Experiment

12

Atomic Spectra and Atomic Structure

OBJECTIVE

To gain some understanding of the relationship between emission (line) spectra and atomic structure.

APPARATUS AND CHEMICALS

Apparatus

- spectroscope with illuminated scale or diffraction grating
- hydrogen lamp
- mercury-vapor lamp
- high-voltage power supply with lamp holder
- Nichrome wire loop
- Bunsen burner and hose
- wood splints

Chemicals

- 6 *M* HCl
- 0.1 *M* $CaCl_2$
- 0.1 *M* LiCl
- unknown solution (mixture containing two or more cations from above)
- 0.1 *M* NaCl
- 0.1 *M* $SrCl_2$
- 0.1 *M* KCl
- 0.1 *M* $BaCl_2$
- unknown solution (one cation from above)

INTRODUCTION

Our present understanding of atomic structure has come from studies of the properties of light or radiant energy and emission and absorption spectra. Radiant energy is characterized by two variables: its wavelength, λ, and its frequency, ν. The wavelength and frequency are related to one another by the relation

$$\nu\lambda = c \qquad [1]$$

where c is the speed of light, 3.00×10^8 meters per second, or m/s; wavelength is usually expressed in nanometers, or nm (10^{-9} m); and frequency is given in cycles per second, or hertz (Hz).

EXAMPLE 12.1

What is the frequency that corresponds to a wavelength of 500 nm?

SOLUTION:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.00 \times 10^8\ \text{m/s}}{500\ \text{nm}}\right)\left(\frac{10^9\ \text{nm}}{1\ \text{m}}\right)$$

$$= 6.00 \times 10^{14}\ \text{s}^{-1} \text{ or } 6.00 \times 10^{14}\ \text{Hz}$$

Radiation of different wavelengths affects matter differently. Infrared radiation may cause a "heat burn"; visible and near-ultraviolet light may cause a sunburn or suntan; and X rays may cause tissue damage or even cancer. Some wavelength units for various types of radiation are given in Table 12.1.

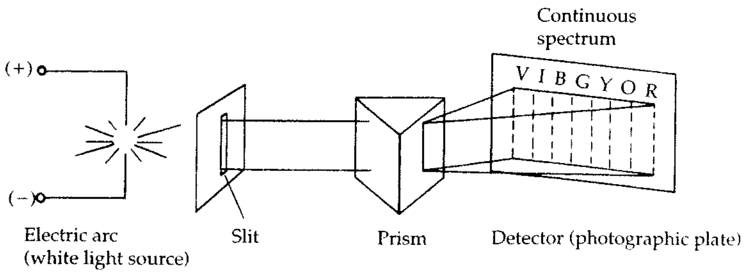
TABLE 12.1 **Wavelength Units for Electromagnetic Radiation**

Unit	Symbol	Length (m)	Type of radiation
Ångstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	ultraviolet, visible light
Micrometer	μm	10^{-6}	infrared
Millimeter	mm	10^{-3}	infrared
Centimeter	cm	10^{-2}	microwaves
Meter	m	1	TV, radio

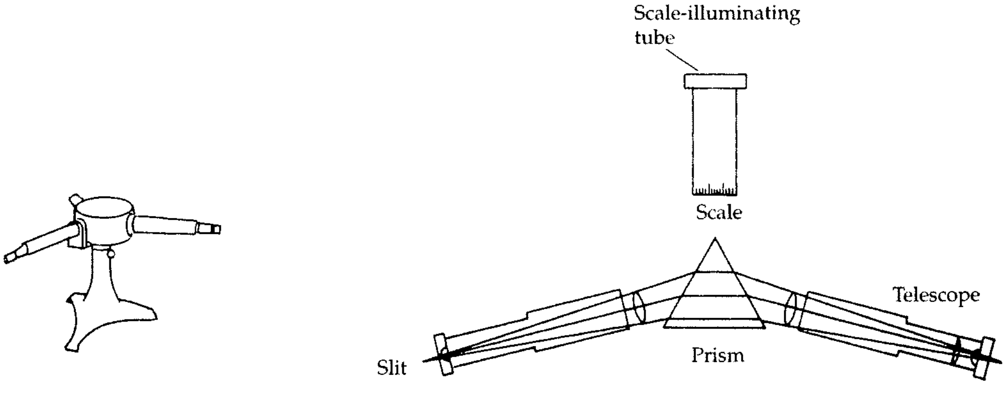
A particular source of radiant energy may emit a single wavelength, as in the light from a laser, or many different wavelengths, as in the radiations from an incandescent lightbulb or a star. Radiation composed of a single wavelength is termed *monochromatic*. When the radiation from a source such as the sun, or other stars, is separated into its components, a *spectrum* is produced. This separation of radiations of differing wavelengths can be achieved by passing the radiation through a prism. Each component of the polychromatic radiation is bent to a different extent by the prism, as shown in Figure 12.1. This rainbow of colors, containing light of all wavelengths, is called a *continuous spectrum*. The most familiar example of a continuous spectrum is the rainbow, produced by the dispersion of sunlight by raindrops or mist.

It was found that by placing a narrow slit between the source of radiation and the prism, the quality of the spectrum was improved and the monochromatic components were more sharply resolved. An instrument used for studying line spectra is called a *spectroscope*. A spectroscope (Figure 12.2) contains the following: a slit for admitting a narrow, collimated beam of light; a prism for dispersing the light into its components; an eyepiece for viewing the spectrum; and an illuminated scale against which the spectrum may be viewed.

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 emit bright red light when excited with a sufficiently high electrical voltage. When energy is absorbed by a substance, electrons within the atoms of the substance may be excited to positions of higher potential energy, farther away from the nucleus. When



▲ **FIGURE 12.1** 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.



(a)

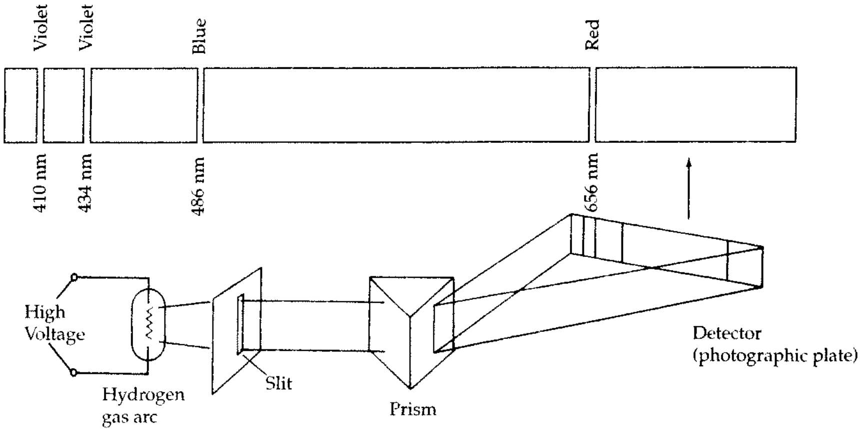
(b)

▲ **FIGURE 12.2** (a) A sketch of the spectroscope to be used. (b) A diagram showing its component parts. When viewed through the telescope, the spectrum will appear superimposed on the numerical scale.

these electrons return to their normal, or ground-state, position, energy will be emitted. Usually some of the energy emitted occurs in the visible region of the electromagnetic spectrum (4000 to 7000 Å, or 400 to 700 nm).

Excited atoms do not emit a continuous spectrum, but rather emit radiation at only certain discrete, well-defined, fixed wavelengths. For example, if you have ever spilled table salt (NaCl) into a flame, you have seen the characteristic yellow emission of excited sodium atoms. If the light emitted by the atoms of a particular element is viewed in a spectroscope, only certain bright-colored lines are seen in the spectrum. See Figure 12.3, which illustrates the emission spectrum of hydrogen.

The observation that a given excited atom emits radiation at only certain fixed wavelengths indicates that the atom can undergo energy changes only of certain fixed, definite amounts. An atom does not emit continuous radiation, but rather emits energy corresponding to definite regular changes in the energies of its component electrons. The experimental demonstration of



▲ **FIGURE 12.3** The emission spectrum of hydrogen.

bright-line atomic emission spectra implied a regular, fixed electronic microstructure for the atom and led to the Bohr model for the hydrogen atom.

In this experiment, you will obtain emission spectra for a few elements and explain your results in terms of the Bohr model. You will use a spectroscope like the one illustrated in Figure 12.2 to obtain your data.

CALIBRATION OF THE SPECTROSCOPE

The scale of the spectroscope has arbitrary divisions and must be calibrated with a known spectrum before the spectrum of an unknown may be obtained. Calibration is accomplished by viewing the emission spectrum of mercury because the emission wavelengths for mercury are very precisely known. You will record the positions on the spectroscope scale of the mercury emission lines and prepare a calibration curve by plotting these positions against the known wavelengths of the lines, which are:

Violet: 404.7 nm
Blue: 435.8 nm
Green: 546.1 nm
Yellow: 579.0 nm

Instructor: Check the electrical connections before the students turn on the power supply.

Turn on the illuminated scale of the spectroscope, and look through the eyepiece to make sure that the scale is visible but not so brightly lighted that the mercury spectral lines will be obscured when the mercury lamp is turned on. With the power supply unplugged, position the power supply and mercury lamp directly in front of the slit opening of the spectroscope. **(CAUTION:** ***The power supply develops 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. In addition to visible light, the lamps may emit ultraviolet radiation. Ultraviolet radiation is damaging to your eyes. Wear your safety glasses at all times during this experiment, since they will absorb some of the ultraviolet radiation. Do not look directly at any of the lamps while they are illuminated.*** **DO NOT LET THE POWER SUPPLY OR LAMP TOUCH THE SPECTROSCOPE.)** With your Instructor's permission, turn on the power supply and then turn on the power-supply switch to illuminate the mercury lamp. Look into the eyepiece and adjust the slit opening so as to maximize the brightness and sharpness of the emission lines on the scale. If necessary, adjust the position of the illuminated scale so that the numbered divisions are easily read but they do not obscure the mercury spectral lines. Once the slit and scale have been adjusted, do not move them during the course of the rest of the experiment. Record on your report sheet the color and location of the mercury lines on the numbered scale for each line in the visible spectrum of mercury. On the graph paper provided, plot the observed scale reading versus the known wavelength for each line. You will then use this calibration curve to determine the wavelengths of the emission lines for some other atoms.

DISCUSSION

A. Emission Spectrum of Atomic Hydrogen

Atoms absorb and emit radiation with characteristic wavelengths. This was one of the observations that led the Danish physicist Niels Bohr to develop a model for the structure of the hydrogen atom. Within this model the electron of the hydrogen atom moves about the central proton in a circular orbit. Only orbits of certain radii and having certain energies are allowed. In the absence of radiant energy, an electron in an atom remains indefinitely in one of the allowed energy states or orbits. When electromagnetic energy impinges upon the atom, the atom may absorb energy, and in the process an electron will be promoted from one energy state to another. The frequency of energy absorbed is related to the energy difference:

$$\Delta E = h\nu = \frac{hc}{\lambda} \qquad [2]$$

In the Bohr model, the radius of the orbit is related to the principal quantum number, n:

$$\text{radius} = n^2(5.3 \times 10^{-11}\ \text{m}) \qquad [3]$$

and the energy of the electron is also related to n:

$$E_n = -R_H\left(\frac{1}{n^2}\right) \qquad [4]$$

Thus, as n increases, the electron moves farther from the nucleus and its energy increases. The constant R_H in Equation [4] is called the *Rydberg constant;* it has the value 2.18×10^{-18} J.

EXAMPLE 12.2

What is the energy of a hydrogen electron when $n = 3$? When $n = 2$?

SOLUTION:

$$E_3 = (-2.18 \times 10^{-18}\ \text{J})\left(\frac{1}{3^2}\right)$$

$$= -2.42 \times 10^{-19}\ \text{J}$$

$$E_2 = (-2.18 \times 10^{-18}\ \text{J})\left(\frac{1}{2^2}\right)$$

$$= -5.45 \times 10^{-19}\ \text{J}$$

The orbital radii and energies are illustrated for $n = 1, 2$, and 3 in Figure 12.4.

According to Bohr's theory, if an electron were to move from an outer orbit to an inner orbit, a photon of light should be emitted having the energy

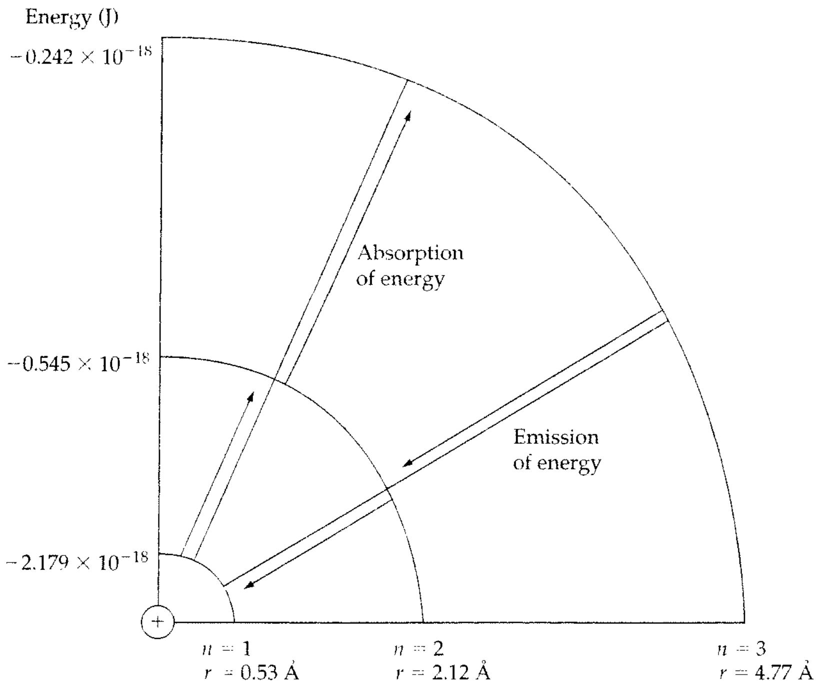
$$\Delta E = E_{\text{inner}} - E_{\text{outer}} = -R_H\left(\frac{1}{n^2_{\text{inner}}} - \frac{1}{n^2_{\text{outer}}}\right) \qquad [5]$$

Thus, from Example 12.2, an electron moving from $n = 3$ to $n = 2$ would emit light of energy

$$[(-5.45) - (-2.42)](10^{-19}\ \text{J}) = -3.03 \times 10^{-19}\ \text{J}$$

The wavelength of this photon is given by the Planck relation

$$\lambda = \frac{hc}{\Delta E} \qquad [6]$$



▲ **FIGURE 12.4** Radii and energies of the three lowest energy orbits in the Bohr model of hydrogen. The arrows refer to transitions of the electron from one allowed energy state to another. When the transition takes the electron from a lower- to a higher-energy state, absorption occurs. When the transition is from a higher- to a lower-energy state, emission occurs.

EXAMPLE 12.3

Calculate the wavelength of light emitted for the $n = 3 \longrightarrow n = 2$ transition.

SOLUTION:

$$\begin{aligned}\lambda &= \frac{(6.63 \times 10^{-34}\ \text{J} - \text{S})(3.00 \times 10^{8}\ \text{m/s})}{3.03 \times 10^{-19}\ \text{J}} \\ &= 6.56 \times 10^{-7}\ \text{m} \\ &= 656\ \text{nm}\end{aligned}$$

By similar calculations Bohr predicted wavelengths for the hydrogen emission spectrum that agreed exactly with the experimental values. He even predicted emission wavelengths in the infrared and ultraviolet regions of the spectrum that had not yet been measured but were later confirmed.

You will measure the emission wavelengths in the visible region for hydrogen with the spectroscope and assign these wavelengths to their corresponding transitions by calculations similar to those in Examples 12.2 and 12.3.

PROCEDURE

Turn on the illuminated scale of the spectroscope and look through the eyepiece to make sure that the scale is visible but not so brightly lighted that the hydrogen spectral lines will be obscured when the hydrogen lamp is turned on. ~~With the power supply unplugged, position the power supply and hy~~drogen lamp directly in front of the slit opening of the spectroscope. **(CAUTION:** ***The power supply develops 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. In addition to visible light, the lamps may emit ultraviolet radiation. Ultraviolet radiation is damaging to your eyes. Wear your safety glasses at all times during this experiment, since they will absorb some of the ultraviolet radiation. Do not look directly at any of the lamps while they are illuminated.* **DO NOT LET THE POWER SUPPLY OR LAMP TOUCH THE SPECTROSCOPE.)** With your instructor's permission, turn on the power supply and then turn on the power-supply switch to illuminate the hydrogen lamp. You should have adjusted the slit and the illuminated scale in the calibration step. Should they require further adjustment, adjust the slit so as to maximize the line intensity and sharpness. On your report sheet, record the color and location of the hydrogen lines on the numbered scale for each line in the visible spectrum of hydrogen. You should easily observe the red, blue-green, and violet lines. A second, faint violet line may also be visible if the room and scale illumination are not too bright.

Instructor: Check the set up before the power supply is turned on.

Use the calibration curve that you constructed to determine the wavelengths of the lines in the hydrogen emission spectrum. Find the true wavelengths of these lines in your textbook or a handbook and calculate the percent error in your determination of the wavelength of each line:

$$\%\ \text{error} = \frac{(\text{true value} - \text{experimental value})}{(\text{true value})} \times 100 \qquad [7]$$

Use Equations [5] and [6] to calculate the wavelengths in nanometers for the $n = 3 \longrightarrow n = 2$, $n = 4 \longrightarrow n = 2$, $n = 5 \longrightarrow n = 2$, and $n = 6 \longrightarrow n = 2$ transitions. How do these calculated values compare with your experimental values? Assign the transitions.

B. Emission Spectra of Group 1A and Group 2A Elements

DISCUSSION

Since the energies of the electrons in the atoms of different elements are different, the emission spectrum of each element is unique. The emission spectrum may be used to detect the presence of an element in both a qualitative and a quantitative way. A number of common metallic elements emit light strongly in the visible region, allowing their detection with a spectroscope. For these elements, the emissions are so intense that the elements may often be recognized by the gross color that they impart to a flame. For example, lithium ions impart a red color to a flame; sodium ions, a yellow color; potassium ions, a violet color; calcium ions, a brick-red color; strontium ions, a bright red color; and barium ions, a green color. If we examine the emission spectra of these ions with a spectroscope, we find that as with mercury and hydrogen, the emission spectra are composed of a series of lines. The series is unique for each metal. Consequently, a flame into which both lithium and strontium, for example, had been placed would be red, and we could not tell with our naked eye that both these ions were present. However, with the aid of a spectroscope, we could detect the presence of both ions.

PROCEDURE

You will obtain the emission spectra of the ions of each of the elements listed in the preceding discussion. You will use a Bunsen burner as an excitation source and observe the gross color imparted to the flame by these ions. With this information, you will determine the contents of two unknown solutions—one containing only one of these metal ions, and the other a mixture containing two or more of these ions.

There are three ways to introduce the metal ions into the flame. First, wood splints can be soaked in each salt solution. The splints can then be ignited by a Bunsen burner. If sufficiently soaked, this procedure produces a substantial burst of color. Second, you can use a wire loop to pick up a drop of the metal-ion solution and then place the drop into the flame for vaporization. Although this method is simple and inexpensive, it produces only a brief burst of color before the sample evaporates completely. Third, you can introduce a fine mist of sample into the flame by using a spray bottle. This method produces a longer-lived emission that is therefore easier to see. Your instructor will tell you which method to use.

Instructor: Tell the students which method to use. A perfume atomizer works very well.

WORK IN PAIRS FOR THIS PART OF THE EXPERIMENT

If you use the wire-loop method, obtain several 6-in. lengths of Nichrome wire and about 10 mL of 6 *M* HCl. Bend the last $^1/_4$-in. of each wire into a small circular loop for picking up the sample solutions. Dip the loop into the 6 *M* HCl solution to remove any oxides that are present, rinse the loop in distilled water, and then heat the loop in the hottest part of the flame until no color is imparted to the flame by the wires.

If the sprayer is used, check to ensure that the sprayer produces a *fine* mist. If the sprayer nozzle is adjustable, try adjusting it to make a very fine mist. If the nozzle cannot be adjusted, ask your instructor how to clean it to improve the mist that it produces.

Instructor: Check the position of the Bunsen burner.

Set up a Bunsen burner directly in front of the slit of the spectroscope but at a sufficient distance to avoid damage to the spectroscope. Have your instructor check the burner placement before you ignite the burner. Ignite the burner and adjust the flame so that it is as hot as possible. Adjust the illuminated scale of the spectroscope so that approximate positions of the emission lines may be determined. It is not necessary to make exact measurements of the emission wavelengths.

With either method of introduction (loop or mist), introduce the metal-ion solution into the flame and note the gross color of the flame. Record your observations on your report sheet. Then, while looking through the eyepiece of the spectroscope, have your partner introduce the metal-ion solution into the flame, noting the color, intensity, and approximate scale position of the brightest lines in the emission spectrum of the metal ions. Repeat the above with each of the other metal-ion solutions. If you use the wire-loop method, use a new loop for each solution, or clean the wire loop with HCl and then distilled water and place the wire loop in the flame until it imparts no color to the flame.

After obtaining the emission spectrum of each of the known metal-ion solutions, obtain the emission spectrum of a single metal unknown, and by matching the colors, intensities, and positions of the lines in the emission spectrum to those of a known metal, identify your unknown. Record your results on your report sheet.

Obtain an unknown mixture and its emission spectrum as above. Then compare the color, intensity, and positions of the brightest lines in this spectrum with those of the knowns. In this way, *determine which metal ions are present in the unknown mixture*. Record your results on your report sheet.

PRE LAB QUESTIONS

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. Name the colors of visible light, beginning with that of lowest energy (longest wavelength).
2. Distinguish between absorption and emission of energy.
3. A system proposed by the U.S. Navy for underwater submarine communication, called ELF (for "extremely low frequency"), operates with a frequency of 76 Hz. What is the wavelength of this radiation in meters? In miles? (1 mile = 1.61 km).
4. What is the energy in joules of the frequency given in question 3?
5. Red and green light have wavelengths of about 650 nm and 490 nm, respectively. Which light has the higher frequency—red or green? Which light has the higher energy—red or green?
6. Mg emits radiation at 285 nm. Could a spectroscope be used to detect this emission?
7. If boron emits radiation at 518 nm, what color will boron impart to a flame?
8. From the wavelengths and colors given for the mercury emission spectrum in this experiment, construct a graphical representation of the mercury emission spectrum as it would appear on the scale of a spectroscope.