3.4 The Bohr Atomic Theory

The development of modern atomic theory involved some key experiments and many hypotheses that attempted to explain empirical results. Along the way, some ideas were never completed and some hypotheses were never accepted. For example, Thomson and his students worked long and hard to explain the number and arrangement of electrons and relate this to the periodic table and the spectra of the elements. Their attempts did not even come close to agreeing with the evidence that existed. Eventually, this work was abandoned.

Rutherford's model of a nuclear atom was a significant advance in the overall understanding of the atom, but it did little to solve the problem of the electrons that frustrated Thomson. In fact, the Rutherford model created some new difficulties. Before looking at Bohr's atomic theory, let us look at some of the problems Bohr was to solve—the stability of the Rutherford atom and the explanation of atomic spectra.

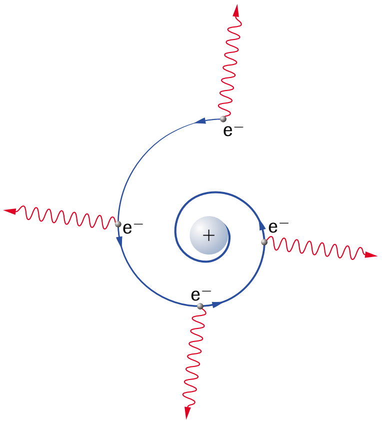


Figure 1
According to existing scientific knowledge at the time of the Rutherford atom, an orbiting electron should continuously emit electromagnetic radiation, lose energy, and collapse the atom. The evidence is to the contrary.

The Big Problem with the Rutherford Model

Rutherford and other scientists had guessed that the electrons move around the nucleus as planets orbit the Sun or moths flutter around a light bulb. This seemed like a logical idea. Planets are attracted to the Sun by gravity but maintain their orbit because they are moving. The same could be said for negatively charged electrons orbiting a positively charged nucleus. However, it was already well established, both experimentally and conceptually, that accelerating charges continuously produce some type of light (electromagnetic radiation). As you may have learned in your study of physics, bodies are accelerating when they change speed and/or direction. An electron travelling in a circular orbit is constantly changing its direction, and is, therefore, accelerating. According to classical theory, the orbiting electron should emit photons of electromagnetic radiation, losing energy in the process, and so spiral in toward the nucleus and collapse the atom (**Figure 1**). This prediction from classical theory of what happens in an atom is obviously not correct. Materials we see around us are very stable and so the atoms that compose them must be very stable and not in immediate danger of collapse. Even the most vigorous supporter of the existing science did not believe that, if atoms contained electrons, the electrons would be motionless and not accelerating.

Atomic Spectra

spectroscopy a technique for analyzing spectra; the spectra may be visible light, infrared, ultraviolet, X-ray, and other types

bright-line spectrum a series of bright lines of light produced or emitted by a gas excited by, for example, heat or electricity

Robert Bunsen and Gustav Kirchhoff worked together to invent the spectroscope (**Figure 2**). The spectroscope forms the basis of an analytic method called **spectroscopy**, a method first reported to the scientific community by Bunsen and Kirchhoff in 1859. They studied the spectra of chemicals, especially elements, heated in a Bunsen burner flame, and the spectrum of the Sun. What they discovered was that an element not only produced a characteristic flame colour but, on closer examination through a spectroscope, also produced a **bright-line spectrum** that was characteristic of the element (**Figure 2**). The spectra of known elements were quickly catalogued and when a new spectrum was found, the spectrum was used as evidence of a new element. The elements cesium and rubidium were discovered within a year of the invention of spectroscopy. Once you quantitatively know the line spectrum of an element, it can be used as an analytic technique to identify an unknown element — a powerful technique that goes beyond the flame tests you have used previously.

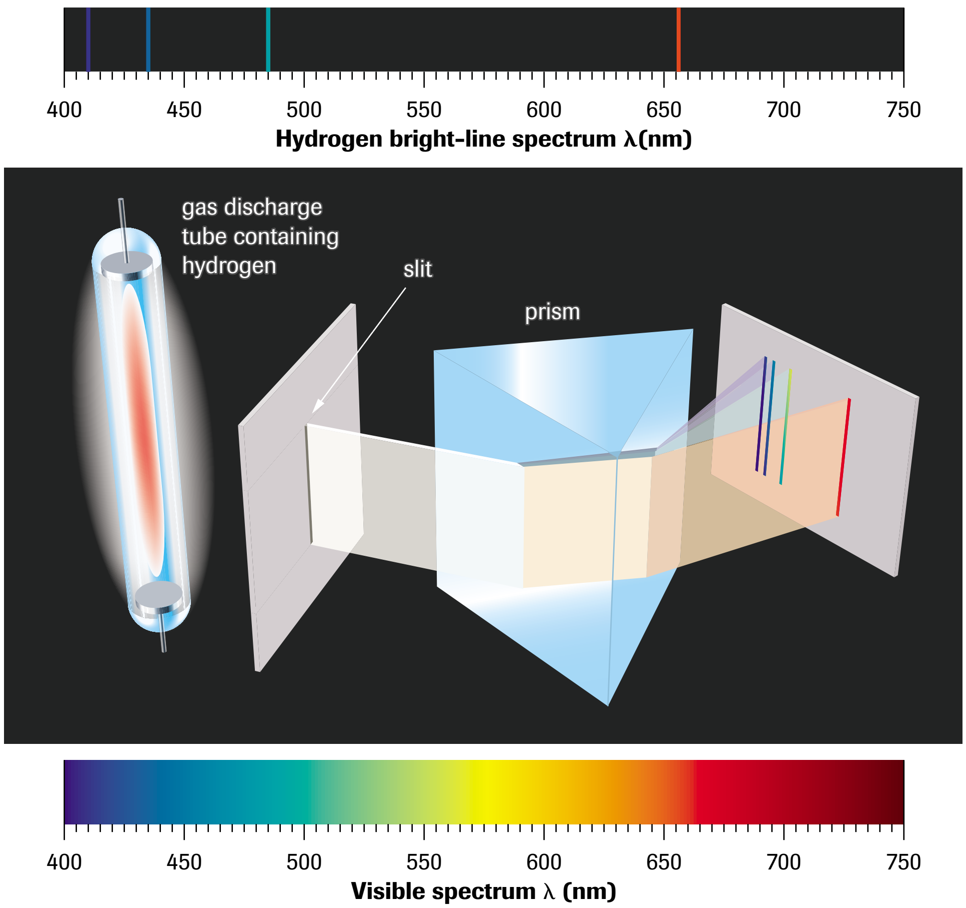


Figure 2
Light from a flame test, or any other source of light, is passed through slits to form a narrow beam. This beam is split into its components by the prism to produce a series of coloured lines. This kind of spectroscope was invented by Bunsen and Kirchhoff. The visible region of the hydrogen spectrum includes four coloured lines at the wavelengths shown by the scale. (1 nm = 10^{-9} m)

As early as 1814, **absorption** or dark-line **spectra** (**Figure 3**) were investigated qualitatively and quantitatively by Joseph von Fraunhofer. Kirchhoff, among others, was able to show in the 1860s that dark lines in an element's spectrum were in the same position as the bright lines in the spectrum of the same element. This provided a powerful tool to determine the composition of gases far away in the universe. When light passes through a gas, for example, the atmosphere around the Sun, some light is absorbed by the atoms present in the gas. This refuted the statement by the French philosopher Auguste Comte who said in 1835 that the composition of the stars was an example of something that scientists could never know.

absorption spectrum a series of dark lines (i.e., missing parts) of a continuous spectrum; produced by placing a gas between the continuous spectrum source and the observer; also known as a dark-line spectrum

Spectroscopes may separate the light by using a prism (**Figure 2**) or a diffraction grating. The most modern, compact, and inexpensive school spectrometers use a diffraction grating.

ACTIVITY 3.4.1

Line Spectra (p. 212)
Use a spectroscope to "dissect" light into its components.

Bohr's Model of the Atom

In his mid-20s, Niels Bohr went to Cambridge University in England to join the group working under the famous J. J. Thomson. At this time, Thomson's group was attempting, quite unsuccessfully, to explain electrons in atoms and atomic spectra. Bohr suggested that tinkering with this model would never work, and some revolutionary change was required. Bohr's hunch was that a new model required using the new quantum theory of light developed by Planck and Einstein. Thomson did not like these revolutionary ideas, especially from a young man fresh out of university in Denmark. There were many heated arguments and Bohr decided to abandon Thomson's group in Cambridge and go to the University of Manchester to work with Rutherford, one of Thomson's former students.

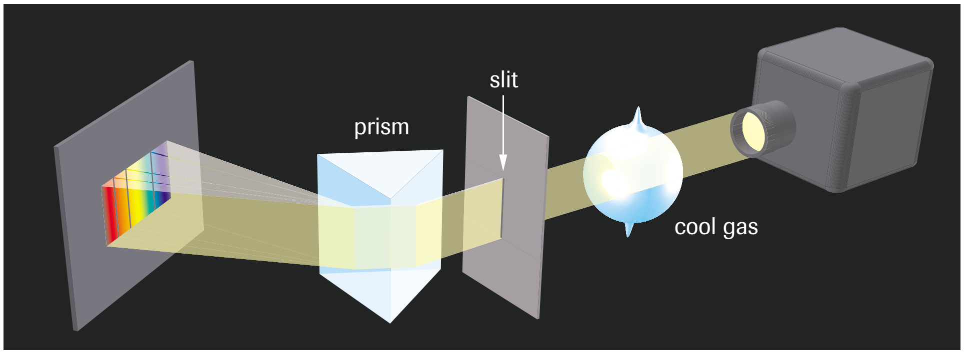


Figure 3
If you start with a complete colour spectrum of all possible colours, then pass this light through a gas and analyze what is left, you get a dark-line spectrum; in other words, the complete spectrum with some lines missing.

This turned out to be a much better environment for Bohr to develop his still vague ideas about the quantum theory and electrons in atoms.

The bright- and dark-line spectra of the elements mean that only certain quanta of light (certain photon energies) can be emitted or absorbed by an atom. Bohr reasoned that if the light released or absorbed from an atom was quantized, then the energy of the electron inside the atom must also be quantized. In other words, an electron can only have certain energies, just as the gearbox in a car can only have certain gears — first, second, third,.... The simplest arrangement would be a planetary model with each electron orbit at a fixed distance and with a fixed energy (**Figure 4**). In this way, the energy of the electron was quantized; in other words, the electrons could not have any energy, only certain allowed energies. To avoid the problem of the Rutherford model, Bohr boldly stated that these were special energy states (called **stationary states**), and the existing rules did not apply inside an atom.

ACTIVITY 3.4.2

The Hydrogen Line Spectrum and the Bohr Theory (p. 213)
This computer simulation helps illustrate the electron transitions that produce bright lines in a spectrum.

stationary state a stable energy state of an atomic system that does not involve any emission of radiation

transition the jump of an electron from one stationary state to another

Bohr's First Postulate

Electrons do not radiate energy as they orbit the nucleus. Each orbit corresponds to a state of constant energy (called a stationary state).

Like many other scientists of the time, Bohr was familiar with the long history of atomic spectra and shared the general feeling that the electrons were somehow responsible for producing the light observed in the line spectra. But no one knew how or why. The visible hydrogen spectrum (**Figure 2**) was the simplest spectrum and corresponded to the smallest and simplest atom. This was obviously the place to start. Although Bohr was familiar with atomic spectra, he did not know about the mathematical analysis of the hydrogen spectrum by Jacob Balmer, a teacher at a girls' school in Switzerland. According to a common story, someone showed Bohr the formula. "As soon as I saw Balmer's equation, the whole thing was immediately clear to me" (Niels Bohr).

Without going into the mathematical detail, what was clear to Bohr was that electrons "jump" from one orbit and energy level to another. This is called an electron **transition**. A transition from a higher energy state to a lower energy state means that the electron loses energy and this energy is released as a photon of light, explaining a bright line in a bright-line spectrum (**Figure 5a**). When some energy is absorbed, for example from a photon of light, the electron undergoes a transition from a lower energy state to a higher one, explaining a dark line in an absorption spectrum (**Figure 5b**). This was the crucial idea that Bohr was seeking.

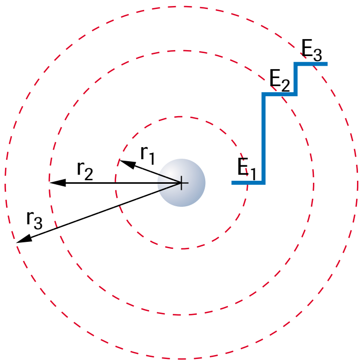
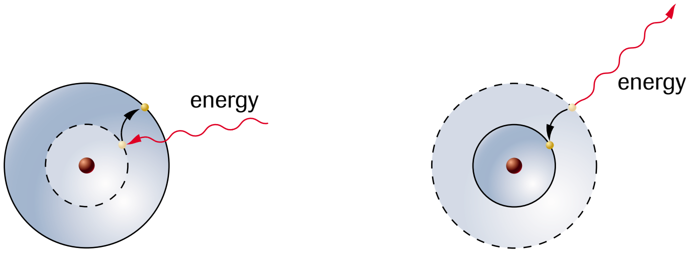


Figure 4
In the Bohr model of the atom, electrons orbit the nucleus, as the planets orbit the Sun. However, only certain orbits are allowed, and an electron in each orbit has a specific energy.

Bohr's Second Postulate

Electrons can change their energy only by undergoing a transition from one stationary state to another.



(a) An electron gains a quantum of energy.

(b) An electron loses a quantum of energy.

Figure 5
In both types of transitions, the energy of the photon must match the difference in energies of the two electron states.
(a) The energy of a photon is absorbed by the electron to move it from a lower to a higher energy state.
(b) When the electron returns from a higher to a lower energy state, a photon is released.

Bohr recognized the need to use Planck's quantum theory to explain the spectral evidence from several decades of experiments. Fifty-four years after line spectra were first observed by Bunsen and Kirchhoff, and twenty-eight years after line spectra were described quantitatively by Balmer, an acceptable theoretical description was created by Bohr. The Bohr theory was another significant step forward in the evolution of modern atomic theories, which started with Dalton.

The Successes and Failure of the Bohr Model

Most importantly for our everyday work in chemistry, the Bohr model of the atom is able to offer a reasonable explanation of Mendeleev's periodic law and its representation in the periodic table. According to the Bohr model, periods in the periodic table result from the filling of electron energy levels in the atom; e.g., atoms in Period 3 have electrons in three energy levels. A period comes to an end when the maximum number of electrons is reached for the outer level. The maximum number of electrons in each energy level is given by the number of elements in each period of the periodic table; i.e., 2, 8, 8, 18, etc. You may also recall that the last digit of the group number in the periodic table provides the number of electrons in the valence (outer) energy level. Although Bohr did his calculations as if electrons were in circular orbits, the most important property of the electrons was their energy, not their motion. Energy-level diagrams for Bohr atoms are presented in the sample problem below. These diagrams have the same procedure and rationale as the orbit diagrams that you have drawn in past years. Since the emphasis here is on the energy of the electron, rather than the motion or position of the electron, orbits are not used.

DID YOU KNOW?

Analogy for Electron Transitions

In an automobile, the transmission shifts the gears from lower to higher gears such as first to second, or downshifts from higher to lower gears. The gears are fixed, for example, first, second, third. You cannot shift to "$2\frac{1}{2}$." Similarly, electron energies in the Bohr model are fixed and electron transitions can only be up or down between specific energy levels. A satellite is not a good analogy for electron energy levels, because a satellite can be in any orbit, so any change in its energy is continuous, not in jumps.

Bohr Energy-Level Diagram — SAMPLE problem

Use the Bohr theory and the periodic table to draw energy-level diagrams for the phosphorus atom.

First, we need to refer to the periodic table to find the position of phosphorus. Use your finger or eye to move through the periodic table from the top left along each period until you get to the element phosphorus. Starting with period 1, your finger must pass through 2 elements, indicating that there is the maximum of 2 electrons in energy level 1. Moving on to period 2, your finger moves through the full 8 elements, indicating 8 electrons in energy level 2. Finally, moving on to period 3, your finger moves 5 positions to phosphorus, indicating 5 electrons in energy level 3 for this element.

The position of 2, 8, and 5 elements per period for phosphorus tells you that there are 2, 8, and 5 electrons per energy level for this atom. The information about phosphorus atoms in the periodic table can be interpreted as follows:

atomic number, 15: 15 protons and 15 electrons (for the atom)
period number, 3: electrons in 3 energy levels
group number, 15: 5 valence electrons (the last digit of the group number)

To draw the energy-level diagram, work from the bottom up:

Sixth, the 3rd energy level,	5 e^-	(from group 15)
Fifth, the 2nd energy level,	8 e^-	(from eight elements in period 2)
Fourth, the 1st energy level,	2 e^-	(from two elements in period 1)
Third, the protons:	15 p^+	(from the atomic number)
Second, the symbol:	P	(uppercase symbol from the table)
First, the name of the atom:	phosphorus	(lowercase name)

Although the energy levels in these diagrams are (for convenience) shown as equal distance apart, we must understand that this is contrary to the evidence. Line spectra evidence indicates that the energy levels are increasingly closer together at higher energy levels.

Example

Use the Bohr theory and the periodic table to draw energy-level diagrams for hydrogen, carbon, and sulfur atoms.

Solution

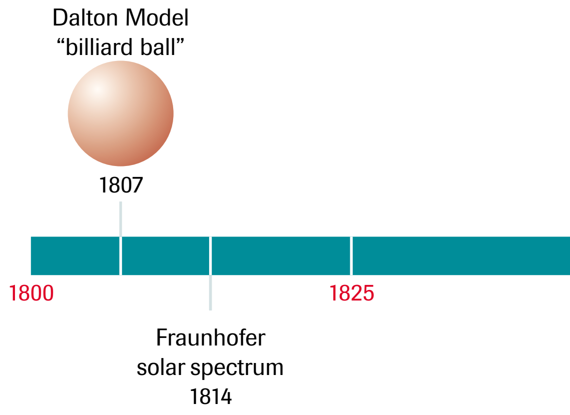
		6 e^-
	4 e^-	8 e^-
1e^-	2 e^-	2 e^-
1p^+	6 p^+	16 p^+
H	C	S
hydrogen atom	carbon atom	sulfur atom

Practice

Understanding Concepts

1. Draw energy-level diagrams for each of the following:
   (a) an atom of boron
   (b) an atom of aluminum
   (c) an atom of helium

Not only was Bohr able to explain the visible spectrum for hydrogen, he was also able to successfully predict the infrared and ultraviolet spectra for hydrogen. For a theory to be able to explain past observations is good; for it to be able to predict some future observations is very good. Unfortunately, Bohr's theory was not excellent, because it works very well only for the spectrum for hydrogen atoms (or ions with only one electron). The calculations of spectral lines using Bohr's theory for any atom or ion containing more than one electron did not agree with the empirical results. In fact, the discrepancy became worse as the number of electrons increased. Nevertheless, Bohr's theory was a great success because it was the start of a new approach — including the new quantum ideas in a model of the atom (**Figure 6**).



SUMMARY Creating the Bohr Atomic Theory (1913)

Table 1

Key Experimental evidence	Theoretical explanation	Bohr's atomic theory
Mendeleev (1869–1872): There is a periodicity of the physical and chemical properties of the elements.	A new period begins in the periodic table when a new energy level of electrons is started in the atom.	• Electrons travel in the atom in circular orbits with quantized energy—energy is restricted to only certain discrete quantities. • There is a maximum number of electrons allowed in each orbit. • Electrons "jump" to a higher level when a photon is absorbed. A photon is emitted when the electron "drops" to a lower level.
Mendeleev (1872): There are two elements in the first period and eight elements in the second period of the periodic table.	There are two electrons maximum in the first electron energy level and eight in the next level.	
Kirchhoff, Bunsen (1859), Johann Balmer (1885): Emission and absorption line spectra, and not continuous spectra, exist for gaseous elements.	Since the energy of light absorbed and emitted is quantized, the energy of electrons in atoms is quantized.	

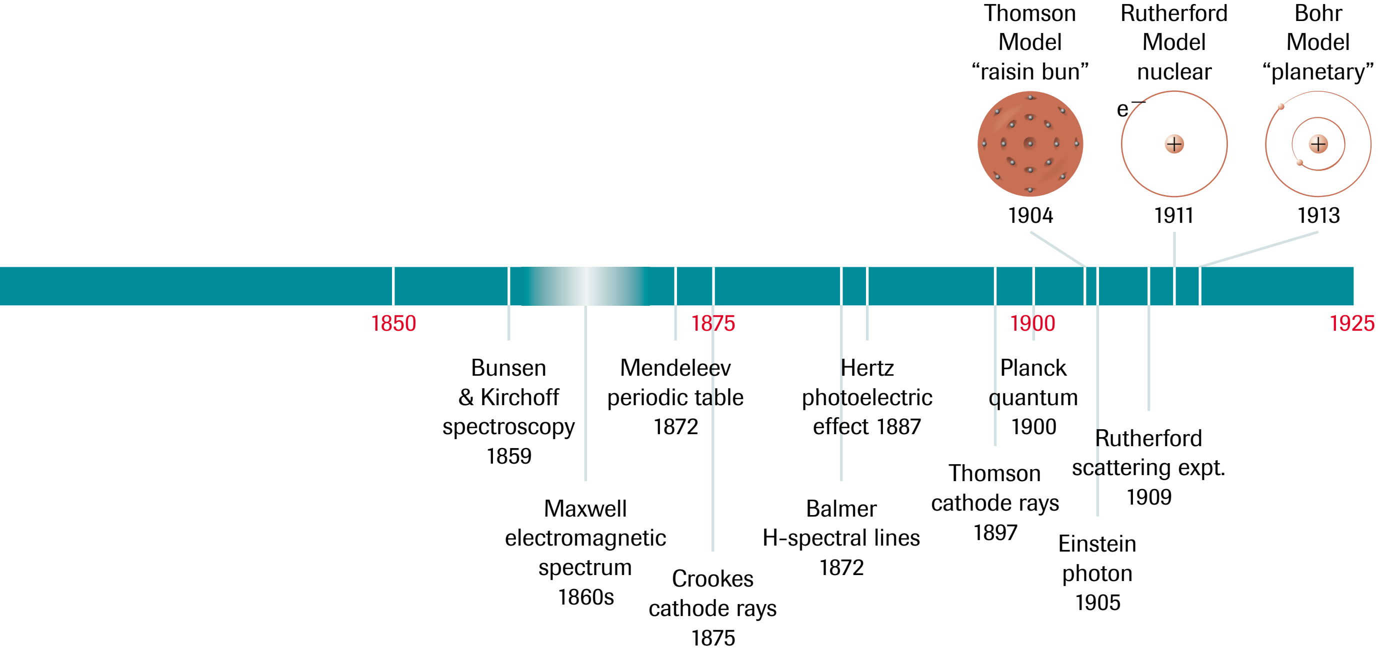
DID YOU KNOW?

A Hydrogen Line Is Red...

Several scientists have struck on a connection between science and the literary arts, especially poetry. Niels Bohr was one of those who felt this connection profoundly. "When it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images."

Figure 6

In a little over a hundred years, the idea of an atom has changed from the original indivisible sphere of Dalton to a particle with several components and an internal organization.



Section 3.4 Questions

Understanding Concepts

1. What was the main achievement of the Rutherford model? What was the main problem with this model?

2. State Bohr's solution to the problem with the Rutherford atomic model.

3. When creating his new atomic theory, Bohr used one important new idea (theory) and primarily one important experimental area of study. Identify each of these.

4. (a) What is the empirical distinction between emission and absorption spectra?
(b) In general terms, how did Niels Bohr explain each of these spectra?

5. Niels Bohr and Ernest Rutherford both worked at the same university at approximately the same time. In this text, their work has been largely separated for simplicity, but scientists often refer to the "Bohr–Rutherford" model. How did the accomplishments of Rutherford and Bohr complement each other?

6. Draw an energy-level diagram for each of the following:
(a) fluorine atom
(b) neon atom
(c) sodium atom

7. What do the atomic, period, and group numbers contribute in energy-level diagrams?

8. State two or more reasons why Bohr's theory was considered a success.

9. Identify one significant problem with the Bohr theory.

Applying Inquiry Skills

10. Element 118 was reported to have been discovered in 1999. However, as of July 2001 no one, including the original researchers, has been able to replicate the experiments. Using your present knowledge, you can make predictions about this element. Predict the properties of element 118 based on the periodic law and the Bohr theory of the atom.

Making Connections

11. Read as much as you can from Bohr's original paper about the periodic table. List the content presented in Bohr's writing that you recognize. Approximately how much of the content is beyond your understanding at this time?

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12. Use your knowledge from this section to determine if a sample of table salt ($NaCl_{(s)}$) contains some potassium chloride.

Extension

13. In 1885 Balmer created an equation that described the visible light spectrum for hydrogen. This evolved to become the Rydberg equation presented below. Bohr used Balmer's work as an insight into the structure of the hydrogen atom.

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

$$R_H = 1.10 \times 10^7 \text{ /m}$$

(a) The visible portion of the hydrogen spectrum is called the Balmer series. The visible light photons emitted from the hydrogen atom all involve electron transitions from higher (excited) energy levels down to the $n_f = 2$ level. Calculate the wavelength of the light emitted from the quantum leap of an electron from the $n_i = 4$ level to the $n_f = 2$ level.
(b) Use the wave equation, $\lambda = c/f$, to calculate the frequency of the light emitted ($c = 3.00 \times 10^8$ m/s).
(c) Use the Planck equation, $E = hf$, to calculate the energy of the electron transition and, therefore, the difference in energy between the $n_i = 4$ and the $n_f = 2$ levels ($h = 6.63 \times 10^{-34}$ J/Hz).
(d) Repeat (a) through (c) for the $n_i = 3$ to the $n_f = 2$ electron transition.
(e) Draw an energy-level diagram for hydrogen showing the $n_i = 3$ and 4 to the $n_f = 2$ transitions. Add the energy difference values to the diagram. From these values, what is the energy difference between $n = 4$ and $n = 3$?

14. Using your knowledge of the history of atomic theories from Dalton to Bohr, state what you think will happen next in the historical story. Provide some general comments without concerning yourself with any details.