

■ EXERCISES

19. For singly ionized helium, calculate the energies of the first three lines of the series equivalent to the Lyman and Balmer series.
20. Show that some of the “Balmer-series” lines of singly ionized helium are the same as lines of the hydrogen Lyman series. Which ones are they, in general? This correspondence was a source of confusion when spectral lines of He ions were first observed in the solar spectrum; some people speculated that they were seeing a new form of hydrogen not found on Earth.
21. Find the energies of the first lines of the series in doubly ionized lithium that are equivalent to the Lyman and Balmer series.

17.5 HOW ATOMS GOT THEIR (ATOMIC) NUMBERS

Introduction

Mendeleev’s periodic table of the elements was a significant advance in chemistry. It made explicit the empirical observation that similarities in the chemical properties of the elements recur periodically as atomic mass increases. For over 40 years it was a useful guide for scientists, but it provided no explanation for the periodicity of properties of the elements. Then, in the early decades of the twentieth century dramatic advances in physics revealed the structure of atoms and uncovered the physical basis of the periodic table. This section tells you about one of these great advances: how physicists learned that the atomic number—the number that specifies the position of an atom in the periodic table—is the number of positive charges in the atomic nucleus.

How many Elements can there be?

In his 1869 table Mendeleev exhibited the periodic recurrence of the chemical properties of the elements by putting elements with similar chemical behavior in rows and ordering them in columns according to their atomic weights. Thus, in one row he put lithium ($A = 7$), sodium ($A = 23$), potassium ($A = 39$), rubidium ($A = 85.4$), and cesium ($A = 133$). These alkali metals show similar chemical behavior; for example, they all form similar compounds with oxygen: Li_2O , Na_2O , Rb_2O , and Cs_2O .

Modern periodic tables like the one on p. 642 put elements with similar properties in columns and with increasing mass along the rows. Modern

periodic tables are also complete and correctly ordered, while Mendeleev's table had empty spaces corresponding to undiscovered elements, and it had some elements in wrong places.

In the 1890s physicists and chemists discovered the noble gases—helium, neon, argon, krypton, and, later, radon—and added an entire new column to the table. Given that discovery, you might ask: Is today's periodic table complete? Might there be other elements that have been overlooked? The fact that the atomic number is the number of charges in the nucleus Z assures us that the answer to this last question is “No.”

Immediately after Rutherford discovered the atom's nuclear core (Chap. 16), Bohr showed that the nuclear charge Ze determines the scale of the energy states of an atom (p. 535). In 1913 H. G. J. Moseley measured the wavelengths of x-rays emitted by many different kinds of atoms and showed that each chemical element is uniquely identified by its nuclear charge Ze , that there is a one-to-one correspondence between Z and a chemical element. In other words, the nuclear charge number Z specifies the position of an element in the periodic table and is, therefore, the same as the atomic number—the serial number of the element in the periodic table. Up to the time Moseley did his experiments the atomic number could only be determined empirically. Moseley found its physical basis: It is the number of positive charges in the nucleus.

From this fact it follows that there can only be as many elements as there are integers Z ; once you have found 83 elements with values of Z from 1 to 83, you have found all the elements from hydrogen to bismuth. The only other possible elements must have $Z > 83$. Some of these exist in nature, and it is possible to make others by adding charges to the nucleus.¹

The properties of x-ray line spectra were the basis of Moseley's discovery that Z is the atomic number, and you need to learn about them to understand his experiment.

X-Ray Line Spectra

In 1905, a decade after Roentgen discovered x-rays, the British physicist Charles Barkla found that a target struck by a beam of high energy x-rays emitted x-rays distinctly different in behavior from those in the incident beam. He called the incident x-rays “primary,” and the different outgoing

¹Nuclear physicists and nuclear chemists do this. They have made elements up to $Z = 118$, but these high Z elements are difficult to make and are radioactively very unstable. For example, experimentalists have observed only two or three atoms of $Z = 118$, and these lived only a few milliseconds. It takes a while before these are given official names. In 2010 element $Z = 112$ was officially named copernicium and given the symbol Cn.

x-rays “secondary.” By measuring the absorption of the secondary x-rays in sheets of material placed between the emitting target and the x-ray detector, Barkla showed that the energy (frequency) of the secondary x-rays was characteristic of the target (anode) material. For example, secondary x-rays from an iron target were more energetic than those from an aluminum target. He discovered that the secondary x-rays emitted by a target are unique to the chemical element the target is made of, so he called them “characteristic x-rays,” and pointed out that they could be used to identify the target material. Barkla had discovered a new means of chemical analysis.²

From his measurements of the absorption of x-rays Barkla found that an anode emits two distinctly different types of characteristic x-rays—a more penetrating type (shorter wavelengths, higher energy) that he called K radiation or K x-rays, and a more easily absorbed type (longer wavelengths, lower energy) that he called L radiation.

Later, after x-rays were found to be waves and the x-ray spectrometer was developed, it became clear that Barkla’s K and L radiations were x-ray line spectra (see Fig. 17.6). These are x-rays with well defined frequencies that show up as high intensity peaks on the background of continuum radiation discussed in Chap. 14. When the energy of electrons bombarding the anode is increased, the intensity of the emitted x-ray lines increases relative to the background, but their wavelengths remain unchanged. These emissions are called x-ray lines because they are analogous to the spectral lines in the visible light spectra of atoms. And like

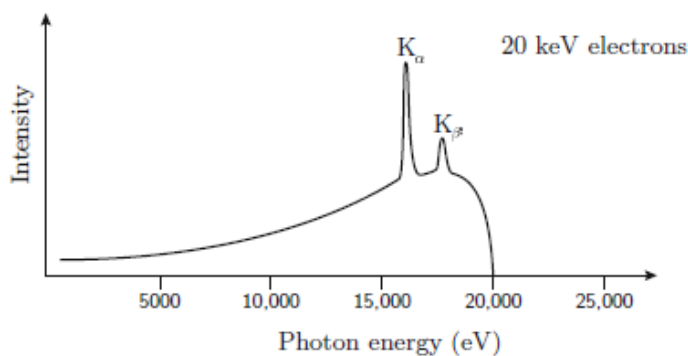


FIGURE 17.6 An x-ray spectrum showing continuum and characteristic x-ray lines from element of atomic number 40 when bombarded with 20 KeV electrons. The subscripts α and β are explained on p. 544 in the text.

²Charles Barkla was awarded the 1917 Nobel Prize in physics. In addition to discovering characteristic x-rays, he confirmed that x-rays are electromagnetic radiation by showing experimentally that they can be polarized. His doctoral advisor was J. J. Thomson.

visible spectral lines, x-ray lines are a unique fingerprint of the emitting atom. Moseley studied x-ray line spectra, (characteristic x-rays) and discovered a simple relationship that allowed him to predict the frequencies (energies) of x-rays from any element and to see that the charge of the atomic nucleus is the property that gives an atom its identity.

Moseley's Experiment

Moseley³ knew from Rutherford's work that an atom has a nucleus with a nuclear charge roughly $A/2$ times the elementary charge e , where A is the atomic mass. (And from Barkla's studies of x-ray absorption, he knew that the number of electrons in an atom was also roughly $A/2$ as necessary to balance the nuclear charge and produce an electrically neutral atom.) Consequently, Mendeleev's ordering of the elements by mass number A was roughly the same as ordering them by nuclear charge number Z . Now Moseley showed that Z gave an exact and unambiguous ordering; Z , not A , was an element's serial number in the periodic table.

Moseley designed and constructed an ingenious spectrometer that allowed him to quickly and accurately measure the wavelengths of the characteristic x-rays emitted by various elements. His spectrometer (Fig. 17.7) had two novel features. First, it used photographic film rather than an electrometer to record x-ray intensities. Second, it had multiple targets (anodes) mounted on a carriage inside the x-ray tube, so that he could change the element he was studying without losing the tube's vacuum. Working mostly on his own, in just over one year of intense effort Moseley measured the line spectra of 38 elements. Some of his early results⁴ are summarized in Table 17.1 and in Fig. 17.8.

Moseley found that when he plotted the square root of the frequency f (or equivalently, as we plot it in Fig. 17.8, the square root of the photon

³From 1910 to 1913 Moseley was at the right place at the right time. He was a graduate student in Rutherford's laboratory at the University of Manchester as Rutherford established the nuclear model of the atom (1911) (Chap. 16). Bohr spent four months at Manchester in 1912, and then went home to Denmark and conceived and published in 1913 his revolutionary model of the hydrogen atom. In 1912 and 1913, von Laue, Friedrich, and Knipping in Germany established the wave nature of x-rays, and the Braggs, at the University of Leeds—36 miles from Manchester—devised the first x-ray spectrometer (Chap. 14). Responding to these advances, Moseley, with Rutherford's support and advice from the Braggs, began studying x-rays. He built an x-ray spectrometer and studied x-ray diffraction, and finished his thesis. Then he built a new spectrometer and, in November, measured K x-rays of some 10 chemical elements. That month he moved to Oxford, set up a new laboratory, rebuilt his apparatus, and measured K and L x-rays from some 20 more elements. This work was published in May. A year later he was shot dead by a sniper in World War I.

⁴ Moseley, "The high-frequency spectra of the elements," *Phil. Mag.* **26**, 1024–1034 (1913); http://web.mit.edu/8.13/www/pdf_files/moseley-1913-high-freq-spectra-elements-part2.pdf.

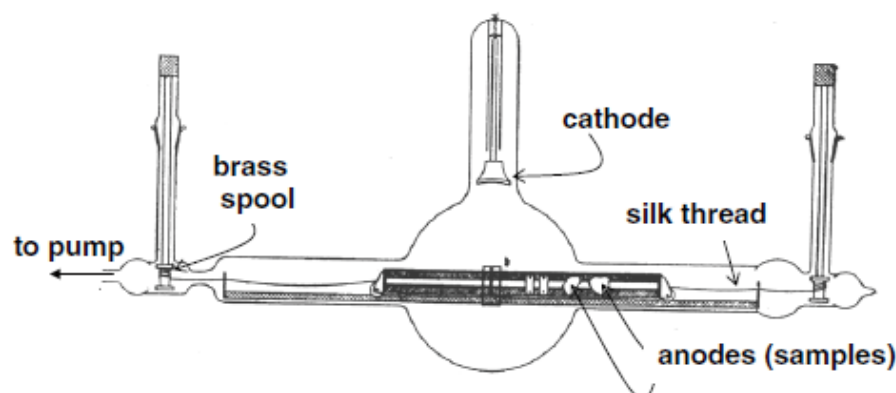


FIGURE 17.7 Moseley's apparatus for measuring K and L x-rays from a succession of samples. The shafts with the brass spools attached can be rotated without breaking the vacuum. When the spool rotates it takes up the silk thread and pulls a carriage along on its wheels. The samples are mounted on the carriage, and when properly positioned a sample becomes the anode struck by electrons from the cathode.

TABLE 17.1 X-ray data for ten elements and Moseley's law

Z	Element	λ (nm)	hf (eV)	Q	A	$Q + 1$
20	Ca	0.3357	3694	19.01	40.09	20.0
21	Sc				44.1	
22	Ti	0.2766	4483	20.97	48.1	22.0
23	V	0.2521	4919	21.97	51.06	23.0
24	Cr	0.2295	5403	23.02	52.0	24.0
25	Mn	0.2117	5854	23.96	54.93	25.0
26	Fe	0.1945	6375	25.00	55.85	26.0
27	Co	0.1796	6904	26.02	58.97	27.0
28	Ni	0.1664	7451	27.03	58.68	28.0
29	Cu	0.1548	8010	28.02	63.57	29.0
30	Zn	0.1446	8575	28.99	65.37	30.0

energy hf) of the K radiation against the atomic number of the emitting substance, a straight line fit the data remarkably well. He saw that he could define a dimensionless constant Q ,

$$Q = \sqrt{\frac{hf}{\frac{3}{4}E_0}}, \quad (16)$$

that had the property that it increased in steps of 1 from one element to the next if E_0 is taken to be 13.6 eV. This behavior of Q is apparent

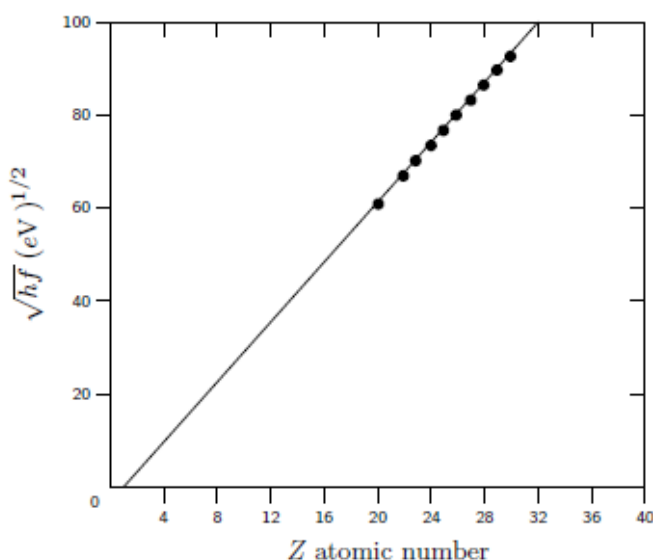


FIGURE 17.8 The data points are the square roots of Moseley's measured x-ray energies vs. atomic number Z . The straight line is the graph Eq. 16.

in Table 17.1, and he observed that $Q + 1$ corresponded to the atomic number of the anode's metal. As he wrote:

We have here a proof that there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus, of the existence of which we already have definite proof [from Rutherford].

EXERCISES

22. Find the wavelength, energy, and Q for the element scandium (Sc), missing from Table 17.1.

Notice from Table 17.1 that if Mendeleev had followed his rule of ordering the elements by their masses, he would have put nickel before cobalt. He broke his rule because of their chemical properties, but Moseley's technique unambiguously established, independently of their chemical properties or their masses, that cobalt's atomic number is one unit less than nickel's.

By establishing that the atomic number is the number of positive charges in the nucleus, Moseley made it clear that the number of possible

elements is limited. In his papers he pointed out that 75 elements were known with atomic numbers up to 79—the atomic number of gold—so as of 1913 there were only 4 chemical elements lighter than gold still to be found. He could specify their atomic numbers and predict the wavelengths of their characteristic x-rays.⁵

X-Ray Line Spectra and the Bohr Model

Moseley observed that the energies of K and L x-rays increased in a regular way as he chose heavier elements further along in the periodic table. He could see that the regularities that he observed were analogous to those in the spectrum of the hydrogen atom, and he felt there must be a connection between the line x-rays and the Bohr model.

Such a connection was established by a simple model of multi-electron atoms. Spectroscopic data suggested that in atoms with several or more electrons the atom's energy states form groups. In each group the states are close together in energy, but between the groups there is a considerable separation in energy. These well defined groups of energy states are called “shells” of energy, and there is one shell for each value of the principal quantum number $n = 1, 2, \dots$. It also turns out that there can not be more than $2n^2$ electrons in a shell with principal quantum number n . This rule is called the “Pauli exclusion principle”⁶ or, for short, the “exclusion principle.”

Here is how shell structure and the exclusion principle explain the generation of characteristic x-rays. Because of the exclusion principle, electrons in higher-energy shells cannot make transitions to lower-energy shells when these shells are filled with electrons. But when electrons accelerated in an x-ray tube strike atoms of the anode, some of the collisions will knock an electron out of the lowest-energy shell. In such an atom there will then be a vacancy in the $n = 1$ shell that can be filled by the transition of an electron from a higher-energy shell to the lower-energy one. When such a transition occurs, a photon is emitted with an energy equal to the difference between the energies of the two shells as illustrated by Fig. 17.9. This photon is one of the characteristic x-rays.

The Bohr model can predict with useful accuracy the energy of a characteristic x-ray photon. As Eq. 15 shows, the Bohr model predicts this will scale as Z^2 . For example, consider the energy of an electron in the $n = 1$ shell of an element with nuclear charge $Z = 40$ (zirconium). According to Eq. 15, its energy will be about $-40^2 \times 13.6 = -22\,000$ eV.

⁵They have all been discovered—hafnium ($_{72}\text{Hf}$), rhenium ($_{75}\text{Rh}$), technetium ($_{43}\text{Tc}$), and promethium ($_{61}\text{Pm}$). These last two are radioactive and must be produced artificially.

⁶Quantum mechanics explains the Pauli exclusion principle, but for now you can be like physicists in the early 1920s and just accept it as an empirically established rule.

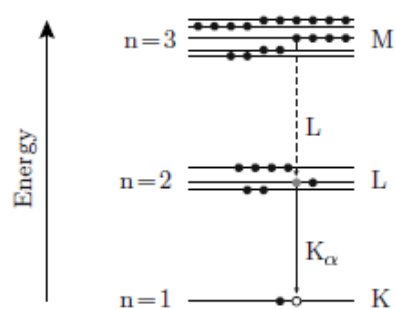


FIGURE 17.9 Schematic representation of energy shells of an atom, illustrating how x-rays can be produced by transitions from a higher-energy shell to a hole in the lower-energy shell.