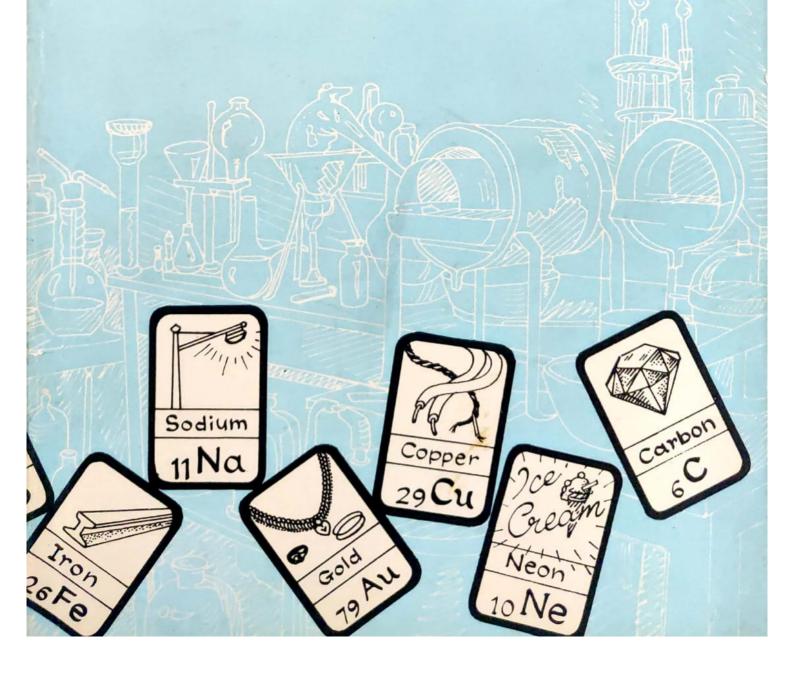


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Model of the Periodic Table

The bunches of papers behind Lanthanum and Actinium list the lanthanides and actinides (rare earths)

# THE FASCINATING STORY OF THE PERIODIC TABLE

#### SAVITA LADAGE V.G. KULKARNI

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Chemistry is a fascinating subject. Even at the elementary level, where one studies the simple properties and composition of some familiar substances, chemistry begins to reveal the beautiful patterns of 'Nature's Architecture'. Indeed, it is at the elementary level that we must pause to understand and admire this brilliant architecture. The purpose of this book is to introduce you to this fascinating world.

While studying the fundamentals of chemistry, we are introduced to various basic concepts and principles. One such important concept in chemistry is the systematic classification of elements based on their properties. This classification is amazingly fruitful. It reveals the periodic nature of the properties of elements and shows clearly how properties are related to the structure of atoms. The arrangement of elements according to their properties gave rise to the *Periodic Table* of elements. As students of chemistry you are familiar with this Table in its widely used form. You also know that the major credit for the discovery of the periodic table and the periodic law goes to the Russian chemist, Dmitry Mendeleev.

Though the discovery of the periodic table is attributed to Mendeleev, several scientists, from the ancient Greek philosophers and alchemists of the middle ages to modern scientists working in well-equipped laboratories, have contributed significantly to its development. In fact, this is how science grows. The work of a large number of scientists accumulates until some exceptionally gifted scientist sees a pattern in the mass of information and explains its 'meaning'. The story of the periodic table illustrates this point perfectly.

The desire to find patterns in nature has been an important aspect of scientific investigation, since ancient times. The Greek philosophers tried to explain all matter on the basis of four natural or basic 'elements'. However, the steady progress of chemistry led to the discovery of elements as we know them today. By 1860 there were 60 known elements. This story in itself is interesting, but we shall not spend too much time on it here. We need cover only the important points which will enable us to understand how the periodic table of elements evolved.

It took several centuries of intelligent hard work together with flashes of genius for humankind to acquire the understanding that is presented in this book. Now, you can read all about it in a few days. But, apart from learning about and understanding the scientific theories of today, it is also useful to study the historical development of various concepts and theories of science. Louis Pasteur (1822–1895), the famous scientist, once wrote a report 'on the usefulness of the historical methods in teaching science'. According to him, the teaching method involving historical developments 'evokes the individual efforts of the most important inventors, adopts preferably their own terms, indicates their essentially simple procedures and tries to transport the audience mentally into the period when the discovery was made'(1).

According to Spencer Weart, Manager of the Centre for History of Physics at the American Institute of Physics, New York, 'The history of science is the story of a community of people with ordinary human flaws

## Recognizing Patterns

Collection of a heap of information does not by itself lead to knowledge. It is only when a law or a pattern in which pieces of information fit is discovered, that one gains insight or understanding. Let us consider a few examples:

- 1. It is easy to observe that the sun rises in the east and sets in the west. The moon and the planets do the same. This information is certainly useful. However, it is only when we realize that the earth spins on its axis once every 24 hours from west to east, that the information about the rising and setting of heavenly bodies acquires a meaning. We then understand that, because of the earth's rotation, all heavenly bodies would appear to rise in the east and set in the west.
- 2. We know that any object thrown up will eventually fall down. We know that if we wish to move an object faster, we have to push harder. However, once we learn Newton's laws of motion, all these experiences become understandable and predictable. Newton's laws provide a framework into which all our mechanical experiences fit.
- 3. As you study chemistry, you will learn that some elements like sodium, potassium and oxygen are very active, and that they form compounds with other elements rather easily. On the other hand, there are some other elements like neon, argon and helium that just do not react with other elements. In the absence of a pattern you will have to remember this information for each individual element. However, the periodic table of elements presents you with a useful pattern in which elements of the same group have similar properties.

who fumble their way to new ideas and then verify them, aided chiefly by hard work and intellectual honesty. Without some knowledge of the history of science, students naturally imagine that science is the story of a few great men who somehow came upon their truths in a flash of genius. . . the work of getting more familiar with history is rewarding — even fun. To the austere world of scientific facts, history brings what one eminent scholar called "the smell of human flesh". Authentic history replaces the old, sterile marble statues of scientists with real men and women. One can watch these people, still vividly alive to the informed mind, struggling with new ideas with all the confusion of the most ignorant student. It is only where such real people are found that real science can be found'.(2)

Human progress in science began in the prehistoric era. The very first observations about trees, animals and different events happening in nature must have prompted human beings to keep records of these things. When such observations became numerous they began to classify them. Thus classification first evolved in biology (the living world), before enriching other branches of science.

The periodic table is the result of such attempts at classification in chemistry. All the known properties of chemical elements were systematically studied and organized to see if a pattern emerged. Eventually, when such a pattern did emerge, it was really successful. It fitted in with all the known information. Besides, it helped predict elements not yet discovered and also acted as a corrective device in some cases.

The periodic table of elements has several distinctions to its credit. It withstood major crises created by discoveries of new elements such as the inert gases, rare earths and radioactive elements. The most amazing fact about the periodic table is that it achieved its final form even before the discovery of atomic structure which eventually and correctly provided the basis for the periodic table.

It will be interesting to read the story of the periodic table. In our book we have taken care to use facts and concepts which will be easily understood by secondary/higher secondary students. Where we have to use concepts or skills somewhat above this level, we have explained them in considerable detail in boxes alongside the main text. Interesting facts about scientists mentioned in the text are also provided in boxes. The six chapters of this book tell you the history of the periodic table. In the appendices you will find some additional useful and interesting information. When there is a quotation in the text you can look up the number in the list of references to find its source.

# 1. THE CONCEPT OF ELEMENTS

The word element has a variety of meanings. The Oxford dictionary gives several meanings for the word, depending on the context in which it is used. For example, an element is (1) one of the simplest parts into which something can be divided, (2) something which is present in small quantities in a larger whole, (3) one of the basic parts of a branch of knowledge, such as the elements of mathematics, (4) a natural element, like wind or water, or (5) in mathematics, a member of a set!

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Even in the context of chemistry, the word element has two distinct meanings:

- 1. the elements of chemistry—the basic principles of chemistry;
- 2. the chemical elements—the basic substances which are fundamental units of complex materials.

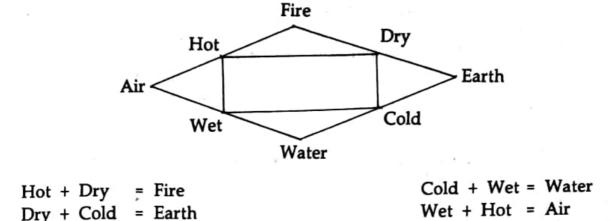
In this book the word 'element' is used in the second context.

While observing the enormous variety of living and non-living objects in nature, thinkers began to wonder whether this complexity could be built up of just a limited number of basic units. This thinking was probably based on their experiences; for example, a variety of words could be produced using a limited number of letters of the alphabet, a few ingredients in the kitchen could produce different dishes, three basic colours could produce a whole variety of shades, etc. The concept of matter being made up of chemical elements probably developed along the same line of thought.

Various attempts were made to identify these 'elements'. The Greek philosophers of ancient times (around 500 BC) tried to identify different substances as elements. Thales (624–546 BC) thought of water as the fundamental substance. Anaximenes (about 570–500 BC) suggested that it was air, whereas Heraclitus (about 540–475 BC) thought it to be fire. Empedocles (around 490–430 BC) suggested that there were four basic elements, namely water, air, fire and earth. To this list Aristotle (384–322 BC) added a fifth—ether, the element of the heavens. However, for centuries the four elements (air, water, fire and earth) were accepted as the elements or building blocks that made the universe.

Other philosophers from different countries (mainly China and India) also suggested similar substances as elements. The number of elements listed rarely exceeded five.

The pioneering attempt at classification of elements (we could call it the first table of elements) was represented as follows:

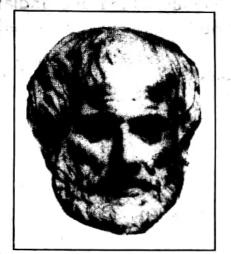


Based on this model, Aristotle explained certain phenomena and certain reactions. For example,

- Hot or cold was explained on the basis of presence or absence of fire.
- 2. Solids were substances devoid of water.
- It was concluded that wood is made of earth and fire, as on burning it gives ash and heat.

The apparent reasonableness of such explanations and the overall respect commanded by Greek philosophers, and especially by Aristotle, gave credibility to this model which prevailed for centuries to come.

Even later, when people began the study of alchemy, false views prevailed with respect to certain elements. One such myth surrounded the element gold. Gold occurs in nature in the elemental or native form. That is, gold is usually found as gold nuggets, and not as an ore from which the metal has to be extracted. Gold was, in fact, one of the first metals to attract man's attention, mainly because of its sparkling yellow colour. It is a beautiful metal, soft, ductile and malleable, easily worked upon and cast. It is, therefore, suitable for artistic work. In ancient times, it was indeed used mainly for ornamental or artistic objects. With the progress of civilization, the exchange and transport of various materials and goods (that is, trade and commerce) gained importance. Soon there was need for a medium of exchange to replace the barter system. Gold, along with silver



## Aristotle (384-322 BC)

Aristotle was a Greek philosopher who achieved great fame and influenced the thinking of scholars for several centuries. His father was a physician attached to the court of Macedonia and is said to have introduced Aristotle to the natural sciences. At the age of 17, Aristotle went to Athens where he attended the school of Plato (another great Greek philosopher) for twenty years. He left Athens when Plato died in 347 BC and tried to establish his own school. Soon, Philip II of Macedonia invited him to teach his son who became the conqueror, Alexander the Great.

When Philip II died in 335 BC Aristotle returned to Athens and founded his school called the Lyceum. The building had a large covered court where Aristotle taught his students, walking as he spoke, as some of your teachers may do in the classroom. After the death of Alexander the Great, there was an anti-Macedonian wave, and Aristotle was forced to flee. He died in exile at Chalcis in 322 BC.

Aristotle was a great teacher and a prolific writer. He wrote exhaustively on many subjects, but most of his writings are lost. For example, his 'Popular Writings' which were in dialogue form, and his 'Memoranda' which was an encyclopedia of known facts, are both lost. However, many of his treatises on philosophy and natural sciences were saved by the Arab philosophers. These books cover an astonishingly wide spectrum from the science of poetry and literature to ethics, morality, political science, and natural sciences.

The influence of Aristotle continued for centuries. His views were accepted as gospel truth and were not questioned. Unfortunately, experimental science was not yet born and some of Aristotle's views were not checked experimentally. Do you know that Aristotle once stated that women have fewer teeth then men, and no one even bothered to verify his statement? His influence was so great that even today, a person who shows off or acts too smart is rebuked: 'Who do you think you are—Aristotle?'

Before you criticize Aristotle for his mistakes, remember that he was the pioneer of organized research. At one time, with the support of Alexander the Great, he had nearly one thousand people working for him in Greece and Asia, collecting material for his 'natural history'. As H.G. Wells observed, '... nothing of the kind had ever been attempted, had even been thought of, as far as we know, before his time. . . . The students of the Lyceum under his direction made an analysis of 158 political constitutions.'(3) Endowed with a remarkable intellect combined with strong common sense and various organizational skills, Aristotle pioneered efforts in the western world to acquire and systematize information.

and copper, became the main medium of exchange. Gold thus gained further value and importance. Efforts were, therefore, made to search for natural gold and also to convert other baser metals like iron and copper into gold. In the middle ages, alchemists (the forerunners of modern chemist) began to search for the mythological *Philosophers' Stone* which they believed could change base metals into gold.

Around AD 800, an Arabian alchemist, Jabir, suggested that all the metals were made of sulphur and mercury. This theory does not seem all that absurd when one remembers that many metals occur in nature as sulphides and that heating these sulphides produces sulphurous fumes and, often, free molten metal which resembles mercury.

#### Gold

The element gold was among the first few metals known to man. Gold has always been synonymous with beauty, wealth and power. Gold is truly 'noble'. It does not get corroded and can be preserved easily. It was, therefore, considered a symbol of immortality. Unlike other metals which have to be extracted from their ores, often using complex and expensive processes, gold is found in pure form. All one has to do is to collect small particles of gold mixed with soil. Simply wash away the soil and you get gold, or collect gold nuggets if you are lucky. For these reasons, ancient people, especially the rich and powerful collected huge quantities of this element. The following story will give you some idea about the quantities of gold collected by ancient peoples.

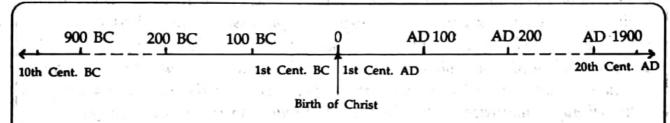
On 6 November 1922, Howard Crater, a British archaeologist, discovered an Egyptian tomb. It was that of Tutankhamun, the boy Pharaoh who died in his eighteenth year, around 1350 BC. He was also known as king Tut, the foremost cultural ambassador of ancient Egypt.

The weight of Tutankhamun's coffin (well over one ton) puzzled Crater. When it was opened, it revealed another coffin decorated with gold leaves and inlaid with a mosaic of multicoloured glass. Inside the second coffin was a third one, made of solid gold. This innermost coffin weighed 1100 kg. (If we take a price of Rs 3000 per 10 g, the approximate value of 1100 kg of gold works out to Rs 33 crores!) Inside the solid gold coffin, lay the mummy of Tutankhamun; this too was covered with a solid gold funerary mask.

Gold has also served as medium of exchange. In ancient times gold was used as currency in international trade. It is interesting to note that even though India never produced much gold, her flourishing trade ensured that gold flowed in from all parts of the world. It is only after the Industrial Revolution in Europe, that the trade began to reverse its direction.

Along with the quest for the Philosophers' Stone, chemistry gained importance as a result of the need for medicines. The growing concern for health and its maintenance generated various views about the elements. People who undertook this search for medicines were referred to as introchemists. Paracelsus, the famous introchemist of the 16th century, suggested that all matter was composed of mercury, sulphur and salt. He considered these substances to be the principles of matter and elevated them to the status of elements.

The 17th century saw the birth of experimental science. It also saw the evolution of the scientific method. Natural philosophers (scientists) started performing experiments in laboratories to identify causes of phenomena observed in nature. Robert Boyle (1627–1691), a noted experimental scientist, gave a new definition of an element, which was indeed close to the modern concept. He defined an element as a substance which cannot be broken down into simpler constituents. He stated further that an element combines with other elements to give a compound (which he referred to as a mixture), but it cannot combine with itself to produce a compound (which he referred to as a texture).



#### How are centuries counted?

Sir Isaac Newton was born in December 1642. In which century was he born? A common mistake is to regard 1642 as being in the 16th century. However, the correct answer is that the year 1642 belongs to the 17th century. If you are perplexed, consider the following example:

Suppose Sunil Gavaskar is batting with (say) 162. Which century is he making? Obviously, the 2nd. Remember the same when you refer to the 17th or 18th century. With this method of counting centuries, it is obvious that we are living in the 20th century and looking forward to the 21st century.

Here's another point to remember: The years of modern calendar are associated with Christ. Periods before Christ are referred to as BC. Thus, the fifth century BC refers to an earlier period than the third century BC. That is why, in the case of people who lived in an era before Christ, the year of birth is larger number than the year of death. For example, Alexander the Great was born in 356 BC and died in 323 BC.



# The basis for chemical equations

The work of alchemists had established that in the process of experiments with chemical compounds one could end up with new ones. What exactly was happening in the process? Were new atoms being created? Was matter 'conserved' or was it created or destroyed? This question bothered the chemists of the 18th century.

The conclusive answer came soon after Joseph Priestley discovered oxygen in 1774. Antoine

Laurent Lavoisier repeated and modified these experiments to prepare oxygen and to test its properties. He also conducted a series of experiments to settle the conservation issue. Remember that Lavoisier, a true scientist, did not jump to any conclusion on the basis of a single experiment. He conducted a large number of experiments which all pointed to the same conclusion.

Lavoisier took mercury in a sealed glass vessel and weighed it accurately. The vessel was then heated in an oven for 14 days. The mercury in the vessel reacted with the oxygen in the air trapped in the vessel to form red oxide of mercury. Slow heating over 14 days ensured that all the mercury was converted into its oxide. He then allowed the vessel to cool and weighed it accurately. The two weights were exactly the same. No mass had been created or lost. It was also noticed that when the seal of the vessel was broken (carefully to preserve the tiny glass fragments) air hissed through. Obviously, air rushed in to replace the oxygen used in the reaction. Lavoisier carefully weighed the vessel (with the broken glass fragments) to determine the weight of the air that had entered the vessel.

You know that red oxide of mercury heated to high temperature decomposes to liberate oxygen leaving behind only mercury. This Lavoisier achieved by focusing sunlight on the red oxide using a convex lens. The oxygen liberated in the reaction was collected carefully and weighed. It was found that the weight of the oxygen collected was precisely equal to that of 'e air that had entered the vessel in the first part of the experiment. In other words, mass was conserved in chemical reactions. The experiments of Lavoisier are often mentioned in the context of preparing oxygen. However, the real importance of these experiments lay in providing conclusive evidence for the conservation of mass. In fact, they provided the justification for writing a chemical equation.

These experiments were the first major blow to Aristotle's choice of elements which had gone unchallenged for almost 2000 years. Science no longer depended on written arguments and suppositions. These had to stand the crucial test of experimental verification.

Unfortunately for the science of chemistry, Lavoisier fell an innocent victim to the French Revolution. He died on the guillotine at the age of 50.

In the year 1776, while studying the reactions of an acid on a metal plate, Henry Cavendish (1731–1810) discovered a highly inflammable gas. He collected the gas over mercury and tested its properties. Another scientist, Joseph Priestley (1733–1804), had discovered in 1774 a gas obtained by heating mercuric oxide, in which substances burned more brightly than in air. Antoine Lavoisier (1743–1794), the French chemist, showed that by burning together the inflammable gas discovered by Cavendish and the gas discovered by Priestley, water was produced. Its weight was equal to the sum of the weights of the two gases. Lavoisier named the inflammable gas hydrogen and the other gas oxygen. Thus, supporting Boyle's theory, he concluded that water was a compound of the elements hydrogen and oxygen.

#### Scientific method

A large number of events occur around us. A stone thrown up first rises and then falls. Sugar dissolves in a cup of tea. Visibility improves after a sharp shower.

What causes such events? We now know, thanks to the efforts of several brilliant scientists, that events such as these occur because of natural forces and properties. It is possible to understand and describe these forces and properties. In other words, we can describe and explain most of events occurring around us. We can also predict some events.

Many thinkers say that this process of generating descriptive and explanatory frameworks is the essence of science. Does that mean that we can know everything? Not at all. For instance, while we generally know why earthquakes occur, we still cannot predict earthquakes. We are also only beginning to learn to predict weather. On the earth and in space, there are still natural events and phenomena which haven't yet been thoroughly understood and explained.

It is scientific method which is the key to these unsolved problems. We should always keep an open mind and be ready to change our descriptive and explanatory frameworks if new information demands such a change. In this book you will come across many examples of scientists changing their views in the light of new information. Remember, this is a continuous process.

What we have said above applies also to social sciences. Why do prices of commodities rise or fall? Why are some nations rich and others poor? Why do groups in a society feel angry and dissatisfied? Why do people go to war? We are just beginning to learn about social forces and understand social behaviour.

# Discovery of new elements

The efforts of alchemists and iatrochemists indirectly led to the discovery of several new substances, mainly acids and alkalis. It also helped in the development of various types of apparatus essential for experiments, and in improving experimental skills. The work of Robert Boyle and Lavoisier in the 17th and 18th centuries clarified the nature of elements. With better understanding of the concept of elements and with better equipped laboratories, scientists began to concentrate on discovering new elements.

In the last decade of the 18th century and in the first decade of the 19th century (from 1794 to 1804), the elements chromium, vanadium, niobium, tantalum, cerium, palladium, rhodium, iridium and osmium were discovered. An important invention which enhanced the rate of discovery of elements was Volta's cell. Alessandro Volta (1745–1827) constructed this cell by piling alternate discs of copper and zinc, each pair separately by a piece of cloth soaked in brine (salt water). This cell provided a steady and reliable source of electricity, and placed in the hands of chemists a new and powerful tool for separating elements. Using the cell, it was possible to pull apart positive and negative ions and to deposit them on electrodes. In later chapters of this book you will come across more examples of how new inventions and techniques have served basic scientific research.

The English chemist, Sir Humphry Davy (1778–1829), working at the Royal Institute, London, isolated extremely active metals using Volta's cell. In 1807, he isolated sodium and potassium by passing an electric current through molten sodium hydroxide and potassium hydroxide, respectively. He used this technique effectively with compounds of other metals and within a year he was able to isolate calcium, strontium, barium and magnesium. The discovery of sodium and potassium was vital as both these elements are powerful reducing agents. These elements thus enriched substantially the tools of chemists who could use them to reduce several elements from their compounds. Jons Jakob Berzelius (1779–1848) discovered selenium, silicon, zirconium, titanium and thorium, all with the help of potassium as a reducing agent. All these elements, along with boron, lithium, cadmium, aluminium and vanadium, were discovered by 1830.

# Who discovered chemical elements?

The history of the discovery of elements is an instructive story that began during prehistoric times when man discovered fire and noticed the carbon from burnt wood left in the forests. Actually, some substances like the seven metals—silver, gold, copper, lead, iron, tin and mercury, and two non-metals—sulphur and carbon, were known from biblical times and even before. But they were not recognized as elements. It is only relatively recently that scientists realized that these substances were elements. All these elements occur either in the free state in nature or in the form of ores composed of compounds that can be decomposed easily using primitive techniques like simple heating or heating in the presence of carbon.

Between the 12th and 15th centuries, that is, in the middle ages, the work of alchemists led to the discovery of elements like arsenic, antimony and bismuth.

Little is known about the individuals who discovered these elements. The first fortunate man to be credited with discovery of a chemical element was German alchemist, Henning Brand (1630-\*) who in 1669 succeeded in isolating a substance which he named phosphorus. This discovery was an important event in the history of chemistry, as it marked the beginning of a new era, when people started keeping detailed records of their experiments.

(\* The year of Brand's death is not known).

## Chemical symbols

From ancient times man has used symbols to denote objects, actions and events, and chemical elements are no exception. The first symbols assigned to elements were pictorial. The simplest ones were those used to represent the four basic elements of ancient times:

Fire	$\triangle$	,	Air	Δ
Water	$\nabla$		Earth	$\forall$

In the case of the seven elements known to the ancients, each one of them was paired with a heavenly body and its symbol was fixed accordingly. For example,

Gold (Sun)	(Solar	disc)
------------	--------	-------

Silver (moon)		(Crescent moon)	
Copper (Venus)	Q	(Mirror of Venus)	
		from time to time. In	

New symbols were added from time to time. In 1787, J.H. Hassenfratz and P.A. Adet presented new and simplified symbols. For example, in the case of non-metals, simple geometric characters were used:

Oxygen — Nitrogen /
Sulphur — Phosphorus —

Circles containing simple abbreviations were used to represent the metals. For example:

Copper © Iron Fe

Around 1805, John Dalton (1776-1844) used circles with different internal markings as symbols of elements. For example:

Oxygen O Sulphur Hydrogen O Nitrogen O

The ultimate credit for developing the symbols used today goes to J.J. Berzelius (1779–1848). He suggested in 1813 that abbreviations of names of elements could be used as their symbols. This simple and powerful idea was soon accepted widely. He suggested certain rules regarding the selection of symbols:

 In the case of non-metals, the initial letter could be used as the symbol for that element. For example, carbon—C, oxygen—O, hydrogen—H.

- In the case of elements whose names start with the same alphabets, the symbols should be formulated using the first two letters of the word. For example, silicon—Si and selenium—Se.
- If the first two letters are found to be common, then the initial letter
  along with the first consonant which is not common should be used
  for one of the elements. For example, calcium—Ca and cadmium—Cd.

Even today, many symbols given by Berzelius are in use. Obviously, there has to be a uniformity in the use of symbols. This is now looked after by the International Union of Pure and Applied Chemistry (IUPAC). It has given English names to all the elements but has retained some symbols which originated from the Latin names of those elements. An appreciation of the origin of chemical names of elements is useful in developing familiarity with the shorthand language of chemistry. For example, Antimony—Sb (from the Latin name Stibium). Similarly, Copper—Cu (from the Latin name Cuprum), Gold—Au (from the Latin name Aurum) and Iron—Fe (from the Latin name Ferrum).

# The language of symbols

Chemical elements are represented by symbols. For example, phosphorus—P, silver—Ag, sodium—Na. Many of you may wonder whether these symbols are really useful, but if you think about it you'll see that we use symbols not only in chemistry but in several other disciplines; in fact in everyday life. These symbols make our life easier.

Consider the following statements:

Ram has a few oranges. If you double the number of his oranges, add four to it and multiply the result by three, you get thirty-six. Can you remember this statement? Now, let us put it in symbolic language.

$$3(2x + 4) = 36$$

Is it not a better way of expressing the same statement?

You will notice symbols almost everywhere, on roads, in hospitals and even in advertisements. Do you know the meaning of the following symbols?









However, in order to ensure that a given symbol conveys the same meaning to everyone, it is necessary to agree to some universal convention. What a mess it would be if you wrote Na for sodium while your friend preferred to write So and few others chose Sd!

#### 2. DALTON'S ATOMIC THEORY

While the credit for proposing the first atomic theory goes to the ancient Greek philosophers of the 5th century BC, these ideas were essentially philosophical. Ideas relating to issues such as the nature of matter and the discontinuity versus continuity of matter, were speculative in nature and were debated on the basis of pure logic.

The Atomic School, originated by the Greek philosopher Leucippus (about 400 BC-?) and his student Democritus (about 470—380 BC) thought that matter was discontinuous and the subdivision of matter could ultimately yield an atom, the ultimate indivisible particle. However, this concept was rejected by Aristotle, and his followers supported the continuous nature of matter. In 1650, that is almost 2000 years later, a French philosopher Pierre Gassendi, reconsidered the concept of atom in the context of the behaviour of gases. Both Robert Boyle (in his book *The Sceptical Chemist* in 1661) and Sir Isaac Newton (in his book *Principia Mathematica* in 1687) supported the concept of atoms.

In the early years of the 19th century, John Dalton revived the concept of atoms in his famous atomic theory and supported it with experimental evidence available to him. Dalton's atomic theory is an important milestone in the history of chemistry. John Dalton had before him laws of chemical combinations which were extracted from data collected over the years by alchemists, and which were also based on precise quantitative measurements made by physicists and chemists. All this mass of information made sense only if one assumed that elements are composed of small indivisible particles called atoms (a—not, tomio—to divide) which participate in a chemical reaction. The genius of John Dalton realized this, and expressed it clearly in three principles:

- Elements are composed of extremely small indivisible particles called atoms. All atoms of an element are identical with respect to their mass, size and properties.
- Atoms of different elements have different properties. In the course of chemical reactions, no atom of one element disappears or is changed into an atom of another element.



# John Dalton (1766-1844)

John Dalton, an English scientist, was the son of a poor weaver. His formal education was very limited and he was essentially a self-made man. For most of his life he worked as a teacher.

Dalton had varied interests. He began his scientific work in the field of meteorology, keeping systematic weather records every day for almost 46 years, and wrote a book on weather. He was one of the first scientists to study colour-blindness, a subject of considerable personal interest since he himself was colour-blind. But John Dalton is best known for his important contribution to chemistry. He revived

the concept of atomicity of matter and put forward his famous atomic theory. There is, however, an important difference between Dalton's theory and the philosophical views of the ancient Greek thinkers. Dalton's theory of atoms 'explained' the laws of conservation of mass. Also, the law of definite proportions followed as a logical consequence of Dalton's theory. It stood yet another crucial test. It was able to predict the law of multiple proportions.

During the years in which Dalton was carrying out his researches in England, the soldiers of the British East India Company were busy extending and strengthening their hold on our country. The armies of a number of Indian kingdoms, including those of the powerful Maratha Empire, were reeling back in the face of superior offensive weapons and military organization. When tracing the history of science, it is interesting to occasionally consider what was happening in our country while major scientific developments were taking place elsewhere. Try and do this in some other cases and think about what the comparisons show.

A compound is formed when atoms of more than one element combine.
 In a given compound, the relative number of atoms present will be definite and constant. These relative numbers can be expressed as integers.

Dalton's theory offered a simple explanation for the basic laws of chemistry known earlier.

#### 1. Law of conservation of mass

The law of conservation of mass was put forward by Antoine Lavoisier (1743–1794) in 1785. It states that there is no detectable change in mass in the course of a chemical reaction. Postulate 2 of Dalton's theory explained this law. As atoms are conserved in chemical reaction, mass also is conserved. (Lavoisier designed direct and convincing experiments to demonstrate conservation of mass. See the box, 'The basis for chemical equations', on page 9.)

#### 2. Law of constant proportion

In 1799 it was suggested by Joseph Proust (1754–1826) that a compound, regardless of its origin or method of preparation, contains the same elements in the same proportion of their masses. If the ratio of atoms in a given compound is constant (postulate 3 of the theory), their proportion by mass must be fixed, since all atoms of one element have to be identical.

The importance of a theory depends upon its ability to fit in with and explain all the available data, and even more importantly on its ability to predict new observations. Dalton's theory stood both these tests and at the same time was simple and elegant. It explained the law of conservation of mass and the law of constant proportion. Dalton used this theory to predict the law of multiple proportion which states that, when two elements combine to form more than one compound, the masses of one element which combine with a fixed mass of the other element are in a simple ratio of small whole numbers.

This law can be illustrated with the help of two compounds of carbon and oxygen, namely, carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>).

The elemental analysis of 1 g of CO shows that it consists of 0.57 g of oxygen and 0.43 g of carbon.

Ratio of oxygen of carbon in CO

$$= \frac{0.57}{0.43} = 1.33$$

That is, 1.33 g of oxygen combines with 1 g of carbon to form CO.

Similar analysis of 1 g of CO<sub>2</sub> shows that it consists of 0.73 g of oxygen and 0.27 g of carbon.

Ratio of oxygen to carbon in CO2

$$= \frac{0.73}{0.27} = 2.67$$

That is, 2.67 g of oxygen combines with 1 g of carbon to give CO<sub>2</sub>.

Thus, in these two compounds the ratio of masses of oxygen that react with 1 g of carbon = 2.67 : 1.33 = 2 : 1 which is a simple integral ratio, supporting Dalton's law of multiple proportion. Dalton assumed that, in the case of carbon monoxide, one atom of oxygen combines with one atom of carbon, while in carbon dioxide, two atoms of oxygen combine with one atom of carbon. That is why we can write carbon monoxide as CO, and carbon dioxide as CO<sub>2</sub>.

This law was found to be valid for analytical data obtained by other workers. Another example of the law of multiple proportion is given below:

Compound	Mass of nitrogen (g)	Mass of oxygen (g)
Nitrous oxide (N2O)	28	16
Nitric oxide (NO)	28	32
Nitrogen trioxide (N2O3)	28	48
Nitrogen dioxide (NO <sub>2</sub> )	28	64

Thus the ratio of masses of oxygen that react with 28 g of nitrogen in the case of above compounds is 16:32:48:64. That is 1:2:3:4 which is an integral ratio. This law is of great importance as it firmly supports the theory of the atomic nature of matter.

In retrospect Dalton's atomic theory seems very simple and convincing. However, it had to face two hurdles in its time. Measurements in those days were few and not as accurate and reliable as those of today. The inaccuracies and uncertainties in experiments concerning the law of multiple proportion led to some scepticism. Moreover, atoms could not be seen. The abstract concept of atoms was so far removed from natural 'real' experiences that several decades had to elapse before this concept was accepted. It is interesting to know that a similar fate awaited relativity and quantum theories.

We have seen that Dalton's theory satisfied two conditions. It explained known facts, and it also predicted something new, that is, the law of multiple proportions. Dalton's theory has one more important facet: it stated that all atoms of the same element are identical in size, mass and properties. This statement indicates that atomic mass is a clear signature of the element. Quite obviously, size is not immediately useful since atoms are too small to be seen without powerful instruments. But mass can be measured readily. Thus, apart from their chemical properties, elements had one distinguishing property: their atomic mass. It is not surprising, therefore, that John Dalton was the first person to try to determine atomic weights.

# 3. ATOMIC WEIGHT DETERMINATION

As described earlier, atomic weight became the signature or identification mark of an element. Various people made efforts to determine the atomic weights of elements. Before describing their efforts, it is essential to understand the difficulties involved.

How can one determine the weight of one atom? In daily life, if we wished to determine the weight of (say) one grain of rice or wheat we would simply count one hundred or one thousand grains and weigh them. The rest would be easy. However, the problem of determining atomic weight was not so simple. How does one count atoms? In spite of this hurdle, the scientists of the nineteenth century devised indirect ways of determining atomic weights. Let us study some of their attempts.

Even to compare atomic weights of different elements, it is necessary to know:

- (1) the correct formula of a chemical compound, and
- (2) the combining weight of an element.

By the early nineteenth century chemists knew how to determine the combining weight of an element by elemental analysis of its compound. However, the correct formulae of compounds were not known. This was a major problem because the concept of the valence of an element was not yet properly understood.

In the absence of knowledge of valence, chemists started working on atomic weight determination by assuming some simple formulae for compounds. While reading about these efforts, it is important to remember that these chemists were groping their way in complete darkness. Credit must be given to them because it was their sustained efforts that ultimately clarified the picture.

#### Dalton

Dalton was the first person to determine the atomic weights of different elements. He calculated atomic weights on a comparative basis. He chose hydrogen, the lightest known element, and assumed its weight to be one.

Two methods to determine the atomic weights of other elements relative to hydrogen seemed possible:

- 1. Comparing the weights of an equal number of hydrogen and (say) oxygen atoms. However, Dalton did not know how to take the same number of atoms for two elements.
- 2. Determining the combining weight of an element with hydrogen.

Dalton used the second method. To find the atomic weight of oxygen relative to hydrogen he used water. It had been established by electrolysis of water that the mass ratio of hydrogen and oxygen in water is 1:8. To start with, Dalton considered two situations:

 In the first situation Dalton assumed that whenever two elements combine to form a compound they do so in a simple ratio, 1:1. Applying this rule to water he assumed the formula of water to be 'HO'.

Mass Ratio = 
$$\frac{1}{8}$$
 =  $\frac{Number\ of\ atoms\ of\ hydrogen\ imes\ weight\ of\ one\ hydrogen\ atom}{Number\ of\ atoms\ of\ oxygen\ imes\ weight\ of\ one\ oxygen\ atom}$ 

When one atom of hydrogen combines with one atom of oxygen, number of hydrogen atoms = number of oxygen atoms. So

$$\frac{1}{8} = \frac{Weight of one hydrogen atom}{Weight of one oxygen atom}$$

Thus, if the atomic weight of hydrogen is one, then according to Dalton, the atomic weight of oxygen is 8.

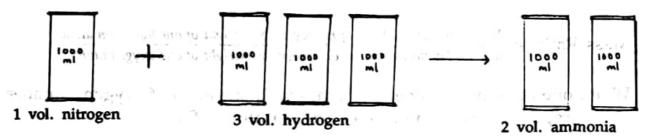
Dalton also considered complex situations where two elements A and B combine to form more than one compound. Dalton assumed that nature was simple. The compounds would be of the type AB, AB<sub>2</sub> or A<sub>2</sub>B, and not (for example) A<sub>13</sub>B<sub>41</sub>. Using this procedure he calculated the atomic weights of elements by analysing their compounds.

Dalton was a good theoretical chemist. However, he was not equally skilled in performing experiments (4). Many of his atomic weights had to be modified later. In spite of this shortcoming, Dalton's contribution is regarded (and rightly so) as a milestone in chemistry. It was Dalton who elevated speculative concepts regarding the atomic nature of matter, to the status of a theory. He also gave a method for comparing atomic weights.

#### Gay-Lussac

While studying chemical reactions in the gaseous phase, Joseph Gay-Lussac noticed that 1000 ml of oxygen gas requires 2000 ml of hydrogen gas to give 2000 ml of water in gaseous form. He further observed that 1000 ml of hydrogen chloride gas reacted with exactly 1000 ml of ammonia gas to give 1000 ml of ammonium chloride gas, whereas 1000 ml of carbon monoxide gas combined with 500 ml of oxygen gas to form 1000 ml of carbon dioxide gas.

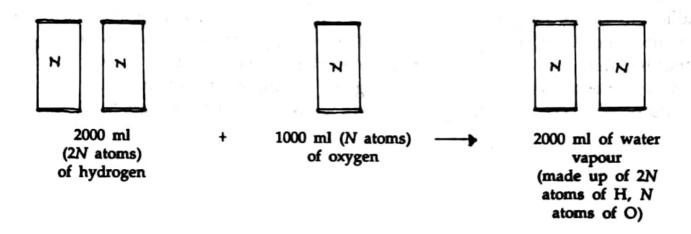
On the basis of these observations, in 1808, he formulated the 'law of combining volumes of gases'. It states that the volumes of gases that react with one another, or are produced in chemical reactions, are in the ratios of small integers, provided the volumes are measured under the same conditions of temperature and pressure. In other words, Gay-Lussac would expect,



But not, for example,

31 vol. nitrogen + 43 vol. hydrogen → 41 vol. ammonia.

We have seen before that mass is conserved in chemical reactions. It is clear from the above reactions that volumes do not obey the conservation law. For example, how do we interpret the process 2 vol. hydrogen + 1 vol. oxygen  $\rightarrow 2$  vol. water vapour? If one supposes that equal volumes of all gases under equal temperature and pressure contain the same number of atoms, then this picture becomes somewhat clearer. Let us assume 1000 ml of any gas contain (say) N atoms. One can therefore, write the reaction of formation of water vapour as follows:





# Gay-Lussac (1788-1850)

Joseph Louis Gay-Lussac was a French chemist. Like most scientists of his day, Gay-Lussac was interested in a variety of subjects. One of his interests was studying the composition of the atmosphere. In 1804, he launched a hot air balloon which rose to a height of 23,000 feet (7000 m), a record that remained unsurpassed for 50 years. Remember, there were no remote sensing electronic gadgets in those days. Gay-Lussac himself travelled in a basket attached to the balloon, to collect data.

Gay-Lussac's most important contributions were in chemistry. He studied chemical reactions

in the gaseous state, and discovered the famous law of combining volumes of gases. What is so great about this law? It is important to realize that Gay-Lussac pointed out that in cases of gases, volumes (at standard temperature and pressure\*, of course) are as important as mass! This insight paved the way for the discovery of molecules and Avogadro's hypothesis.

\* Standard temperature and pressure (STP): 76 cm of mercury and 273 Kelvin

However, the answer is not all that simple. Even if we suppose that one atom of oxygen combines with two atoms of hydrogen, that is, the formula of water is H<sub>2</sub>O, how can we produce two volumes of water vapour? If we have

then shouldn't we have

2 vol. hydrogen + 1 vol. oxygen → 1 vol. water vapour?

If one oxygen atom had to produce two units of vapour, the oxygen atom would have to split into two. Dalton would not allow this. Nor could he ignore Gay-Lussac's law as it was based on experimental observations. This conceptual difficulty led Dalton to propose that Gay-Lussac's experiments with gases were perhaps not accurate enough.

#### Avogadro

It was Avogadro who provided the missing link in 1811. Without splitting atoms, he clarified the conflict between Gay-Lussac's observation and Dalton's atomic theory.

Amedeo Avogadro suggested that gas does not exist in the natural state as single atoms. Two or more atoms group together to form a particle which Avogadro called an elementary particle. If during a chemical reaction such a particle were to split releasing individual atoms, Dalton's and Gay-Lussac's theories could both be satisfied. Today, we know that Avogadro was referring to molecules. Thus, to avoid confusion, we shall refer to Avogadro's 'elementary particles' as molecules. Along with the concept of molecules, he put forward an important hypothesis, now called Avogadro's hypothesis.



## Avogadro (1776-1856)

Amedeo Avogadro, an Italian physicist, was born just a few days before the American Colonies declared their independence from Great Britain. Like Dalton, Avogadro worked as a teacher throughout his life. While he taught physics, Avogadro, like his contemporaries, never hesitated to tackle any problem that caught his attention, whatever branch of science it involved.

He excelled in quantitative thinking and used his knowledge of mathematics in his scientific investigations.

Based on Gay Lussac's observations, Avogadro put forward the important concept of molecules. He also proposed a hypothesis which eventually acquired great importance in physics and chemistry. This hypothesis, which is now called Avogadro's hypothesis, states, 'Equal volumes of all gases contain an equal number of molecules under the same conditions of temperature and pressure.'

Avogadro's hypothesis ultimately enabled chemists to establish the correct relative atomic weights of various elements. Unfortunately, Avogadro's hypothesis was so far ahead of its time that he did not receive any credit for this outstanding work in his lifetime.

Today you know that a gram molecular weight of any element or compound contains the same number of molecules, namely,  $6.023 \times 10^{23}$ , a number known as Avogadro's number.

Avogadro's hypothesis states that equal volumes of all gases under the same conditions of temperature and pressure contain an equal number of molecules. That is, if one volume of gas contains N molecules under the same conditions of temperature and pressure, the reaction of hydrogen and oxygen to form water vapour can be written as:

2N molecules of hydrogen + N molecules of oxygen = 2N molecules of water

Avogadro suggested that each molecule of oxygen must contain two atoms. This diatomic molecule undergoes splitting and then reacts with hydrogen to form water. Thus,

$$2H_2 + O_2 \rightarrow 2H_2O$$

Do you realize the importance of Avogadro's hypothesis? It solves the difficulty of 'counting' atoms or molecules. Remember the difficulty scientists faced in trying to compare atomic masses. They could not count atoms/molecules since they could not see them. So there was no way of taking an equal number of atoms/molecules of two different elements.

## Was Avogadro crazy?

Avogadro's hypothesis is indeed a remarkable example of human brilliance. Remember, our daily experience is very different. Bags of equal size will NOT contain an equal number of grapes, potatoes or pumpkins. Was Avogadro crazy? Not at all. Note that Avogadro was talking of gases. Now, we know that 22.4 litres of any gas at normal pressure and temperature will have exactly 6.023  $\times$  10<sup>23</sup> molecules. What is the actual volume of all these molecules?

A typical small molecule has a radius of approximately  $1\text{\AA}$  (Angstrom, a unit of length,  $10^{-10}$  m or  $10^{-8}$  cm). The approximate volume of one typical molecule (assuming it to be more or less spherical)

$$\frac{4\pi}{3}$$
  $r^3 \approx 4 \times 10^{-8} \times 10^{-8} \times 10^{-8}$   $ml = 4 \times 10^{-24}$ 

[The value of  $\pi$  ( $\approx$  3.14) cancels with 3.]

Thus, the physical volume of  $6.02 \times 10^{23}$  molecules will be  $6.02 \times 10^{23} \times 4 \times 10^{-24}$  ml, which is approximately equal to 2.4 ml. This is just about a spoonful. The molecules are spread over the entire 22.4 litres at STP because they are in a gaseous state—they are darting around at high speed, colliding among themselves and with the walls of the container. They are not idle.

Going further than Avogadro's hypothesis, we now know that one gram mole of any substance in any form will have  $6.023 \times 10^{23}$  molecules. However, if we wish to take the same number of (say) sugar or salt molecules, we cannot go by volume. We have to go by weight.

Avogadro solved this problem for gases. Equal volumes of any two gases under identical conditions of temperature and pressure have the same number of molecules. This discovery was, therefore, very useful in determining atomic weights.

According to Avogadro, Gay-Lussac's observation was correct and the molecular formula of water should be H<sub>2</sub>O. The atomic weight of oxygen, therefore, comes out to be 16 on the basis of Avogadro's hypothesis, and not 8, as calculated by Dalton.

Unfortunately, Avogadro's hypothesis met the same fate as that of Gay-Lussac, and practically nobody paid much attention to it until it was revived by Stanislao Cannizzaro (1826–1910) and was used effectively for atomic weight determination.

#### Berzelius

Let us come back to the story of determining atomic weights. Berzelius's contributions to chemistry, namely the discovery of a number of elements and the development of symbols for chemical elements, have been discussed earlier. He also made important contributions towards the determination of atomic weights. A comparison of the atomic weights determined by Berzelius with their modern values exhibits the remarkable accuracy of his measurements in most cases.

Berzelius realized the importance of Dalton's atomic theory. He felt that if this theory was confirmed, it would have a great impact on the progress of chemistry. He also realized that accurate determination of the atomic weights of elements would provide a crucial test for this theory. He, therefore, set out to solve the problem of atomic weight determination.

To explain Gay-Lussac's observations, Berzelius assumed that a unit volume of any gas (assuming equal temperature and pressure) contained the same number of atoms or molecules. The same was suggested by Avogadro in 1811, though there is no recorded evidence to show that they knew of each other's work.

Berzelius combined the experimental results of Gay-Lussac with his own ideas and concluded that the molecular formula for water was H<sub>2</sub>O. He then inferred that the atomic weight of oxygen was 16. Berzelius used Gay-Lussac's law as a guideline and undertook a study of various compounds of different elements. He used the concept of analogy to assign a formula to a compound and proceeded to determine the atomic weights of various elements. For example, by analogy of sulphides and oxides, he assumed the formula of hydrogen sulphide to be H<sub>2</sub>S like H<sub>2</sub>O. By extending his studies to selenium and tellurium which indicated their relationships with



#### Berzelius (1779-1848)

Jöns Jakob Berzelius, a Swedish chemist, made several contributions to the field of chemistry. In fact, he is considered as one of the pioneers of modern chemistry. By meticulous analysis of about 2000 compounds, he obtained accurate atomic weights for most of the known chemical elements. The language of symbols and formulae is based essentially on the system suggested by Berzelius. He also played a major role in the discovery of of several elements and contributed to the development of electrochemistry.

At the age of 29, Berzelius was elected to the Stockholm Academy of Sciences. He was honoured on his wedding day with the title of Baron by the king of Sweden, Charles XIV.

sulphur, he assumed their hydrides to be H<sub>2</sub>Se and H<sub>2</sub>Te respectively. Berzelius had to work with gases since Gay-Lussac's law is applicable only to gases. He also had to study compounds containing hydrogen (whose weight was taken as the standard).

Choice of hydrogen as the reference element meant that Berzelius's work had to be confined to a few elements that combine with hydrogen to form hydrides. What about the elements that did not form hydrides? Berzelius therefore changed his reference from hydrogen to oxygen, whose atomic weight was already inferred as 16. From the determination of the elemental composition of oxides by chemical analysis, one can find the atomic weight of an element provided the formula of its oxide is known. Berzelius assumed certain rules to arrive at the formulae of oxides. Chemists of that era believed that if two elements A and B combined to form a compound, they did so in simple ratios like AB, AB<sub>2</sub> or A<sub>2</sub>B. Berzelius extended this list to include AB<sub>3</sub>, AB<sub>4</sub> and also A<sub>3</sub>B and A<sub>4</sub>B, but insisted that either A or B must be one. Thus, Berzelius extended the ideas of his colleagues, but ignored, to begin with, the possibility of combinations like A<sub>2</sub>B<sub>3</sub>.

Subsequently, Berzelius filled this lacuna. After 1818 he made an exhaustive study of oxides. He prepared oxides of different elements and then analysed them for their oxygen and metal contents. Altogether, he analysed almost 2000 compounds, and each several times. This gives us some idea of the enormous amount of work that he carried out for the careful determination of atomic weights.

In 1819, two important discoveries were made in physical chemistry which were exploited fruitfully by Berzelius for atomic weight determination. These were:

- (1) the law of Dulong and Petit, and
- (2) the law of isomorphism.

#### Law of Dulong and Petit

The relationship between the specific heat and the atomic weight of an element is known as the Law of Dulong and Petit. It was published in 1819 by two French scientists, Pierre Dulong (1785–1838) and Alexis Petit (1791–1820).

Dulong and Petit noticed that in the case of elements in the solid state, especially metals, the product of specific heat and atomic weight was a constant. (The specific heat of a substance is defined as the amount of heat required to raise the temperature of one gram of the substance through 1°C.)

The results obtained by Dulong and Petit are shown below:

Element	Specific heat cal/°C/g	Atomic weight O=1g	Product of atomic weight and specific heat cal/°C	Atomic weight O=16g	Product of atomic weight and specific heat cal/°C
Bismuth	0.0288	13.30	0.3830	209.0	6.0
Lead	0.0293	12.95	0.3794	206.0	6.1
Gold	0.0298	12.43	0.3704	197.0	5.9
Platinum	0.0314	11.16	0.3740	195.0	6.1
Tin	0.0514	7.35	0.3779	119.0	6.1
Silver	0.0557	6.75	0.3759	108.0	6.0
Zinc	0.0927	4.03	0.3736	65.4	6.1
Tellurium	0.0912	4.03	0.3675	128.0	11.7
Copper	0.0949	3.957	0.3755	63.5	6.0
Nickel	0.1035	3.69	0.3819	58.7	6.1
Iron	0.1100	3.392	0.3731	55.8	6.1
Cobalt	0.1498	2.46	0.3685	58.9	8.8
Sulphur	0.1880	2.11	0.3780	32.1	6.0

Note that Dulong and Petit took the atomic weight of oxygen as 1. If, however, they had used the correct atomic weight, that is 16, the product of atomic weight and specific heat would be about 6 cal/°C as shown in the last column. In the above table the products for elements tellurium and cobalt differ from the constant, that is, from 6 cal/°C. This was due to the fact that Dulong and Petit had incorrectly estimated the values of specific heats for these elements.

Even though the law was an empirical one (that is, there was no theoretical proof or explanation available), Dulong and Petit suggested that it could be used for the determination of approximate atomic weights. To determine the atomic weights of the element, it would be enough to know its specific heat.

Berzelius used this law to cross-check the atomic weights he had obtained by chemical methods of analysis. In some cases he noted discrepancies, that is, his value of atomic weight × specific weight did not tally with the table of Dulong and Petit. In such cases, Berzelius changed the formula of oxides of certain metals from XO<sub>2</sub> to XO (X=metal) and obtained the correct atomic weights for metals like gold, zinc, lead, copper, iron and tellurium.

What does the law suggest? The law indicates that the same amount of heat (that is, 6 cal) is required to raise the temperature of one gram atomic weight of an element through 1°C irrespective of whether the element is gold, copper, lead or iron. It means that the heat absorbed depends mainly

# Heat capacity and specific heat

Usually the word specific means relative. Thus, density is expressed as weight/volume but specific gravity of any substance is the ratio of its density to the density of water. Since the density of water is 1 g/cm³, the two numbers, that is, density and speific gravity are the same. However, density is expressed in units, e.g. g/cm³, while specific gravity is a pure number. Similarly, the heat capacity of a substance is the heat in calories required by one gram of the substance to raise its temperature by 1°C. Specific heat was then defined as ratio of the heat capacity of that substance to the heat capacity of water. Interestingly, the heat capacity of water is the highest, and turns out to be 1. You need 1 calorie of heat to raise the temperature of 1 ml or 1 g of water by 1°C. Once again the two numbers expressing heat capacity and specific heat should be the same, but they would not have the same units. Specific heat would be a pure number. However, these days this difference is dropped and specific heat is defined as heat required to raise temperature of one gram of the material by one degree celsius (callg/°C).

on the number of atoms present in one gram atomic weight of the substance and not on the kind of atoms. We now know that one gram molecular weight of any element (that is, one mole) contains the same number of molecules (particles) equal to Avogadro's number,  $6.023 \times 10^{23}$ . We also know that the molecules of metals are monoatomic. That is, in the case of metals, one gram atomic weight will contain  $6.023 \times 10^{23}$  atoms. As the number of particles receiving heat is constant, the product, atomic weight  $\times$  specific heat, turns out to be a constant.

## Law of Isomorphism

We said at the beginning of this book that chemistry is a fascinating subject. Here is yet another instance where nature reveals its magnificent architecture. You know that several substances crystallize. Diamond is a crystal. Common salt, potassium permanganate, copper sulphate, alum and several other chemicals crystallize. But not all crystals are alike. Some common forms are described in the box on page 32. Do you think that the crystal structure and the nature of the chemical could be related? Why should these two seemingly unrelated things be related? Here is a surprise for you.

Eilhardt Mitscherlich (1794–1863) studied various chemical compounds and their crystalline forms. He found a relationship between crystal forms and chemical composition. From such a study, he inferred the law of isomorphism which states that compounds which form similar types of crystals have similar chemical compositions.

Mitscherlich found that the compounds potassium sulphate  $(K_2SO_4)$  and potassium selenate  $(K_2SeO_4)$  are isomorphous compounds, that is, they form similar types of crystals (rhombic). He studied the isomorphism between perchlorates and permanganates; arsenates and phosphates, chromates, sulphates and manganates and also among other compounds.

By using this law, it became possible to infer the chemical formula of an unknown compound. For example, suppose we know that potassium perchlorate is isomorphous to another compound which is made of potassium, manganese and oxygen. The chemical formula of potassium perchlorate is known to be KClO<sub>4</sub>. By using the law of isomorphism, we can infer the chemical formula of the unknown compound to be KMnO<sub>4</sub>.

This law can also be used for the determination of atomic weights. For example, we want to determine the atomic weight of selenium (Se). The salts potassium sulphate and potassium selenate are found to be isomorphic, that is, they form a similar type of crystal (rhombic). Elemental analysis of these compounds gives the following results:

% of elements	In Potassium sulphate	In Potass selen	ium
Potassium (K)	44.83%	(K)	35.29%
Oxygen (O)	36.78%	(O)	28.96%
Sulphur (S)	18.39%	Selenium (Se)	35.75%

The total % of weight of potassium and oxygen in potassium sulphate = 44.83 + 36.78 = 81.61.

Similarly, the total % weight of potassium and oxygen in potassium selenate = 35.29 + 28.96 = 64.25.

The law of isomorphism says that isomorphic compounds have similar chemical compositions. In this example, the ratios K:O:Se must be the same. If the proportional weights of sulphur and selenium combining with the same amount of potassium and oxygen are calculated, then it is possible to determine the atomic weight of selenium. We must first of all have the same scale for these ratios.

From the table above, it is clear that 81.61% of potassium and oxygen require 18.39% of sulphur. To calculate the weight of selenium which will combine with the same amount of potassium and oxygen (that is, 81.61%),

$$64.25 \% \text{ of } (K + O) = 35.75 \% \text{ of Se (from he table)}$$

:. 81.61 % of (K + O) = 
$$\frac{81.61 \times 35.75}{64.25}$$
 = 45.40% of Se

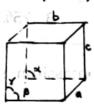
In other words, the ratio of weights of Se and S combining with the same weights of K and O is 45.40/18.40 = 2.47. If we know that the atomic weight of S is 32, we can predict that of Se to be  $32 \times 2.47 = 79.04$ .

Remember, in the above calculations, we have not used the actual chemical formulae of the compounds. Do you now realize the importance of the law of isomorphism? With the help of this law, one can calculate the atomic weight of an element without knowing the actual chemical formula of its compound.

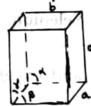
Berzelius used this law to correct the chemical formulae of compounds and, hence, the atomic weights of the elements. For example, he observed isomorphism between chromic oxide (Cr<sub>2</sub>O<sub>3</sub>) and oxides of aluminium, iron and manganese. Using the law of isomorphism, he concluded that the

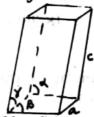
# Common forms of crystals

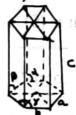
You are aware that many solids substances like common salt, sugar and potassium permanganate crystallize in different forms. All these different complex crystal forms can be resolved into seven fundamental types of crystals. The following table describes these fundamental forms along with their characteristics. It also gives examples of chemical compounds which crystallize in that form.

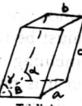


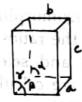
Cubic













Rhombohedral

Type	Characteristics	Examples
Cubic (add)	a = b = c $\alpha = \beta = \gamma = 90^{\circ}$	NaCl, KCl
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$	MgF <sub>2</sub>
Orthorhombic (or rhombic)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$	BaSO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub>
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$	AlCl <sub>3</sub> , graphite
	$a \neq b \neq c$ $\alpha = \beta = 90^{\circ}, \gamma \neq 90^{\circ}$	Sulphur
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	CuSO <sub>4</sub> .5H <sub>2</sub> O
	a = b = c $\alpha \neq 90^{\circ}, \beta \neq 90^{\circ}, \gamma \neq 90^{\circ}$	Al <sub>2</sub> O <sub>3</sub>

formulae of the oxides of these elements were Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> respectively. Using these formulae, he recalculated the atomic weights of these elements.

Thus, using Dulong and Petit's law and the law of isomorphism, Berzelius corrected the atomic weights of a number of elements. He published a revised version of the table of atomic weights in 1826. Comparison of this table with the currently accepted atomic weight values reveals the remarkable accuracy of his results. It also reveals the ingenuity of Berzelius, who worked without modern, sophisticated tools and techniques.

As discussed earlier, atomic weight determination used information about the elements that made up a compound as well as the number of atoms of each element in a molecule of the compound, i.e., its molecular formula. From this information, the atomic weight of one element in the compound could be calculated if the atomic weights of the other elements were known.

Dalton calculated the atomic weight of oxygen to be 8 by assuming the molecular formula of water to be HO and the weight of hydrogen to be 1. Further, the work of Gay-Lussac and Avogadro showed that the molecular formula of water was H<sub>2</sub>O giving an atomic weight of 16 for oxygen.

The determination of the atomic weight of oxygen was crucial as the weights of many elements could be determined using oxygen as the reference element. This was possible because oxygen forms oxides with almost all the elements. Moreover, unlike hydrides, many of these oxides are stable. By analysing carbon monoxide and carbon dioxide, the atomic weight of carbon was determined. It was found to be 6 if the atomic weight of oxygen was taken as 8, and 12 if the atomic weight of oxygen was taken as 16.

Thus, different assumptions gave different atomic weights for the same element. For these reasons, a chaotic situation existed in the first half of the nineteenth century regarding the atomic weights of the chemical elements.

#### Cannizzaro

Cannizzaro solved this problem with the help of Avogadro's hypothesis. In 1858, he published a paper which summarized the application of Avogadro's hypothesis for the determination of the molecular weights of gaseous compounds. He also showed how the data on correct molecular weights could be used to calculate the atomic weight of an element present in a compound. Let us see how Cannizzaro utilized Avogadro's hypothesis.

Let us choose equal volumes of the two compounds A and B in gaseous state under the same conditions of temperature and pressure.



#### Cannizzaro (1826-1910)

Stanislao Cannizzaro, an Italian chemist, made two important contributions to chemistry—one to the field of organic chemistry and the other to the field of atomic science.

He developed a method of decomposing an aldehyde (which is an organic compound) into a mixture of an organic acid and an alcohol. This reaction is today called Cannizzaro's reaction, and is used in the industrial preparation of alcohol.

Benzaldehyde

Sodium benzoate Benzyl alcohol

Cannizzaro was the first person to realize the significance of Avogadro's hypothesis. In 1858, two years after the death of Avogadro, he explained how Avogadro's hypothesis could be used effectively for determining molecular and atomic weights. Cannizzaro's work enabled chemists to determine atomic weights of several elements accurately, which paved the way for later work on the periodic law and periodic table.

In 1891, the Royal Society of Britain recognized his contributions and bestowed the prestigious Copley Medal on him.

. Let  $M_A$  = molecular weight of gaseous compound A,

3 M<sub>B</sub> = molecular weight of gaseous compound B,

V = volume of A = volume of B,

N<sub>1</sub> = number of molecules of A present in volume V, and

 $N_2$  = number of molecules of B present in volume V.

Now, the weight of compound A present in volume V is a compound V is a compoun

$$W_A = M_A \times N_1$$

Similarly, the weight of compound B present in volume V is

$$W_B = M_B \times N_2$$

If DA is the density of A, then

$$D_A = \frac{W_A}{V}$$

Substituting  $W_A = M_A \times N_1$ 

$$D_A = \frac{M_A \times N_1}{V}$$

Similarly,

$$D_B = \frac{M_B \times N_2}{V}$$

Now we can measure the densities and volumes of A and B.  $M_A$  can be compared with  $M_B$  only if we count  $N_1$  and  $N_2$ . But how do you count  $N_1$  and  $N_2$  molecules? You don't need to, if you recall Avogadro's hypothesis. If you take equal volumes, then  $N_1 = N_2 = N$  (say).

In the language of algebra,

$$D_{A} = \frac{M_{A} \times N}{V}$$

$$D_{B} = \frac{M_{B} \times N}{V}$$

$$\frac{M_{A}}{D_{A}} = \frac{V}{N}$$

$$\frac{M_{B}}{D_{B}} = \frac{V}{N}$$

$$\frac{M_{B}}{D_{B}} = \frac{V}{N}$$

(This is an example of how the use of even elementary mathematics can give us a better insight into a practical problem.)

In other words, the molecular weight of a compound in gaseous phase

is proportional to its density.

The constant K can be calculated if the molecular weight and the density of a compound are known. The value of K can be calculated from the data for oxygen, as Avogadro established that oxygen is a diatomic molecule and its atomic weight is 16, that is, its molecular weight is 32.

Cannizzaro observed that one litre of oxygen gas weighs 1.429 g under STP (pressure = 76 cm of Hg, temperature = 273 K), that is, the density of oxygen under STP is 1.429 g/litre. He calculated the value of K.

$$K = \frac{\text{molecular weight of oxygen}}{\text{Density of oxygen}}$$

$$= \frac{32}{1.429} = 22.4 \text{ litres}$$

Remember the formula for K was K = V/N where V = volume and N = number of molecules. Hence the constant K should have the same unit as that of volume. Thus, one gram of molecular weight of any gaseous substance occupies a volume of 22.4 litres at STP. This is the most valuable

and useful conclusion for the molecular weight determination of gaseous substances. Thus, the molecular weight of any element which vaporizes easily can be found, provided the gaseous density is measured under STP conditions. We noted that the volume of the gas is measured at STP. How do you maintain pressure = 76 cm of mercury and temperature = 273°K in the laboratory? You do not have to. You can conduct your experiment in your laboratory at room temperature and pressure and use the relation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P = pressure}{T = temperature}$$

$$V = volume$$

to convert your measurements to STP. Gases are indeed co-operative!

The density of the compound in gaseous state is then calculated from the weight of the compound taken and the volume in litres calculated under STP conditions. The molecular weight of the compound is found by multiplying the calculated density by 22.4.

Thus, Cannizzaro, first used Avogadro's hypothesis to calculate the molecular weight of an element or a compound which exists in (or can be converted into) a gaseous state. Why are we saying 'exists' or 'can be converted'? There are compounds which will not be in the gaseous phase at room temperature. We can change the temperature and pressure to get them into the gaseous state. Remember, we can use the relation stated above to convert our observations to STP.

For an element which cannot be vaporized easily, Cannizzaro suggested another method for determination of its atomic weight, provided the element forms a number of easily volatilizable compounds. The molecular weights of a number of such compounds are determined by taking their measured densities (g/litre) under STP conditions and multiplying these by 22.4.

According to Cannizzaro, the atomic weight of an element can be determined from the molecular weight of its compound as follows:

An atom is the smallest part of an element which participates in the formation of chemical compounds. The atomic weight, therefore, must be the smallest weight of the element that can be found in the molecular weight of its compound. This is illustrated by the following example:

Suppose we want to calculate the atomic weight of carbon. For this purpose a number of different compounds of carbon which are gaseous or can be vaporized, are selected and their gaseous densities (D) under STP conditions are measured. The compounds chosen are methane, ethane, benzene and chloroform. From their densities under STP conditions, the molecular weights are determined by using the formula M = KD, where K = 22.4 litres.



# Now in telestation a route for the carbo

In 1815, William Prout (1785–1850), a British chemist, put forward an important hypothesis which stated that the atomic weights of all the elements were exact multiples of the atomic weight of hydrogen (atomic weight = 1). This hypothesis indicates that Prout probably considered hydrogen to be an integral part of all the elements. The analytical data available at that time were found to support this hypothesis. However, it was essential to determine the atomic weights of elements very accurately in order to test this

hypothesis. Prout's hypothesis, therefore, acted as a trigger to intensify the existing efforts aimed at accurate determination of atomic weights.

Jean Stas (1813–1891), a Belgian scientist, started working on this problem around the mid-1850s. He worked for almost a decade and succeeded in determining atomic weights more accurately than any others before him. His work showed that the atomic weights of a number of elements were not integral values. Rejecting Prout's hypothesis, Stas said in 1860, that it was '. . . only an illusion, a pure hypothesis absolutely contradicted by experiments. . . '(5)

Stas's results were accepted as standard for more than fifty years until they were improved upon by Theodore Richards (1868–1928), the first American chemist to win the Nobel Prize in chemistry for his work on atomic weights of chemical elements.

But ultimately, the work done in the beginning of the 20th century showed that the proton, that is, the hydrogen ion H<sup>+</sup>, is an integral part of all atoms. Prout had probably guessed correctly and he cannot really be blamed for not distinguishing between the hydrogen atom and the hydrogen ion.

The percentage of carbon is measured by chemical analysis of these compounds and then the weight of carbon per molecular weight is determined. The data obtained are shown in the following table:

Compound	Density D (g/l) at STP	Molecular weight M=22.4×D	% of Carbon (C)	$\frac{\% C \times mol. \ wt.}{100}$
Methane	0.715	16.02	74.80	12
Ethane	. 1.340	30.02	79.80	24
Benzene	3.480	75.95	92.30	72
Chloroform	5.340	119.62	10.05	12

Now in the last column, the weight of carbon present in each molecule of the different compounds is shown. According to Cannizzaro the smallest of all these must be the atomic weight of carbon, and hence 12 is the atomic weight of carbon.

Another example is that for chlorine.

Compound	Density D (g/l) at STP	Molecular weight M= 22.4×D	% of Chlorine (Cl)	% Cl × mol. wt. 100
Ethyl chloride	2.88	64.51	55.0	35.48
Carbon tetrachloride	6.38	152.99	92.20	<b>141.05</b>

Reasoning in the same way as above, the atomic weight of chlorine is found to be 35.48.

The knowledge of the atomic weight of an element enables us to calculate the number of atoms of that element present in the molecule of a given compound. For example, ethane will contain 2 atoms of carbon (as the atomic weight of carbon is 12 and the total weight of carbon present is 24), benzene will contain 6 atoms of carbon, and carbon tetrachloride will contain 4 atoms of chlorine (as the atomic weight of chlorine is 35.48 and the total weight of chlorine is 141.05)

In the development of methods for the determination of atomic weights of elements, Cannizaro's contributions are very important. Reliable atomic weights of elements led to further progress in chemistry, as will be discussed in the next chapter.

# 4. THE KARLSRUHE CONGRESS

The discussion in the previous chapter gave us some idea about the problems which existed with respect to the determination of atomic and molecular weights in the first half of the nineteenth century. We know that two elements, hydrogen and oxygen, were used as reference elements for determination of atomic weights. Oxygen was used more widely as it forms compounds, that is, oxides, with almost all other elements. But unfortunately, different people assigned different atomic weights to oxygen, for example, 8 (Dalton), 16 (Gay Lussac and Avogadro) and 1 (Dulong and Petit.)

As atomic weights of other elements were determined with respect to oxygen, these also varied when different values of the atomic weight of oxygen were assumed. For example, the atomic weight of carbon determined by analysis of its oxides led to two values:

- (a) 6, when the atomic weight of oxygen was taken as 8, and
- (b) 12, when the atomic weight of oxygen was taken as 16.

Thus, for the same element, different atomic weights were used by different people.

Apart from this confusion in atomic weights, another source of error was the use of the equivalent weight of an element rather than its atomic weight. (This error was a result of the fact that equivalent weight can be found more easily by experiment than atomic weight).

Another problem was the lack of a clear understanding of the valence of an element, hence the molecular formula proposed for a single compound varied widely, so much so that, around 1860, Friedrich Kekule listed 19 different formulae for acetic acid. For example,  $C_4H_3O_2 + H_2O$ ,  $C_2O_3 + C_2H_3 + H_2O$ ,  $C_4H_3O_4$ . All these problems became critical around the middle of the nineteenth century. It had become essential for chemists to come together to resolve them. This was the main objective of the first International Congress of Chemists which was held at Karlsruhe in Germany on 3 September 1860. Fredrich Kekule, an eminent chemist, was the main spirit behind the Congress. Almost all the renowned chemists of the day, including Stas, Berzelius, Bunsen, Cannizzaro and Dumas, participated in the Congress.

#### What is a Standard?

In everyday life we use the second, the metre and the kilogram as standard units of time, length and mass, respectively. In this book you have seen how chemists tried several alternatives to provide a standard unit of atomic weight. Why did they have to do this?

An element whose atomic weight could be used as a standard unit had to have several virtues. Firstly, it had to be an active element, forming compounds with several other elements. Secondly, it had to be light enough so that other weights could be expressed as easy multiples. (You cannot use kilograms in goldsmith's shop!) Hydrogen was the lightest element, but not many elements formed hydrides. Oxygen was active and many elements formed oxides, but it was a little too heavy. Carbon, too, formed many compounds. Should they have tried carbon?

Just to get an idea of the problem, you can play the following game. Imagine that you are in a grocer's shop, and that the weighing balance is available but the standard weights are missing. Can you construct standard weights from items in the shop so that you can carry on the business? Here are some hints. You may discover that toothpaste tubes come in three or four sizes and that tubes of the same size weigh about the same. Cardboard boxes containing tea can be used similarly. Do cakes of soap have roughly the same weight?

Maybe you can use these items to run the shop and sell rice, wheat and other commodities by weighing them against toothpaste tubes or soap cakes. But how do you choose a standard weight? Why not try a matchbox or a small piece of toffee? The predicament of chemists in the past was not very different.

During the Congress, Cannizzaro explained and emphasized the effective use of Avogadro's hypothesis for molecular weight and atomic weight determination. A pamphlet setting out the atomic weights of elements derived on the basis of Avogadro's hypothesis was also distributed to all the participants. Even though Cannizzaro's explanation was not approved immediately, it had a great impact on the chemists present at the Congress. Both Lothar Meyer and Mendeleev, who eventually shared the honours for the discovery of the periodic table and the periodic law, were present at the Congress. Lothar Meyer, who was profoundly impressed by Cannizzaro's explanation, described the effect it had: '. . . The scales fell from my eyes, uncertainty vanished and in its place came a feeling of calmest assurance. . . '(6).

## **Equivalent Weight**

The concept of equivalent weight is rather important. Consider, for example, two compounds, NaCl and  $MgCl_2$ . We can say that 23 g of Na combine with 35.5 g of Cl. Now, if we wish to compare the abilities of Na and Mg to combine with Cl, we will have to note that 24 g of Mg combine with 71 g of Cl. Normalizing with respect to 35.5 g of Cl, the equivalent weight of Mg will be half of 24, that is, 12.

Such a concept of equivalence is not used only in chemistry. It is used also in a variety of other disciplines. For example, you know that the water equivalent of a copper calorimeter is the weight of the calorimeter  $\times$  0.1 which is the specific heat of copper. In other words, 100 g of copper will be equivalent to 10 g of water, in that both will need 10 cal to show a temperature rise of 1°C. However, that does not mean that you can buy 100 kg of copper by bartering 10 kg of water! All statements about equivalence are in relation to something specific. Equivalence and equality are very different concepts.

In daily life we use the concept of equivalence. When you are told (look up your text-book on arithmetic) that 10 men, 15 women and 30 children are equivalent, one is referring to their ability to do work. In some other context like rail-fare, an infant would be equivalent to zero, while a ten-year-old child will be equivalent to half and a man or woman will be equivalent to one.

At present, one US dollar is equivalent to about 30 Indian rupees and one British pound sterling is equal to about 50 Indian rupees. How does one get this equivalence? It is arrived at on the basis of trade. If we want to import large quantities of goods from (say) the USA, and we do not export goods to the USA in comparable quantities, then the dollar will become more valuable in terms of rupees. On the other hand, if a country has to buy many goods from us and has nothing to sell to us, the value of our rupee will rise with respect to the currency of that country. Do you think that the value of the rupee will increase substantially if India finds large deposits of oil?

The meaning of the terms 'atomic weight' and 'molecular weight' became clear from Cannizzaro's explanation. Uncertainties regarding the atomic weights of most of the elements vanished. With the availability of accurate molecular weights (from Cannizzaro's work), it also became possible to distinguish between the empirical and the molecular formula of a compound. Thus, the chemists of the nineteenth century came together, exchanged ideas, clarified fundamental concepts like those of molecular and atomic weights and paved the way for further progress in chemistry.

# Molecular and empirical formulae

Consider the following example:

Elemental analysis of an unknown compound shows that it contains 40% carbon, 6.67% hydrogen and 53.33% oxygen. The molecular weight of the compound was found to be 180. We also know that the atomic weights of carbon, oxygen and hydrogen are 12, 16 and 1 respectively.

Using this information, we wish to determine the molecular and empirical

formulae of the compound.

Let us first calculate the weight in grams of individual elements present in 180 g of this compound.

Grams of carbon present = molecular weight  $\times$  % of carbon =  $180 \times \frac{40}{100}$  = 72 g

Grams of oxygen present =  $180 \times \frac{53.33}{100} = 95.99 \ g = 96 \ g$ 

Grams of hydrogen present =  $180 \times \frac{6.67}{100} = 12 g$ 

To know the number of atoms of carbon present in a molecule of given compound, use the following relation:

Number of atoms =  $\frac{grams\ of\ carbon}{atomic\ weight\ of\ carbon} = \frac{72}{12} = 6$ 

Similarly, number of oxygen atoms =  $\frac{96}{16}$  = 6

Number of hydrogen atoms =  $\frac{12}{1}$  = 12

The given compound can now be represented as  $C_6H_{12}O_6$ .

This formula which shows the number of atoms of different elements present in a molecule of a given compound, is called the molecular formula of the compound.

Now, consider the proportion of different elements in a given compound, that is, the ratio C:H:O = 6:12:6 or 1:2:1. If we are not interested in the molecular weight of the compound and wish to consider only the relative proportion of elements forming the compound, we can say it is of the type  $CH_2O$ . Such a formula is called the empirical formula of the compound. In some cases, the molecular and the empirical formula would be identical (for example  $H_2O$ ,  $CO_2$ , HCl). If you are interested in knowing the arrangement of atoms of different elements in the molecule of a given compound, you need yet another formula called the structural formula of the compound.

Examples of Structural Formulae

Name	Empirical formula	Molecular formula	Structural formula
Acetylene	СН	C <sub>2</sub> H <sub>2</sub>	$\frac{H}{C} = \frac{H}{C}$
Benzene	СН	C <sub>6</sub> H <sub>6</sub>	# or O
Water	H <sub>2</sub> O	H <sub>2</sub> O	H O H

What is the significance of this account of Karlsruhe Congress? It showed that the leading chemists of that era were not only ingenious and hard-working, they also exhibited what is now called a scientific attitude. They came together, exchanged views and settled their differences in opinions and beliefs. In the face of new evidence, they were willing to discard their old theories for newer, more correct ones. The need to question and improve on existing ideas is the basis of all scientific progress.

#### ATTEMPTS PRIOR TO 1860

By 1860, 60 to 63 chemical elements were known. Moreover, chemists knew with certainty which substances were elements and which were compounds. The atomic weights of elements were also known fairly accurately due to the work of several chemists. While studying the physical and chemical properties of elements and compounds, chemists had also noticed that some elements exhibited similar properties. For example, sodium, potassium and rubidium were all very active, reacted violently with water and formed hydroxides, and were strong reducing agents. Similarly, flourine, chlorine, bromine and iodine were strong oxidizing agents. Moreover, chemists had also noted that elements having similar properties replaced one another rather easily in chemical reactions. For example, calcium, strontium and barium have similar properties and calcium can be replaced easily by strontium.

With the clarification of various concepts like atomic weight and molecular weight and with the settlement of issues like standardization and choice of reference element (oxygen = 16, hydrogen = 1), scientists turned their attention to other unsolved problems in chemistry. One such problem was why some elements had similar properties. As a first step, some scientists thought they could use the tool of classification to get a better insight into the properties of elements.

Even before these issues were resolved, attempts at classifying chemical elements were made as early as 1829, by a scientist called Johann Döbereiner (1780–1849). He identified groups of elements having similar properties. He further noticed that each group had three elements and called them triads. He found that when the elements of the triad were arranged according to increasing atomic weights, the atomic weight of the middle element was approximately the average of the atomic weights of the remaining two elements. Some of his triads were lithium, sodium and potassium; sulphur, selenium and tellurium; chlorine, bromine and iodine. It was also possible to infer the properties of the middle element from the properties of the other two elements. This finding is illustrated by the following example:

Property	Calcium	Barium	Strontium	
			Mean	Actual
Atomic Mass	40.00	137.30	88.70	88.60
Density (g/cm <sup>3</sup> )	1.60	3.50	2.55	2.60
Melting point (°C)	850	704	777	770
Boiling point (°C)	1490	1638	1564	1370

Döbereiner published his law of triads in 1829. By 1843, ten different triads were found. However, three tetrads and even one pentad—nitrogen, phosphorus, arsenic, antimony and bismuth—were also identified. The concept of grouping elements with similar properties looked promising, though the number three lost its magic.

But all these efforts before 1860 had little success, mainly because the confusion regarding atomic weights of chemical elements was yet to be clarified.

#### CLASSIFICATION OF ELEMENTS AFTER 1860

### Begauyer de Chancourtois

The first post-Karlsruhe Congress attempt to classify chemical elements was made in 1862, just two years after the Congress was held. It is a pleasant surprise that it was made, not by a chemist, but by a geologist called Chancourtois.

In his model, Chancourtois arranged the elements on a line or helix that descended at an angle of 45° from the top of the cylinder. If you draw such a line on a right circular cylinder, you will find that it forms a helix like a winding staircase. In order to place elements on this line, Chancourtois decided to divide the circumference of the cylinder into sixteen parts, since oxygen = 16 was used as a reference element. He expressed the atomic weights of other elements as whole numbers in accordance with Prout's hypothesis.

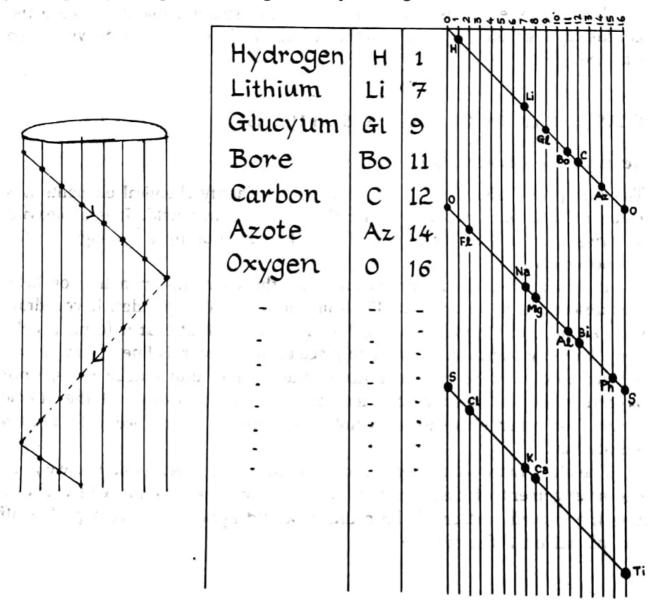
The elements were arranged according to their increasing atomic weights. The arrangement of elements will be clear from the diagram which shows how the curved surface of the cylinder would appear if it were peeled off and placed on a flat surface.

It is clear from the figure that the elements of some triads appeared in one vertical line in the model. But for some other elements the model did not work that well. For example, boron and aluminium were followed by nickel, arsenic, lanthanum and palladium, which did not have similar chemical properties.

Chancourtois called this three-dimensional model the 'Telluric Screw' as the element tellurium was almost at the centre of the model.

The 'Telluric Screw' was a step in the right direction, as it demonstrated the existence of several groups of elements having similar properties. However, it lacked precision as it failed to bring similar elements together in some cases. In other words, Chancourtois had discovered periodicity, but had got the frequency wrong.

When Chancourtois reported his model to the French Academy in 1862, not much attention was paid to it. Thus, his efforts did not gain any contemporary recognition though history now gives him due credit.



Chancourtis's model: cylinder and one-dimensional representation



## Chancourtois (1820-1866)

Begauyer de Chancourtois, a geologist, was the first person to try and classify the chemical elements after the Karlsruhe Congress. He had studied classification as a tool, and had applied it to fields such as mineralogy, geology, geography and even philosophy.

Chancourtois was studying the nature and composition of rocks and was looking for a system of simple substances. At that stage his attention was drawn to a book written by one of his colleagues on volcanic and metal-rich rocks. This book discussed the geographical distribution of elements and classified the 59 then known elements

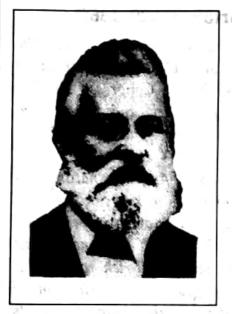
according to their electro-positivity. Inspired by this approach, Chancourtois began his work on classification of elements. He systematically collected data for the atomic weights of all 59 elements. He also decided to use whole numbers for these weights in accordance with Prout's hypothesis. Chancourtois then arranged all these elements on the basis of their atomic weights on the curved surface of a cylinder. He called this model a 'Telluric Screw'.

Unfortunately, the contemporary scientific community regarded this Telluric Screw Model merely as an amusing curiosity and did not take it seriously.

## John Newlands

John Newlands, a teacher of chemistry and an expert in sugar chemistry, came very close to the crucial understanding of the periodicity of chemical elements.

Newlands presented his paper in March 1866 to the Chemical Society, London. It was promptly rejected by the Society. Dr Olding, the President of the Society stated that they had 'made a rule not to publish a paper of purely theoretical (speculative) nature since it was likely to lead to correspondence of controversial character' (7). G.C. Foster, professor of Physics at the University College, London, made a comment ridiculing Newlands and suggested that he might as well try to arrange the elements in alphabetical order (8). If you really try to arrange the periodic table in alphabetical order it will appear as shown in the picture. You can clearly see the futility of such an effort. Suppose Indians had discovered most of the elements and had given them Sanskrit names, the alphabetical order



# John Newlands (1838-1898)

John Alexander Reina Newlands was born in 1838 only a short distance away from Faraday's birthplace (in London). He was educated privately by his father, and developed a love for music from his mother who was of Italian descent. In 1860, he participated in the insurrectionary movement in Italy under Garibaldi. For most of his professional life, he worked as an expert in sugar chemistry.

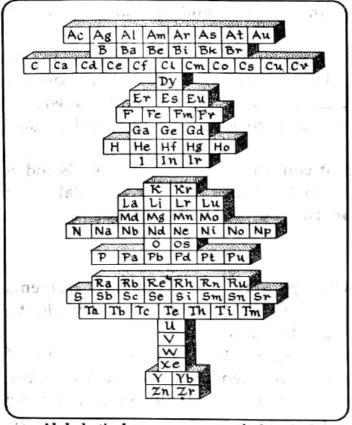
Even though Newlands did not attend the Karlsruhe Congress, he was among the first people to accept the atomic weights determined by Cannizzaro. He arranged the then known chemical

elements on the basis of these atomic weights. In doing so, he observed that the analogous elements differed either by 7, or by multiples of 7. Comparing this relationship with octaves in music, he called it the law of octaves. Newlands thus saw the essential nature of periodicity in the properties of chemical elements even before Mendeleev. However, he could not give his periodic table the necessary finishing touches, like identifying and interpreting the gaps. The history of science is full of examples of brilliant minds who saw the broad outline of a new idea, but who could not give it complete shape. Eventually, the credit goes to the scientist who provides the finishing touches and perfects the theory.

Newlands' contribution to the formation of the periodic table was recognized only 23 years after his first publication. In 1887, he was awarded the prestigious Davy Medal by the Royal Society, London.

would be very different! The classification of chemical elements has to be based on the properties of elements, not their names.

Unfortunately, Newlands did not enjoy a high standing among his contemporaries. Discouraged by their attitude he did not pursue his ideas further until Mendeleev's paper appeared in 1869. After the publication of this paper, Newlands staked his claim for credit in the discovery of the periodic law. It was in 1887, almost twenty-two years after Newlands' paper, that his contribution were recognized by the Royal Society which awarded him the prestigious Davy Medal. Similar honours had been bestowed upon Mendeleev and Meyer in recognition of their contributions to the periodic classification of elements five years earlier, in 1882.



Alphabetical arrangement of chemical elements (Source: Education in Chemistry, Sept., 1988)

Newlands was among the first to accept the atomic weights suggested by Cannizzaro. He arranged the elements on the basis of these atomic weights. He also numbered these elements and called these numbers ordinal numbers. Newlands noticed that there was a periodicity and that the eighth element exhibited properties similar to the first one. Because of the similarity between the periodicity and octaves in music (which he was fond of), he christened it 'the Law of Octaves'. In August 1865 he published a table of the 62 known elements arranged in eight vertical columns and seven horizontal rows. In 1865-66 he worked on the law of octaves and in March 1866 he

published a revised version of the periodic table (see Table 1 on page 59).

Newlands arranged elements in the increasing order of their atomic weights. He placed all his confidence on atomic weights rather than on the elements' physical and chemical properties. His table exhibits several anomalies:

- Some elements having similar properties are separated from one another.
   For example, iron is separated from cobalt and nickel and osmium is separated from iridium and platinum.
- Some elements having different properties fell into the same category.
   For example, chromium was placed below aluminium, manganese was placed below phosphorus, and tungsten was placed below tin.
- 3. In addition, incorrect atomic weights for elements like indium (In), cerium (Ce), lanthanum (La), uranium (U), vanadium (V) and gold (Au) resulted in their being put in the wrong place. (Newlands was primarily wrong in the placement of transition elements and rare earths.)

Actually, Newland's earlier table of 1864 showed that he was aware of the existence of certain elements that had yet to be discovered. This table had gaps in it, which Newlands predicted would be filled by newly discovered elements, including scandium, yttrium and germanium, which were actually discovered later.

Unfortunately, Newlands did not pursue this line of thought. In the 1866 table he removed all the gaps. Did he feel that all new discoveries would be fitted into new columns? This, too, did not prove totally wrong, as the inert gases, which were still to be discovered, did eventually make up a separate column.

In any case Newlands' work was of considerable value, and he is today recognized as one of the predecessors of Mendeleev in the formulation of the concept of periodicity in the properties of chemical elements.

#### **DMITRI MENDELEEV**

The major credit for the discovery of the periodic law of chemical elements is rightly given to the Russian chemist, Dmitri Mendeleev. It would be interesting to know what Mendeleev did to deserve this credit.

Mendeleev attended the Karlsruhe Congress of 1860 and was aware of the atomic weights suggested by Cannizzaro. Mendeleev began his studies of the chemical and physical properties of chemical elements and their compounds in 1867 when he decided to write a textbook of chemistry. At that time he was a professor of inorganic chemistry at the University of St Petersburg (later and till recently called Leningrad). He decided to group the elements according to their valence with respect to hydrogen (atomic weight 1). In his study of compounds, Mendeleev primarily and very effectively used the law of isomorphism. He grouped the isomorphous compounds together and then inferred their general formula. Such a grouping of isomorphous compounds gave him an idea about analogous elements, that is, elements with similar chemical and physical properties.

Mendeleev was so possessed by these ideas that he prepared 63 different cards, one each for the 63 known chemical elements. He wrote the name, the atomic weight and the chemical and physical properties of each element on a separate card. He shuffled his cards and tried a large number of arrangements which would display the periodicity of elements.

On 17 February 1869, Mendeleev cancelled his visit to a cheese factory (where he was going to investigate the methods used for making cheese) and stayed at home to resolve the problem of the arrangement of chemical elements. On the same day, he succeeded in formulating a system for such an arrangement. The elements were arranged on the basis of increasing atomic weights and the valencies of the elements were represented with respect to the elements oxygen (valence 2) and hydrogen (valence 1). On 1 March, the table was sent for printing, as Mendeleev intended to send

copies of it to eminent chemists all around the world. This first table published in 1869 is shown in Table 2. In 1871, Mendeleev published his Periodic Table which is shown in Table 3 (see pages 60–61 for Tables 2 and 3).

Mendeleev stated the Periodic Law: 'Elements placed according to the values of their atomic weights present a clear periodicity of properties.'

In arranging the elements, Mendeleev utilized two different attributes in two directions, that is, family likeness in the vertical direction and a progression of atomic weights in the horizontal direction. However, he emphasized the family likeness more than atomic weight sequence. Where these two did not match, he openly challenged the existing atomic weights or left vacant spaces in his arrangement. He never sacrificed family likeness for the sake of atomic weights.

He found that the physical and chemical properties of the element indium were similar to those of group III elements. However, the current atomic weight of indium which was 75.6 presented a problem. Mendeleev was confident enough to question the atomic weight which had been calculated assuming the valency of indium to be 2. Mendeleev placed the element indium in Group III. From the available chemical data and by assigning the valency 3 instead of 2, he recalculated the atomic weight of indium to be 113. In retrospect it looks like a very logical decision. After all, atomic weights were being revised all the time, whereas chemical properties were firmly established. But remember, everything looks simple in retrospect! Mendeleev also changed the atomic weights of certain heavy metals. By observing family likenesses, he placed uranium in group VI and thorium in group IV and modified their atomic weights from 116 to 240 and 118 to 231 respectively. Simtlarly, he placed the element tellurium where it belonged chemically, in the sixth row in group VI, even though this placement caused an anomaly with tellurium (128) coming before iodine (127). To remove this anomaly, he later changed the atomic weight of tellurium from 128 to 125. (See underlined parts of Tables 2 and 3 on pages 60-61).

But what about the vacant spaces? Mendeleev was confident enough to predict that the vacant spaces represented elements yet to be discovered. He even ventured to predict the physical and chemical properties of these absent elements. Sure enough, elements with these predicted properties were eventually discovered.

J. Bronowski in his book, The Ascent of Man, brings out the importance of Mendeleev's work in the following words: '. . . The conception of the gaps or missing elements was scientific inspiration. It expressed in practical terms what Francis Bacon proposed in general terms long ago, the belief that new instances of a law of nature can be guessed or induced in advance



### Dmitri Mendeleev (1834–1907)

The genius who conceived, nursed and gave the finishing touches to the periodic table was a Russian chemist, Dmitri Mendeleev.

Mendeleev, the youngest child of his parents, was unfortunate enough to lose them in his early childhood. Even so, Mendeleev was greatly influenced by his mother. Later in life, he mentioned the advice she gave him on her deathbed: 'Refrain from illusions, insist on work and not on words. Patiently seek divine and scientific truth.' (9)

Mendeleev followed his mother's advice. After an outstanding academic career, he became a

professor of chemistry at St Petersburg University. He soon acquired a reputation as one of the most inspiring teachers in Europe. His book 'Principles of Chemistry', is considered the best Russian chemistry book ever written.

Mendeleev successfully classified the 63 known chemical elements. He emphasized mainly the similarities and differences in chemical and physical properties, and used his outstanding judgement to ignore, where necessary, the atomic weight sequence. His greatest achievements were the decision to leave vacant places in the periodic table for undiscovered elements and to predict their properties. For example, while leaving the gap for gallium, Mendeleev predicted that it would be a metal with a low melting point. His confidence can be judged by the legendary statement attributed to him: 'If I hold it in my hand, it will melt.' Sure enough, gallium is a metal and it melts at 27°C (the temperature of the human body is 37°C). The eventual discovery of these elements and their placement in the very gaps left for them by Mendeleev brings out the fundamental nature of his work. In fact, Mendeleev's periodic table guided chemists in their search for new elements.

The problem that Mendeleev faced was very formidable. It is almost unbelievable that he was able to build the periodic table when atomic structure and the concept of atomic number were yet to be discovered. Try solving the following puzzle and you will appreciate the genius that was Mendeleev:

Once upon a time, a chemistry teacher had a peculiar class of students. There were 30 students in the class. Roll numbers were assigned according to marks scored in a chemistry test in the previous year. Thus, the student with roll number 1 had 95 marks, number 2 had 93 marks, number 3 had 79 marks and so on. It also turned out that roll numbers divisible by 3 belonged to girls,

while roll numbers divisible by 5 had marks divisible by 10. On the first day only 20 students turned up. The teacher had to seat them according to their roll numbers, leaving appropriate vacant seats for those who had not yet turned up. However, the students did not know their roll numbers. They knew only the marks they had scored and, of course, you could spot the girls. Could the teacher manage to seat them correctly?

This amusing but fictitious puzzle illustrates the nature of the problem that Mendeleev set out to tackle. He had, of course, one advantage. The atomic weights were related to the properties of atoms rather more reasonably than marks were to roll numbers!

from old instances. And Mendeleev's guesses showed that induction is a more subtle process in the hands of a scientist than Bacon and other philosophers supposed. In science, we do not simply march along a linear progression of known instances to unknown ones. Rather, we work as in a crossword puzzle, scanning two separate progressions for the point at which they intersect: that is where the unknown instances should lie in hiding. . . '(10)

Mendeleev provided a perfect example of the above philosophy. For example, according to the then known atomic weight sequence, the element next to calcium was titanium. Mendeleev noticed that titanium had physical and chemical properties similar to those of carbon and silicon. He, therefore, placed titanium below silicon. The place next to calcium was left vacant. Mendeleev interpreted it as the place of an undiscovered element. It represented the first gap in Mendeleev's periodic table. The next two successive gaps were left after the element zinc. Mendeleev was sure that three undiscovered elements with properties similar to those of boron, aluminium and silicon, respectively, would eventually fill the gaps left for them. He was so sure that these elements would exhibit properties similar to boron, aluminium and silicon, that he decided to name them (even before birth) as eka-boron, eka-aluminium and eka-silicon. It is interesting to note that Mendeleev turned to Sanskrit to select the prefix eka meaning one. Today we know that eka-boron is scandium, eka-aluminium is gallium and eka-silicon is germanium.

In 1875, Boisbaudran, a French spectroscopist, discovered a new element by emission spectroscopic analysis. He named it gallium. Surprisingly, the properties of this element were found to match exactly those predicted by Mendeleev for the element eka-aluminium, except for density (gallium—4.7 g/cm³, eka-aluminium—5.9 g/cm³). But Mendeleev was so confident about

his value that he asked Boisbaudran to re-determine the density. Boisbaudran did this and found that value was was actually 5.956 g/cm<sup>3</sup> (see Table 4 on page 61).

Such precise agreement between Mendeleev's predicted properties of eka-aluminium and those of gallium elevated Mendeleev's periodic law and periodic table from a mere laboratory curiosity to the status of a prestigious theory capable of explaining what was known and making verifiable predictions of the unknown. In science, the predictive ability of a hypothesis and subsequent confirmations of such predictions signify real success.

Subsequent discoveries of scandium, (that is, eka-boron) by Nilson in 1879, and of germanium (that is, eka-silicon) by Winkler in 1886, and the agreement between their predicted and actual properties, reinforced the value of the periodic law (see Tables 5 and 6 on page 62).

Mendeleev formulated his periodic table in 1871 when 63 elements had been discovered. New elements discovered subsequently had appropriate places waiting for them. However, at that time, the atom was still undivisible. It was like a billiard ball, with no structure. The concepts of atomic number, the nucleus, the proton and neutron, and hence isotopes, were simply not known. It is thus remarkable that modern understanding of atomic structure led to only marginal changes in Mendeleev's periodic table.

In 1955, tribute was paid to Mendeleev, the father of the periodic table, by naming the 101st element, a man-made one, 'Mendelevium'.

## Lothar Meyer

Lothar Meyer, a German professor of chemistry, has also received recognition for the periodic classification of chemical elements as he achieved this independently of Mendeleev.

Like Mendeleev, Meyer too had attended the Karlsruhe Congress in 1860, which prompted him to look for the numerical relationships between the elements. He felt it necessary that a textbook which he was writing should be based on a classification of chemical elements.

In 1864 Meyer published a set of two periodic tables for chemical elements in which the elements were grouped according to their valence. The first table with six columns did not include all the then known elements. For example, Meyer did not include the transition elements like iron, copper, manganese, vanadium and chromium. Meyer's second table which included mainly transition elements was divided into seven groups. He believed that most atoms in the second table were tetravalent (valence = 4), with a few exceptions. The two systems Meyer proposed are shown in Tables 7 and 8 on page 63.



## Lothar Meyer (1830-1895)

Lothar Meyer was a German chemist who independently discovered the periodic law and the periodic table. He began his career as a science teacher holding various appointments until he became professor of chemistry. Lothar Meyer tried to arrange the elements on the basis of atomic weights. Interestingly, he took into account (like Mendeleev) the chemical properties of elements, and went one step ahead to study the physical properties of elements. In 1864, he formulated his first periodic table.

The most important feature of Meyer's work is his study of the physical properties of elements.

He plotted a graph of atomic volume as a function of atomic weight. The graph (shown later in this section) clearly revealed the periodicity of elements with respect to atomic volume. Meyer also studied physical properties such as compressibility, hardness, and boiling and melting points of analogous compounds as a function of atomic weights.

The Royal Society of London recognized Meyer's contribution to the periodic table and honoured him with the prestigious Davy Medal.

Study of these tables clearly indicates that valence was not the only criterion used for the grouping of elements. Even though Meyer did not make any mention of atomic weight sequence, the elements were arranged according to their increasing atomic weights, as seen in his tables. He also realized that the difference in the atomic weights of analogous elements was either 16 or a multiple of 16.

By 1868, Meyer had prepared a new and consolidated version of the periodic table which incorporated almost all of the then known chemical elements. But unfortunately this was not published until 1895, the year in which Meyer died. This table in which the elements were divided into 15 columns is shown as Table 9 on page 64.

The elements were arranged in increasing order of their atomic weights. The only exceptions to the increasing atomic weight sequence were the elements aluminium, molybdenum, vanadium and tungsten. Actually, Meyer could have placed aluminium (atomic weight 27.3) before silicon or magnesium (see Table 9 on page 64). Why he did not do so is not known.

# Transition elements

Transition elements are metals which occur in three rows of the block in the middle of the periodic table we use today, from scandium to zinc, from yttrium to cadmium, and from lanthanum to mercury. Their atomic structure gives rise to their typical properties of variable valency and colour. They are hard and strong, have high melting and boiling points, and are good conductors of heat and electricity.

Lothar Meyer published his first article on the periodic system of elements in 1870, that is, one year after the publication of Mendeleev's first periodic table. When he wrote this article, he had already seen a German abstract of Mendeleev's Russian publication. It is, therefore, possible that Meyer may have benefited from Mendeleev's paper. Meyer's own remarks indicated the probability of this. He wrote '. . . The table below is in important aspects, identical to the one given by Mendeleev. . . '(11)

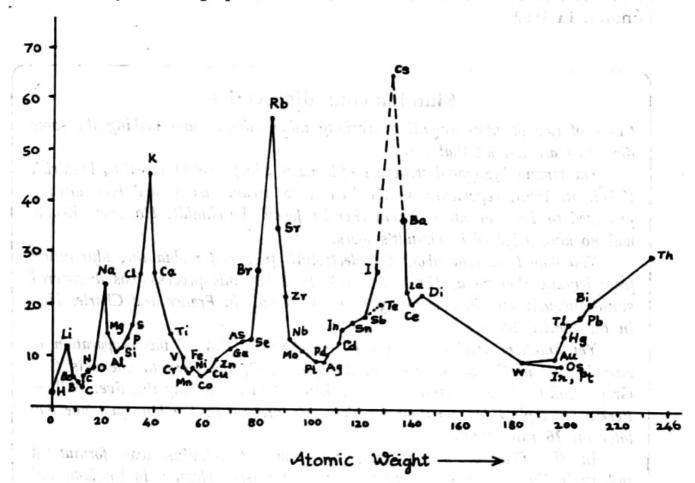
But the fact that Meyer worked independently and that he did not imitate Mendeleev's system can be seen by a comparison of the two tables, that is, Mendeleev's 1869 table and Meyer's 1870 table. (see Tables 2 and 10).

It is clear that both the tables have striking similarities. But unlike Mendeleev, Meyer did not separate the main and sub-group elements. The distinct transition element groups were thus formed in his table. (For example, see Gr. IV or Gr. VI of Table 10 on page 65.) On the other hand, transition elements were placed in various groups by Mendeleev (see Table 2).

Meyer correctly placed the elements mercury and lead as homologues of cadmium and tin, respectively. Mendeleev went wrong in placing these elements as homologues of silver and barium, respectively. Meyer properly placed thallium in the boron group, while it was wrongly placed in the alkaline group by Mendeleev. Meyer changed the atomic weight of indium from 75.6 to 113.4 and placed it in Gr. III. All these differences indicate that Meyer had conceived the periodic table independently of and almost simultaneously with Mendeleev, whose revised version of the periodic table in 1871 does incorporate several positive features of Meyer's table published in 1870. How much they gained from each other will probably never be known. It is best to assume that each arrived at his result independently.

Meyer pointed out that the properties of elements were periodic functions of their atomic weights. He attempted what no chemist had tried so far: plotting a graph of atomic volume vs. atomic weight. The term atomic volume was defined as the ratio of atomic weight and density, using hydrogen as

having unit atomic weight and water as having unit density. The periodicity is seen clearly in this graph.



Meyer's plot of atomic volume against atomic weight

Even though Meyer was conservative about changing the atomic weights of elements on the basis of this graph, he did do this in some cases: for example, changing indium from 75.6 to 113. He also studied other physical properties such as specific weight (that is, density), coefficient of expansion, melting point, etc. to show such periodic variations with atomic weights of elements. It is obvious from this discussion that Meyer took both physical and chemical properties into account. In fact, he paid more attention to the physical properties, whereas Mendeleev concentrated on the chemical properties in arranging the elements.

Mendeleev's firm belief in the validity of his periodic law led him to predict unknown elements. Meyer did leave many gaps for undiscovered elements in his table but did not predict chemical and physical properties of these elements. Mendeleev's predictions which came true in a brilliant manner proved the strength of the periodic table and rightly earned him the major credit for the periodic classification of chemical elements.

As independent discoverers of the periodic system, Mendeleev and Meyer were jointly awarded the prestigious Davy Medal by the Royal Society, London, in 1882.

#### Simultaneous discoveries

Cases of two or more scientists working independently and making the same discovery are not all that rare.

The famous hexagonal structure of benzene which was proposed by Friedrich Kekule in 1865, reportedly on the basis of a dream vision, had been already proposed in 1861 by an Austrian chemist Joseph Loschmidt. However, Kekule had no knowledge of Loschmidt's work.

You may have read about the electrolytic process for obtaining aluminium from bauxite (known as Hall's process). In 1886, this process was discovered simultaneously and independently by Paul Heroult in France and Charles Hall in the United States.

Yet another striking example of this type is that of the preparation of alizarin dye in the laboratory. On 25 June 1869, the German chemists Carl Graebe and Carl Liebermann submitted their patent for making this dye. William Perkinson applied for a patent for the same process in London, just one day later on 26 June 1869.

In the field of mathematics, the basis of calculus was formulated independently and almost simultaneously by Sir Isaac Newton in England and Gottfried Liebnitz in Germany. You perhaps already know that in the 19th century, radio-waves were discovered simultaneously by Sir J.C. Bose and M.G. Marconi, once again independently of each other. When the double helix model of DNA was proposed by Watson and Crick, other scientists like Linus Pauling were about to achieve the same breakthrough.

As chemists gathered valuable information about properties of elements, several scientists attempted to search for a pattern. You can see from examples given in this book that many scientists noted similar patterns simultaneously.

These examples tell you that often a scientist's hard work can remain unknown to the world, and unrewarded by recognition, merely because another scientist happens to publish his or her results earlier. However, a true scientist will be glad to have other scientists working on the same subject, and will not hesitate to share the credit where this is due.

Table 1: Newlands' Periodic Table (1866)

¥ 97.	;					H <sup>1</sup>
<b>Li<sup>2</sup></b> 7	<b>Be</b> <sup>3</sup> 9	<b>B</b> <sup>4</sup>	<b>C</b> <sup>5</sup>	<b>N</b> <sup>6</sup> 14	<b>0</b> <sup>7</sup> 16	<b>F</b> <sup>8</sup> 19
Na <sup>9</sup> 23	Mg <sup>10</sup>	<b>Al</b> <sup>11</sup> 27.5	Si <sup>12</sup>	<b>P</b> <sup>13</sup> 31	<b>S</b> <sup>14</sup> 32	CI <sup>15</sup> 35.5
K <sup>16</sup>	<b>Ca</b> <sup>17</sup>	Cr <sup>19</sup> 52.5	<b>Ti</b> <sup>18</sup> (50)	Mn <sup>20</sup> 55	<b>Fe</b> <sup>21</sup> 56	<b>Co,Ni</b> <sup>22</sup> 58.5
Cu <sup>23</sup> 63.5	<b>Zn</b> <sup>25</sup> 65	<b>Y</b> <sup>24</sup> (64)	In <sup>26</sup> (72)	<b>As</b> <sup>27</sup> 75	<b>Se</b> <sup>28</sup> 79.5	<b>Br</b> <sup>29</sup> 80
Rb <sup>30</sup> 85	<b>Sr</b> <sup>31</sup> 87.5	Ce,La <sup>33</sup> (92)	<b>Zr</b> <sup>32</sup> 89.5	<b>Di,Mo</b> <sup>34</sup> 96	Rh,Ru <sup>35</sup>	<b>Pd</b> <sup>36</sup> 106.5
<b>Ag</b> <sup>37</sup> 108	Cd <sup>38</sup>	<b>U</b> <sup>40</sup> (120)	<b>Sn</b> <sup>39</sup>	<b>Sb</b> <sup>41</sup> 122	<b>Te</b> <sup>43</sup>	<b>I<sup>42</sup></b> 127
<b>Cs</b> <sup>44</sup>	<b>Ba,V</b> <sup>45</sup> (137)	<b>Ta</b> <sup>46</sup> (138)	<b>W</b> <sup>47</sup> 184	<b>Nb</b> <sup>48</sup> (195)	<b>Au</b> <sup>49</sup> (196)	<b>Pt,Ir</b> <sup>50</sup> (197)
<b>Os</b> <sup>51</sup> (199)	Hg <sup>52</sup> 200	TI <sup>53</sup> 203	<b>Pb</b> <sup>54</sup> 207	<b>Bi</b> <sup>55</sup> 210	Th <sup>56</sup> 238	

Source: Journal of Chemical Education, Vol. 26 (1949), pp. 491-96.

Note: It has been mentioned in the 3rd point of discussion on page 49 that incorrect atomic weights of some elements led to the wrong placements in the periodic table. This is especially true for those elements whose atomic weights are given in parentheses (i.e. the atomic weights given in parentheses are incorrect). Why Newlands reversed the order in the case of these elements is not known. Perhaps Newlands might have paid attention to similarities in the properties of elements.

Table 2: System of Mendeleev (1869)

			Ti = 50	Zr = 90	? = 180
7	V 8		V = 51	Nb = 94	Ta = 182
ĭ	+		Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104.4	Pt = 197.4
	12.3	the 1 th	Fe = 56	Ru = 104.4	Ir = 198
\$1.1	er; 1	1) 0	Ni = Co = 59	Pd = 106.6	Os = 199
H = 1			Cu = 63.4	Ag = 108	Hg = 200
77.0	Be = 9.4	Mg = 24	2n = 65.2	Cd = 112	a.
	B = 11	Al = 27.4	? = 68	U - 116 *	Au = 197 ?
	C = 12	Si = 28	? = 70	Sn = 118	
100	N - 14	P - 31	As = 75	Sb = 122	Bi - 210
1	O = 16	5 - 32	Se = 79.4	Te = 128 ?	
	F - 19	C1 = 35.5	Br - 80	I = 127	
Li = 7	Na - 23	K = 39	Rb = 85.4	Cs = 133	T1 - 204
	5.45	Ca - 40	Sr = 87.6	Ba = 137	Pb = 207
	** 11 ##	? = 45	Ce = 92	* *	
	4. a . a . F.	? Er - 56	La = 94	5 15 15	
	3.00	?Yt = 60	Di = 95	8.48	23
		? In = 75.6	Th - 118?		

<sup>.</sup> The symbol for element U is Ur in the original table.

Source: (for tables 2 and 3) Interdisciplinary Science Review, Vol. 12 (1987), pp. 23-31.

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Table 3: Periodic Table of Mendeleev (1871)

Group I R <sub>2</sub> O	Group II RO	Group III R <sub>2</sub> O <sub>3</sub>	Group IV	Group V	Group VI RO <sub>3</sub>	Group Vil	Group IV
-			RH <sub>4</sub>	RH <sub>3</sub>	RH <sub>2</sub>	RH	-
H=1						idgless	
Li=7	Be=9.4	B=11	C=12	N-14	O=16	F=19	-
Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	C1-35.5	
K=39	Ca=40	?=44	Ti=48	V-51	Cr=52	Mn-55	Fe=56 Co=59 Ni=59 Cu=63
(Cu=63)	Zn=65	?=68	?=72	As=75	Se=78	Br=80	
Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	?=100	Ru=104 Rh=104 Pd=106 Ag=108
(Ag=108)	Cd=112	<u>In=113</u>	Sn=118	Sb=122	Te=125	<u>I=127</u> •	-
Cs=133	Ba=137	?Di=138	?Ce=140	-	-	-	
(-)	- 10 <u>-</u> 15 m =	derageng i	370 <u>1</u> 3. 171	e la <u>t</u> ina	Nasaujed	പുട്ടും	i na prima
_	71.6	?Er=178	?La=180	Ta=182	W=184		Os=195 Ir=197 Pt=198 Au=199
(Au=199)	Hg=200	TI=204	Pb=207	Bi=208	_ = ,	-	17
_	-	-8.3	<u>Th=231</u>	- ,	<u>U=240</u>	₹8. KL 0.15	x- ,

The symol for element I is J in the original table. Also, valency is represented by superscripts in the column headings of the original table, i.e. R<sup>2</sup>O instead of R<sub>2</sub>O.

Table 4: Comparison between predicted and observed properties (for eka-aluminium)

Property	Eka-aluminium	Gallium (Boisbaudran)
Atomic weight	68	69.9
Specific gravity	5.9	5.94
Melting point	Low	303.15°K
Formula of oxide	Ea <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>
Solubility in acid and alkali	Dissolves slowly in	Dissolves slowly in both

Table 5: Comparison between predicted and observed properties (for eka-boron)

Property	Eka-boron	Scandium (Nilson)
Atomic weight	44	43.79
Oxide	Eb <sub>2</sub> O <sub>3</sub>	Sc <sub>2</sub> O <sub>3</sub>
Specific gravity	3.5	3.864
Sulphate	Eb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Sc <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>

Table 6: Comparison between predicted and observed properties (for eka-silicon)

Property	Eka-silicon	Germanium (Winkler)
Atomic weight	72	72.32
Specific gravity	5.5	5.47
Melting point	High	958°C
Valence	4	4
Reaction with acid and alkali	Slightly attacked by acid, resists attack by alkali	Dissolved neither by HCl nor NaOH

Table 7: Meyer's 1864 System (Part I)

Valence*	4	3	2	1	1	2	
	-	-	-	-	Li = 7.03	(Be = 9.3?)	
Diff. =	-	_ "	-	-,	16.02	(14.7)	
	C = 12.0	N - 14.04	O - 16.00	F - 19.00°	Na = 23.05	Mg = 24.0	
Diff. =	16.5	16.96	16.07	16.46	16.08	16.0	
	Si = 28.5	P = 31.0	S = 32.07	Cl = 35.46	K - 39.13	Ca - 40.0	
Diff. =	89.1 = 44.55	44.0	46.7	44.51	46.3	47.6	
	-	As = 75.0	Se = 78.8	Br = 79.97	Rb = 85.4	Sr = 87.6	
Diff. =	$\frac{89.1}{2}$ = 44.55	45.6	49.5	46.8	47.6	49.5	
	Sn = 117.6	Sb = 120.6	Te = 128.3	I = 126.8°	Cs = 133.0	Ba = 137.1	
Diff. =	89.4 = 2×44.7	87.4 = 2×43.7		- 3	(71 = 2×35.5)	- 7	
	Pb = 207.0	Bi = 208.0	_ *_ *		T1 = (204?)		

<sup>•</sup> The symbols for elements F and I are Fl and J in the orignal table.

Table 8: Meyer's 1864 System (Part II)

Valence*	4	6	4 , ,	4	4 .	2	
	27		Mn = 55.1			1	
	Ti = 48	Mo = 92		Ni = 58.7	Co = 58.7	Zn = 65	Cu = 63.5
		1	Fe = 56				
	29	7	49.2				
Diff. •	42	45		45.6	47.3	46.9	44.4
			48.3			1	,
	Zr = 90	Vd = 137	Ru = 104.3	Rh = 104.3	Pd = 106	Cd = 111.9	Ag- 107.94
Diff. =	47.6	47	92.8=2×46.8	92.8=2×46.4	93=2×46.5	88.3=2×44.2	88.8=2×44.4
	Ta = 137.6	W = 184	Pt = 197.1	Ir = 197.1	Os = 199	Hg = 200.2	Au = 196.7

In the original table the word werthig is used for valence.

Source: (For tables 7-10) Journal of Chemical Education, Vol. 46 (1969), pp. 136-39.)

Table 9: System of Meyer (1868) published after his death

		Т			Т	_	T.		Τ	Т	1
15					Mo - 92	3	Vd - 137	4	W = 184	-	
14					Ti - 48	2	2r - 90	47.6	Ta = 137.6		
13	Be = 9.3	14.7	Mg = 24.0	16.0	Ca = 40.0	97.2	Sr = 87.6	49.5	Ba = 137.1		
12	LI - 7.03	16.02	Na = 23.05	16.08	K = 39.13	46.3	Nb - 85.4	97.79	Cs - 133.0	71-2×35.5	74C - ILL
11			F - 19.00	16.46	C = 35.46	44.51	Br = 79.97	8.94	I = 126.8		
10			0 - 16.00	16.07	5 = 32.07	46.7	Se = 78.8	49.5	Te = 128.3	: + >	12:
6			N = 14.04	16.96	P = 31.0	44.0	As = 75.0	9'57	Sb = 120.6	87.4-2×43.7	Bi = 208.0
8		(2)	C - 12.0	16.5	Si = 28.5	89.1 2 -44.55	1	89.1 2 -44.55	Sn = 117.6	88.3=2×44.1 89.4=2×44.7 87.4=2×43.7	Pb = 207.0 Bi = 208.0
2					475.5	S 8 3	Zn = 65.0	6'97		88.3=2×44.1	Hg=200.2
9	The same of the		16				Cu = 63.5	4.4	Ag - 107.94 Cd - 111.9	88.8=2×44.4	Au=196.7
5							Ni = 58.7		15.		
•			Al - 27.3			2 5	Co = 58.7	47.3	Pd = 106.0	93=2×46.5	Os=199.0
6		- G	Al - 27.3	$\frac{28.7}{2}$ =14.3			Fe = 56.0	48.3	Rh - 104.3	92.8=2×46.4	
2		 				eşe.	- 1	49.2	Ru = 104.3 Rh = 104.3	928=2×46.4 92.8=2×46.4 93=2×46.5	Pt = 197.1 Ir = 197.1
1							Cr = 52.6 Mn = 55.1				
		Diff.	Diff.			Diff.		Diff. •		Diff. •	

Note for Tables 7, 8, 9: This is the difference between the atomic weights of two successive elements in the column. If the successive element is missing, then the next element in the same column is considered and the difference is then divided by two
e.g. Si = 28.5
C = 12.0

Diff. = 16.5

Note the element after Si is missing and the next element is Sn = 117.6
Difference in atomic weights of Sn and Si = 89.1

.: Diff. • 89.1 • 44.55.

· See footnote to table 7.

Table 10: System of Meyer (1870)

1	п	ш	īv	v	VI	VII	VIII	İX
	B = 11.0	Al = 27.3		1,-	12-	?In = 113.4	- ,	TI = 202.7
	C = 11.97	Si = 28				Sn = 117.8	-	Pb = 206.4
			Ti = 48	Ť,	Zr = 89.7			
	N = 14.01	P = 30.9	37 13	As = 74.9	У	Sb = 112.1	4	Bi = 207.5
			V = 51.2		Nb = 93.7		Ta = 182.2	
,		S = 31.98		Se = 78		Te = 128?		-
		4 .	Cr = 52.4		Mo = 95.6		W = 183.5	
	F = 19.1	Cl = 35.38		Br = 79.75		I = 126.5 •		-
		B 1	Mn = 54.8	75 .	Ru = 103.5		Os = 198.6?	
			Fe = 55.9	6	Rh = 104.1		Ir = 196.7	
			Co=Ni=58.6	F1	Pd = 106.2		Pt = 196.7	
Li = 7.01	Na = 22.99	K = 39.04		Rb = 85.2		Cs = 132.7	ù.	-
		,	Cu = 63.3	77.77	Ag =107.66		Au = 196.2	
?Be = 9.3	Mg = 23.9	Ca = 39.9		Sr = 87.0		Ba = 136.8		-
		,	Zn = 64.9		Cd = 111.6		Hg = 199.8	

<sup>·</sup> See footnote to table 7.

Table 11: Werner's Periodic Table (1905) showing the rare earths

Consister in the consis		ች 4	<b>2</b> 8	A 39.9	Br Kr 79.96 81.12	%e. 128			
Catalara Than Than Than Than Than Than Than Tha	,		F 19	G. 35.4	Br 79.96	ا 126.9			
Catalana Than Than Than Than Than Than Than T			0	S 32.06	Se 79.1	Te 127.6	,	Tea ?	
California	1		N 41		<b>As</b> 75.0		Bi 208.5		
California			O 24	28.4 4.8	38	Sn 118.5	Pb 206.9	Pa ~	
Catalogy and the catalo			<b>8</b> =	Z7.1	88		E 2		
Cate At 1 48 1 5 1 2 5 2 1 5 5 0 5 5 9 9 0 5 8 7 1			9. G	Mg 24.36	Z 55.4	Cd 112.4	F 00.3	- + - +	
Cate At 1 48 1 5 1 2 5 2 1 5 5 0 5 5 9 9 0 5 8 7 1					2 g	Ag 107.9	Au 197.2		
Call 40.1 Sr					₹ 28.7	\$ 8		9	
Call 40.1 Sr				7	88	₽ 103.0	lr 193.0		
Ca 40.1 Sr 87.6 Sr 87.6 Sr 87.7 Sr 89.0 So.7 94 96.0 Sr 87.6 Sr 97.7 S					55.9	101.7			
CA-40.1 Sr 87.6 Ra La Ce Nd Pr 150.3 151.8 156 160 162 166 171 173 183 Ra La Ca Th 225 7 232.5	1				M⊓ 55.0				
Ca 40.1 Sr 87.6 87.6 87.6 87.6 87.6 87.7 87. Zr 89.0 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.					Ω 29	96.0	W 184.0		
Ca 40.1 Sr 87.6 87.6 87.6 87.6 87.6 87.7 87. Zr 89.0 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.7 80.0 80.						€ \$	å <u>s</u> 58		1
Ca 40.1 Sr 87.6 Ba La Ca Nd Pr 137.4 138 140.5 140.5 150.3 151.8 156 160 162 166 177 173 173 173 173 152.5 173 173 173 173 173 173 173 173 173 173					_	Z 200.7	100		1
Ca 40.1 Sr 87.4 138 140 143.6 140.5 150.3 151.8 156 160 162 166 171 137.4 138 140 143.6 140.5 150.3 151.8 156 160 162 166 171 171 171 171 171 171 171 171 171	0.				8 4			i .	1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 151.8 156 160 162 166 Ra La a Th U U U 239.5							δ <u>ξ</u>		1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 151.8 156 160 162 Ra La C Th C 143.6 140.5 150.3 151.8 156 160 162 Ra La C Th C 143.6 140.5 150.3 151.8 156 160 162		,					5 5	₽~	1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 151.8 156 160 162 Ra La C Th C 143.6 140.5 150.3 151.8 156 160 162 Ra La C Th C 143.6 140.5 150.3 151.8 156 160 162									1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 151.8 156 160 Pa La Th U 143.6 140.5 150.3 151.8 156 160							<u>т</u> 8		1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 151.8 156 Pa La Th U 143.6 140.5 150.3 151.8 156 225 7 232.5 U							<b>동</b> 형		1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 Ra La C Th 150.3 151.8 Ra La C Th 150.3 151.8							5 8		1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 Ra La 7 Th 150.3							8 %		1
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 150.3 Ra La 7 Th 150.3							Eu 151.8	U 230.5	
Ca 40.1 Sr 87.6 Ba La Ce Nd Pr 137.4 138 140 143.6 140.5 Ra La C Th 23.2.5							\$ 03	-	٦
Ca 40.1 87.6 87.6 87.6 137.4 138 140 143.6 137.4 138 140 143.6									1
Ca 40.1 87.6 87.6 87.6 137.4 138 140 143.6 137.4 138 140 143.6									1
Ca 40.1 87.6 87.6 87.6 137.4 138 140 143.6 137.4 138 140 143.6							F 6.5		1
Ca 40.1 87.6 87.6 137.4 138 140 137.4 138 140 7 2225 7 232.5							-		1
Ca 40.1 87.6 137.4 138 137.4 138							-	₹ 25	
40.1 40.1 87.6 137.4 137.4							ब <u>छ</u>		_
					2 3	9.78 87.6	37.4 4.78	2 %	
+ 5   - 5   5 8   × 8   4 8   Q 5		± 8	٦ 8	₹ 50 80 80 80	_		1		1

Source: Van Spronsen, J. W., The Periodic System of the Chemical Elements: A History of the First Hundred Years, Elselvier, Amsterdam, (1969).

. In the original table, the symbols for F, I, and Xe are Fl, J and X.

## 6. PROBLEMS POSED BY DISCOVERIES OF NEW ELEMENTS

The turn of the century witnessed revolutionary changes in human understanding of nature. With the mechanics formulated by Sir Isaac Newton, the laws of electromagnetism and thermodynamics enunciated by James Clerk Maxwell and other physicists, and the entire body of chemical reactions and properties of elements and compounds culminating in the elegant 'Periodic Table', it was possible to suggest that the framework of science was complete, and what remained to be done was just filling in the gaps. However, in the span of just ten years from 1895 to 1905, this confidence received several rude shocks. Around 1895-97 the German physicist Roentgen discovered x-rays-rays far more powerful than visible light, which could penetrate matter, and in England Sir J. J. Thomson discovered the electron, the first subatomic particle. It was also discovered around this time that atoms of some elements could be recorded on a photographic plate—the phenomenon of radioactivity. These 'rays' were found to be made up of electrically charged particles—alpha particles (positively charged) and beta particles (negatively Thus, it was becoming evident that Dalton's atoms were not charged). innocent billiard balls; that they had structure and some of them were unstable. In the light of these revolutionary ideas, the entire stock of scientific knowledge on the nature of matter had to be reconsidered. How did the periodic table withstand this revolution?

The development of the periodic table and the periodic law has been discussed in detail in previous chapters. The discovery of gallium, scandium and germanium, and the excellent agreement between the physical and chemical properties, predicted and observed, firmly established the periodic table of chemical elements. The periodic table, a little over 26 years old, had stood the test of time. Besides, chemists now knew what kind of new elements to look for, since the gaps in the periodic table carried an approximate description of the chemical and physical properties of the absent elements. It was an era of hope, confidence and excitement.

With the revolutionary scientific discoveries at the end of the nineteenth century came the discovery of new elements. The three major discoveries



#### Robert Bunsen (1811-1899)

You must have often used a bunsen burner in your laboratory. This burner is named after the renowned German chemist, Robert Wilhelm Bunsen, who invented it in 1855. As a chemist, he studied the burning gases and noticed that a mixture of air and a combustible gas usually burned to give a non-sooty blue flame and also produced higher temperatures. You must have noticed that the Bunsen burner in the laboratory uses some gas and also has a hole at the bottom to admit air. A band around the hole can be turned to cover the hole partly or

fully to control the flow of air. The idea of burning a gas mixed with air has turned out to be important and useful. The liquid petroleum gas burner you use at home for cooking also works on the same principle.

Bunsen did substantial work in the field of chemistry. He had investigated gases produced in blast furnaces and suggested methods for minimizing heat loss. In the course of this work, he invented new methods of gas analyses and different calorimeters for heat measurement.

Bunsen produced magnesium in large quantities and showed that it could be burnt to obtain extremely bright light. This discovery proved to be of great importance in the field of photography. (Magnesium was used to produce brilliant flashes.) In his career as a chemist, he was bold and determined enough to conduct some hazardous experiments with organic compounds containing poisonous aresenic. While working with these compounds, he lost one eye in an explosion and twice nearly died of arsenic poisoning. In spite of these accidents he continued his work in the field of chemistry.

Bunsen's most important contribution to the advancement of science was the spectroscope. In 1859, Bunsen and Kirchoff (a well known physicist), working together, invented the spectroscope which played an important role in discovering new chemical elements. In fact, Bunsen and Kirchoff themselves discovered cesium and rubidium using the spectroscope.

that challenged the validity of the periodic law were the discoveries of the rare earths, the rare gases, and radioactive elements. The main difficulty lay in finding proper places for these new arrivals.

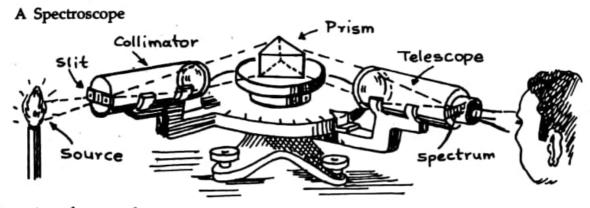
Surprisingly, the periodic table was able to accommodate all these 'problem' elements and emerged even sounder than before. It is interesting

to study these crises in some detail, but let us first learn about an important scientific invention which greatly influenced the discovery of the rare gases and rare earths.

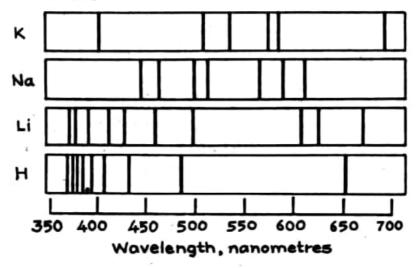
#### The Spectroscope

Since the sixteenth century it was known that certain substances produced characteristic glows when introduced into a flame. To distinguish between similarly coloured flames a method of looking through coloured glass was usually used. In the seventeenth century, Newton observed sunlight through a prism, which split the light into seven different colours. The prism could thus be used to analyse light. Using these two ideas, Robert Bunsen (1811–1899) and Gustav Kirchoff (1824–1887) invented the spectroscope in 1859. This instrument proved to be of great importance in the discovery of new elements.

This is how spectroscope works: A compound (solid or its solution) is introduced into a bunsen flame. As a result, the flame gives out coloured light which is characteristic of the elements present in the compound. This light passes through a narrow slit and then through a prism (set for an angle of minimum deviation), which splits the light further into different colours according to their wavelengths. When viewed through a telescope, a set of bright lines is observed. Chemists in the nineteenth century soon



Line spectra of some elements



noticed that no two elements exhibited the same pattern of spectral lines. Even more importantly, it was seen that the spectral lines due to one element were not affected by the presence of other elements. With the spectroscopic technique, it thus became possible to detect a completely new element in a sample. There was no need to go through complicated methods for separation. The spectroscope, in fact, provided a novel method which did not require knowledge of the chemical properties of an element. It was also a powerful method capable of detecting an element, since the intensities of spectral lines obtained were very bright even though the element was present in minute quantities.

The spectroscope, thus, proved to be far more effective and sensitive than the chemical methods then in use, and it was extensively used by scientists in the nineteenth century as an invaluable tool for the identification of chemical elements. Shortly after the discovery of the spectroscope, Bunsen and Kirchoff announced the discovery of two new elements—cesium (1860) and rubidium (1861), named for their sky-blue and ruby-red flame colours.



## Lord Rayleigh (1842-1919)

John William Rayleigh, an English physicist, discovered the first inert gas 'argon'. This discovery astonished the scientific community, as argon was the first chemical element that did not exhibit any chemical behaviour! Moreover, in the absence of chemical properties argon could not be given a proper place in the periodic table. It is only after other inert gases were discovered that a separate group was created for these elements.

In 1904, Lord Rayleigh won the Nobel Prize for the discovery of argon. He also contributed substantially to physics and studied several types of wave motions such as light (electromagnetic) waves, sound waves, water waves, and earthquake waves. Lord Rayleigh is best known for his theory of the scattering of light by molecules and small particles. He set up mathematical equations to describe the scattering of light by gas molecules in air (now known as Rayleigh scattering) and was able to show that the blue colour of the sky is due to the fact that blue light is scattered most efficiently by the gas molecules.

Using the spectroscopic technique, Crookes discovered the element thallium in 1861 and Reich discovered the element indium in 1863.

The spectroscope played an especially vital role in the discovery of rare earths and rare gases for the study of which the conventional chemical methods then available were not useful, for reasons explained in the subsequent sections.

#### **INERT GASES**

By the end of the 19th century, five different inert gases had been discovered and the spectroscopic technique conclusively established their elemental nature. They were named inert gases (or rare gases or noble gases) as all of them were found to be chemically inactive, that is, they reacted neither with any other metallic or non-metallic elements to form compounds, nor with each other. The lack of any chemical activity made it very difficult to determine their atomic weights by the usual chemical means.

In 1894, the first element of this series was discovered (once again) simultaneously by two British scientists, John Rayleigh (1842–1919) and William Ramsay (1852–1916). When the British Association met at Oxford in August 1894, Rayleigh and Ramsay astonished the members by announcing



## William Ramsay (1852–1916)

William Ramsay, a British chemist, is famous for his discovery of all the inert gases. He was an organic chemist, studying mainly the alkaloids and pyridine, the phenomenon of water loss in salts, and solubility of gases in solids.

Ramsay came across an article published in Nature by Rayleigh describing the difference in the densities of nitrogen obtained from the atmosphere and from compounds of nitrogen. This problem fascinated Ramsay who took up a detailed

investigation of gases. He discovered argon simultaneously and independently of Rayleigh, and later discovered other inert gases like helium, neon, xenon and krypton within the span of four years. The last member of this series, radon, which is radioactive, was also identified from a sample prepared by Ramsay.

the discovery of the first inert gas, which, at the suggestion of Mr G. H. Madan, the Chairman, they proposed to call Argon, 'the lazy one'.

The existence of argon was, in general, not immediately accepted by the scientific community, first because it had not been predicted by the periodic table, and second because it did not exhibit any chemical behaviour. No one had ever come across a chemical reaction involving such an element. More importantly, even if the existence of argon was accepted, there was no place for it in the periodic table which by now was not just established but held sacred! Contemporary thinking just could not accept the existence of an element that had no use or purpose or place!

Since argon was chemically inert, and it was not possible to determine its atomic weight by the conventional methods, Rayleigh and Ramsay determined its atomic weight by the specific heat ratio and vapour density methods.

The specific heat of a substance is defined as the amount of heat required to raise the temperature of 1 gram of a substance through 1°C. It is measured at constant pressure (denoted as  $C_p$ ) and at constant volume (denoted as  $C_v$ ). The ratio of these specific heats, that is,  $C_p/C_v$  is a constant and depends on the atomicity of the given gas. For example, for a monoatomic gas the ratio is 1.6666.

The following table gives values for certain gases.

Gas	Specific heat	Specific heat (kJ/kg - K)	
, , ,	$C_p$	$C_v$	$K = (C_p/C_v)$
Oxygen (O <sub>2</sub> )	0.9198	0.6595	1.395
Nitrogen (N <sub>2</sub> )	1.0414	0.7442	1.399
Hydrogen (H <sub>2</sub> )	14.3338	10.2043	1.400
Ozone (O <sub>3</sub> )	0.8192	0.6456	1.269
Sulphur dioxide (SO <sub>2</sub> )	0.6234	0.4934	1.263
Argon (Ar)	0.5215	0.3132	1.666
Helium (He)	5.2028	3.1233	1.666
Neon (Ne)	0.1039	0.0624	1.666

Note: The units of Cp and Cv are SI units, that is, kilo-joules per kilogram-degree Kelvin.

The specific heat ratios can, thus, be used to determine the atomicity of a given gas. Using the specific heat ratio, Rayleigh and Ramsay found that argon was a monoatomic gas. The atomic weight was then determined using Cannizzaro's method (that is, the density method). They concluded that the atomic weight of argon was 39.9.

With this atomic weight, argon would fall between the elements potassium and calcium; but there being no place between these two elements, the placement of argon created insurmountable problems for the periodic table. As a result of this problem, chemists looked upon argon as an 'intruder'. Several scientists made various suggestions to overcome this chemical 'monster'. Some suggested that argon be considered as a mixture of two elements. But data such as the precise melting point and precise boiling point of argon showed that argon was a pure substance. Others suggested that the atomic weight of argon was 20 instead of 39.9. With this atomic weight, it was possible to accommodate argon between the elements fluorine and sodium. In this context, the attitude of Mendeleev is of special interest. He was not happy with this new 'intruder', as it could neither be included in the periodic table, nor be ignored in the face of so much evidence. To overcome this problem, Mendeleev provided an ingenious solution. He suggested that the new 'monster' was allotrope of the element nitrogen, that is N<sub>3</sub>, like ozone, O<sub>3</sub>, which is an allotrope of oxygen.

The problem became even more critical with the discovery of the second inert gas, helium, which was discovered by Ramsay in 1895. The atomic weight of helium determined by the same methods as used for argon, was found to be 4. Now it became necessary to find places for two newly discovered inert gases. Actually, helium was first discovered in the spectrum of the sun by Janissen and Lockyer in 1868. The name helium comes from the Greek word 'helios' which means sun. Ramsay discovered this element in the atmosphere on earth, and was able to establish that it was an inert gas.

Even though argon (39.9) was marginally heavier than potassium (39), both Rayleigh and Ramsay placed argon before potassium without changing the atomic weight of argon. With this placement, a new pair of elements, namely, argon-potassium, was introduced in the periodic table, in which the atomic weight sequence was reversed.

The plot began to thicken fast. By 1898 Ramsay and Travers had discovered three more intruders. These were 'neon' (from the Greek word neos—new), 'krypton' (from the Greek word kryptos—hidden) and 'xenon' (from the Greek word xenos—stranger). Now it was necessary to find appropriate places, not for one or two strangers, but for five.

## The discovery of Argon

The discovery of argon clearly illustrates the importance of not ignoring minor discrepancies in the results of scientific analysis. It also demonstrates the importance of historical perspective.

In the late 1880s and early 1890s Lord Rayleigh, a physicist, was studying the densities of various gases like oxygen, nitrogen, hydrogen, etc. In these experiments, Lord Rayleigh found that the nitrogen prepared by removing all the other known components from air, was always denser than the nitrogen prepared from chemical compounds. The puzzle was, 'Why should atmospheric nitrogen be heavier than chemical nitrogen?'

Rayleigh's results are shown in the following table:

Atmospheric N2	Density	Chemical N2	Density
By hot copper	2.3103	From nitrous oxide	2.29901
By hot iron	2.3100	From nitric oxide	2.3001
By ferrous hydrate	2.3102	From urea	2.2985
Average	2.3102	Average	2.2992

When Rayleigh published his results, another scientist William Ramsay, a chemist, got interested in the problem and adopted it for further study.

Both Rayleigh and Ramsay suspected the presence of some heavier unknown gas in the atmospheric nitrogen. In order to detect the presence of unknown gases, it was essential to remove the nitrogen from air along with other components, namely oxygen, carbon dioxide and water vapour.

The work of Henry Cavendish in 1785, about 100 years earlier, was brought to the notice of Rayleigh (probably by Ramsay or Dewar). Henry Cavendish had studied the composition of air. He had found that all the atmospheric nitrogen could not be converted to nitrous acid by sparking the air over caustic soda. Cavendish had concluded that '. . . If there is any part of phlogisticated air of our atomosphere which differs from the rest, . . . we might safely conclude that it is not more than 1/128th part of the whole. . . '(12)

In 1894, repeating the experiment of Cavendish, Rayleigh found that 'atmospheric nitrogen' was mixture of nitrogen and another heavier gas, which was found to be a new element. Subsequently, this new element was named argon. Ramsay also discovered argon almost at the same time by passing atmospheric nitrogen over hot magnesium. In this process, the nitrogen reacted with magnesium forming magnesium nitride, leaving behind the new element.

In 1904, Ramsay and Rayleigh were both awarded the Nobel Prize for the discovery of argon. This was for the first time that two Nobel Prizes were awarded for the same discovery in the same year to two different scientists—a chemist (Ramsay) and a physicist (Rayleigh).

The specific heat ratios of these elements showed that they were monoatomic. Using the density method, Ramsay and Travers concluded that the atomic weights of neon, krypton and xenon were 20, 82, and 128, respectively. However, not being sure about these values, they could not assign definite places for these elements in the periodic table. If these values were correct the inert gases would appear between the alkali metals and halogens. The discovery of neon with atomic weight 20, made it clear that the atomic weight of argon could not be 20. It also ruled out the possibility suggested by Mendeleev of argon being an allotrope of nitrogen.

The discovery of the first inert gas had posed an insurmountable problem. But the discovery of more inert gases, in fact, led to the final solution. As long as chemists had to deal with only one intruder, that is, argon, they tried all kinds of adjustments in the periodic table. The arrival of many more strangers at first complicated their task, but later it prompted them to think of a whole new column for these elements. The 'intruders' had, thus, legitimately arrived. Ultimately in 1900, Ramsay and Travers placed all these elements in between the alkali metals and the halogens, forming a new group, the 'Zero' group, in this order:

He (4), Ne (20), Ar (39.9), Kr (82), Xe (128).

With this arrangement, the reversal of the atomic weight sequence in the case of argon and potassium became more acceptable.

The best indication of the final acceptance of the inert gases as a new group in the periodic table, which also noted the appearance of the term 'Group 0,' was the third edition of Mendeleev's *Principles of Chemistry* in which he withdrew his opinion that argon was triatomic nitrogen. However, Mendeleev was not happy with the reversal of atomic sequence and so he assigned the atomic weight 38 to argon, instead of 40.

Thus, a totally new group was added to Me deleev's periodic table, with an additional pair, Ar-K, in the reverse order of their atomic weights. William Ramsay would have been happy to read the following line which appears in a modern textbook of chemistry:

'. . . the inert gases have provided the key to the whole problem of valency and the interpretation of the periodic classification'. (13).

#### RARE EARTHS

The spectroscopic technique made it possible to detect an element present even in a complex sample, a mixture of many difficult compounds, and so spectroscopy played an important role in the discovery of the rare earths.

#### Rare Earths

You are familiar with elements like carbon, hydrogen, iron, copper and calcium. The periodic table of elements lists elements like praseodynium, samarium, gadolinium, promethium, etc. These names are strange and one does not come across them in daily life. The term 'rare earths' given to such elements thus seems quite appropriate.

However, it is interesting to know that the term 'rare earths' has only historical significance. They are not all that 'rare' and are not all necessarily associated with earth! It so happens that the first few rare earths were found in rather rare minerals. Hence the name.

The rare earths (now we can use the name) are extremely useful in the laboratory and in several industrial processes. Cerium oxide is used for polishing lenses, mirrors and television picture tubes. Rare earths are used as catalysts in the petroleum industry. They have an affinity for non-metals like carbon or sulphur. This property comes in handy for removing these unwanted non-metals in the processing of steel. Rare earths are also used as phosphors in colour television screens and for production of high quality magnets (especially samarium). You may have read that yttrium/ytterbium was used for making a high temperature superconductor.

Along with rare gases, the rare earths also posed serious problems regarding their placement in the periodic table. One of the basic criteria for the arrangement of chemical elements in the periodic table was the systematic and progressive change in the chemical properties of elements. Rare earths had nearly identical chemical properties, which meant that they could not be arranged in a row. At the same time, their atomic weights were such that they could not be fitted into a column, either. It was difficult, therefore, to place them in the periodic table. Because of their chemical similarities, their mutual separation was also not acceptable.

When Mendeleev formulated the periodic table in 1869, only five rare earths were known. Even with these few rare earths, Mendeleev faced considerable problems in their placement. In the table published in 1869 and 1871 Mendeleev changed the atomic weights of all the rare earths. In the second table (1871), he placed only the element cerium correctly by assigning it the correct atomic weight (140). In fact, Mendeleev and his contemporaries did not succeed in the proper placement of rare earths, mainly because they all tried to place these elements as homologues of other elements. It will not be wrong to say that if all the rare earths had been discovered at the time, Mendeleev would not have been able to set up his first periodic table so soon after the Karlsruhe Congress.

Bayley, whose periodic table appeared in 1882, was the first person who realized that the rare earths must be placed as a separate group. Doing this, Bayley presented a new version of the periodic table. Bassatte, Thompson and Werner are the other main contributors whose valuable work ultimately solved the crisis of accommodating the rare earth elements. Of these, Werner's periodic table is of greatest importance as it accommodated all the then known rare earths in their proper sequence.

Werner's periodic table which appeared in 1905 is given in Table 11 on page 66. The table shows clearly that Werner placed the rare earths as a special group between the alkaline earth metals and the transition elements. Because of this, his table represents the longest form of the periodic table (containing 33 columns). As Werner started the series of rare earths with the element lanthanum, there were 15 places available for the rare earth elements. (Modern scientists do not include lanthanum, and start with cerium, making the number of rare earths 14.) Werner also introduced the new pair, neodymium and praseodymium, in the reverse order of atomic weight sequence.

It is really remarkable that Werner successfully arranged the rare earths in the periodic table without knowing anything about electronic configuration, which eventually became the basis of the periodic table (and which also revealed that there could be only 14 rare earths).

## RADIOACTIVE ELEMENTS

Even after solving the problems of placement of rare gases and rare earths, the periodic table could not be finalized. It had to face a new challenge at the beginning of the twentieth century. With the discovery of new radioactive elements, the periodic table once again faced a collapse, especially in the region of high atomic weights.

In March 1896, that is just about two months after the discovery of X-rays in Germany by Wilhelm Conrad Roentgen, the French physicist Antoine Henri Becquerel (1852–1908), observed that the salts of uranium emit certain rays, which like X-rays penetrate various substances and darken photographic plates. After Becquerel published his observations, two scientists from Paris, Marie Curie (1867–1934) and her husband Pierre Curie (1859–1906) became interested in this subject and decided to undertake further studies in it. In their work, the Curies studied different substances to find out whether they emit rays similar to those emitted by uranium salts. They found that another element, thorium, also emits similar rays. They named this phenomenon of spontaneous emission of rays radioactivity (which means ray emitting), and described substances exhibiting this property as

## Two ways of getting information

How does one learn about far away lands, foreign cultures or other unknown things? There are two ways. One can get information from messengers or travellers coming from these far-off lands or one can send one's own messengers to these places. Travellers like Hiuen Tsang and Megasthenes visited India and brought knowledge of their countries to us. They also wrote accounts of their travels for the benefit of the rest of the world.

These processes occur in science also. Analysis of lava and other materials thrown out during a volcanic eruption enables geologists to guess about the earth's interior. Similarly, alpha and beta particles and gamma rays ejected by atoms in radioactive decay carry their own story. Of course, one needs to know some physics to understand these messages.

Physicists have also tried to probe the interior of the atom to get information. Lord Rutherford bombarded atoms with alpha particles and made the very significant discovery that all the positive charge and almost all the mass of the atom was concentrated at a tiny active centre called the nucleus. This discovery was an important milestone in the history of science.

Such experiments are conducted in many branches of science. Scientists use accelerators to shoot high energy particles into atomic nuclei. X-rays are used for studying crystal structure. Radioactive trace elements are used to get information about processes and affected parts in animals and humans. Space probes are sent to get information about planets. You can add many more examples to this list.

radioactive. It should be remembered that, at this stage, scientists worked with substances emitting these strange rays and not with pure elements. They were like the early metallurgists working with ores instead of with pure metals.

Initial observations led the Curies to conclude that the amount of radioactivity was proportional to the uranium content of the substances under investigation. However, they soon found that radioactivity in an ore of uranium called pitchblende was several times more than that expected from its uranium content. The Curies, therefore, suspected the presence of a new radioactive element in pitchblende. By investigating the ore further, the Curies discovered two new radioactive elements and called them polonium (in honour of Madam Curie's native country, Poland) and radium (as it was intensely radioactive). In 1899, the French scientist A. Debierne succeeded in isolating yet another radioactive element, actinium, once again from the same ore.

Thus, by 1900, five radioactive elements, namely uranium, thorium, polonium, radium, and actinium were identified. Further work in this field led to the discovery of several new radioactive elements. By 1911, the number of such radioactive elements had reached nearly thirty.

Study of the chemical properties of all these elements indicated that they had to be accommodated in the nine spaces provided by Mendeleev between the elements lead and uranium. The challenge the radioactive elements presented to the periodic table was not their curious behaviour (this was a challenge to the physicists), but the difficulty in housing these thirty elements in nine available slots. If several elements were pushed into one vacant space, the problem could be solved in an ad hoc fashion (ad hoc means only for that single purpose). Obviously, an ad hoc solution would be a blemish on the otherwise smoothly generalized periodic table.

A detailed study of the chemical properties of these elements had also led to an interesting observation. It was found that, in spite of differences in the atomic weights and differences in the radioactive properties, some of these elements were chemically indistinguishable, that is, they had precisely the same chemical properties. It was not possible to separate these elements using chemical methods. For example, radium B, actinium B and thorium B; or thorium A, actinium A and radium C could not be chemically separated. (It was proved later, that the first three elements were isotopes of lead and the next three were isotopes of polonium.)

In 1913, two scientists, Frederick Soddy and K. Fajans, suggested that the chemically inseparable elements, that is, elements with 'identical' chemical properties must be included in a single space, in spite of the differences in their atomic weights. Soddy called such elements isotopic elements. (Iso means same and topos means place.) This solved the puzzle. It provided some logical basis for accommodating several candidates in one space. The most crucial problem was thus successfully resolved.

We thus come to the end of our story, the story of man's attempt to classify the known chemical elements and to arrange them in a manner that revealed a deeper understanding of their properties. In the preceding pages, we have traced the early history of such attempts, culminating in the success of Dmitri Mendeleev.

In the light of modern knowledge, the periodic table acquires a meaning deeper than ever before. The work done in the last decade of the 19th century and the first four decades of the 20th century completely changed the picture of the Daltonian atom. It revealed that Dalton's atom is made of positively charged protons, negatively charged electrons and neutral particles called neutrons. Both protons and neutrons form the atomic nucleus and the

#### Marie Curie (1867-1934) and Pierre Curie (1859-1906)



Marie Curie, a Polish-French chemist, is the only person to win two Nobel prizes in two different disciplines of science. In 1903, she shared the Nobel prize for physics with her husband Pierre Curie and Henri Becquerel. It was awarded for work done in the field of radioactivity. In 1911, she was awarded her second Nobel prize, this time in chemistry, for the discovery of radium. The Curies separated this element (and also the element polonium) from an uranium ore called pitchblende.

After the discovery of radium, the Curies decided to produce radium in visible and weighable quantities. For this purpose, they required several tons of pitchblende which they acquired from

the world's first uranium mine at Jochimstahl in Bohemia.

After four years of hard work in an old wooden shed with leaking roof and unpaved floor, and facing several other difficulties, the Curies ultimately succeeded in separating a tenth of a gram of radium from tons of pitchblende. This accomplishment represents the culmination of a supreme effort of scientific faith and perseverance. Despite their moderate income, the Curies refused to patent the process of radium production.

Madame Curie's fame did not free her from other obligations. During World War I she interrupted her work to drive an ambulance on the battlefields of France. After the war, she spent her years supervising the Paris Institute of Radium which was founded by her. The unit of radioactive decay is named after the Curies; 10<sup>10</sup> disintegrations per second is 1 Curie.

Pierre Curie was a distinguished physicist in his own right. Besides his work in the field of radioactivity, Pierre Curie studied the magnetic properties of metals and found that, above a certain temperature, the magnetic properties either disappear or are substantially reduced. This temperature is now referred to as the Curie temperature.

He also studied the electrical properties of crystals subjected to pressure, and discovered an interesting phenomenon. It was found that certain crystals

subjected to pressure produced an electrical potential. He named the phenomena piezoelectricity. Piezoelectric crystals form an essential component of electronic devices such as microphones and record players.

Unfortunately, Pierre Curie was killed in a road accident in 1906, and could not share in the satisfaction of Marie Curie's second Nobel prize. In 1934, Marie Curie succumbed to cancer which had been caused by her exposure to radioactivity in the course of her dedicated work.



electrons distribute themselves around the nucleus in different shells. The number of protons present in the nucleus is equal to the number of electrons and is called the 'atomic number' of an element. It was further observed that the chemical properties of an element depend entirely on the number of protons present in its nucleus. Scientists learned that once the number of protons was fixed, the arrangement of electrons was also fixed. In fact, you now know that the alkali metals which have similar chemical properties have a single electron in their outermost shell. All these discoveries ultimately revealed the mystery of periodic variations in the physical and chemical properties of the chemical elements. It was also observed that an isotope was an atom of the same element with the same number of protons but a different number of neutrons. As the number of protons in the isotopes of an element is the same, their chemical properties a single space in the periodic table.

Today, you know that almost all the elements in the periodic table, with few exceptions, have isotopes. The concept of isotopes helped in understanding the fractional atomic weights of certain elements. A brief discussion of the modern periodic table is given in Appendix A.

Chemistry is an interesting science. Regardless of how much we know of the subject, it keeps presenting a seemingly inexhaustible supply of unknowns. That is why even today it is considered a growing science. From this host of topics available to us, why did we single out the periodic

## Frederick Soddy (1877-1956) and Kasimir Fajans (1887-1975)







Kasimir Fajans

The work done in the beginning of the 20th century led to the discovery of several new elements. All these elements were radioactive, that is, they spontaneously emitted certain rays. The main problem for chemists was to accommodate almost 30 such radioactive elements in less than 10 spaces available in Mendeleev's periodic table.

The problem was solved simultaneously and independently by two chemists; the British chemist Soddy and the Polish chemist Fajans. Both these chemists suggested that the 'elements' with different atomic weights, but possessing identical chemical properties were merely different forms of the same element. Soddy called the different forms of the same element isotopes.

The concept of isotopes revealed for the first time that the atomic weight was not the signature of a chemical element. For example,  $C^{14}$  and  $N^{14}$  have the same atomic weight but are two different elements!

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table for such a detailed description? We chose the periodic table because it illustrates how science progresses.

Also, the story of the periodic table is a tribute to the great minds who saw so much even when so little was known. One wonders at the fact that knowledge of just Dalton's very simplistic concept of the atom, the concept of atomic weights, and the properties of the 63 then known chemical elements were enough for them to formulate a structure, a model that has been able to survive a century in which science has developed at a faster rate than ever before. New knowledge has led to substantial refinement of the model, but has not yet led to its abandonment.

This story of the periodic table, therefore, highlights capabilities of human ingenuity and is ideally suited to illustrate the merits of a good theory. Maybe it will also tempt you to study various other aspects of the fascinating science of chemistry in greater detail.

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## APPENDIXES

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#### The Modern Periodic Table

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We now know that an atom consists of an atomic nucleus surrounded by electrons in various shells. The nucleus is made of positively charged protons and neutral particles called neutrons. The atom as a whole is electrically neutral because the number of electrons in its shells equals the number of protons in its nucleus. It is this number which identifies the atom of an element and is called the atomic number.

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Why is this atomic number so important? We now know that the chemical properties of an element depend upon how the electrons are distributed in various shells. It is also important to remember that the electrons cannot distribute themselves as they please. There are strict laws, discovered by Wolfgang Pauli (1900–1958), which govern the distribution of electrons in various shells. For example, the first shell can hold a maximum of 2 electrons, the second shell can take 8 electrons, whereas the third shell can accommodate a maximum of 18 electrons, and so on. In fact, if you want to calculate the number

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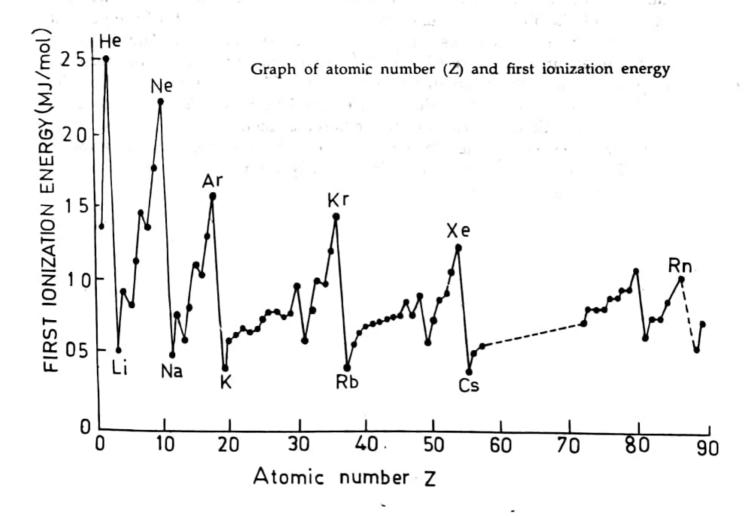
of electrons in any given shell, use the formula  $2n^2$ , where n represents the shell number, that is, 1, 2, 3, etc.

We now know that the periodicity of chemical properties arises out of the periodicity in the filling of shells. For example, consider the alkali metals. Every one of these has an inner shell completely filled with just one electron in the outermost shell, as shown below: Li 2, 1 Na 2, 8, 1 K 2, 8, 8, 1 Rb 2, 8, 18, 8, 1 Cs 2, 8, 18, 8, 1

(Please note that this is a simplified picture. As you go to heavier atoms, the shells lose some of their distinct separate existence. There is some mixing. However, we will not go into such details here.)

What happens when more electrons are added to the same outermost shell? We move horizontally along the period. For example,

Na - 2, 8, 1 Mg - 2, 8, 2 Al - 2, 8, 3 Si - 2, 8, 4 P - 2, 8, 5 S - 2, 8, 6 Cl - 2, 8, 7 Ar - 2, 8, 8



Chemical reactions between elements involve the electrons in the outermost shells. An element with a completely filled outer shell would therefore be most stable. Do you now understand why argon is inert in nature? Consider the elements sodium and chlorine. With a transfer of one electron from sodium to chlorine, both of them acquire a stable octet configuration. You will now understand why alkali metals and halogens are extremely active and react with each other to give halides. What will happen if you go to the elements magnesium and sulphur?

This periodicity is not restricted only to chemical activity. You have already seen the periodic variations in atomic volumes. Here are some other examples. You are aware of the fact that it requires some energy to knock out an electron from an atom to convert it into an ion. This is called the ionization potential of the element. The graph on the previous page shows how ionization potential varies with atomic number. Note that the inert gases have the highest ionization potentials. You can study other properties such as melting point, boiling point, density, etc. Such a study will give you deeper insight into the periodic table.

The modern periodic table is mainly based on atomic numbers rather than atomic weights. It consists of eighteen columns and seven rows. The alkalis and alkaline earth metals are placed at the extreme left of the periodic table, while the inert gases are placed at the extreme right. The transition elements are in the centre of the table. Two series of 14 elements each are displayed below the main frame of the table. The first series is called the lanthanide series as it precedes the element lanthanum. The second series is called the actinide series as it precedes the element actinium. The actinide series includes man-made elements (that is, elements after atomic number 92). This form of the periodic table is widely known as the long form of the periodic table and is shown opposite.

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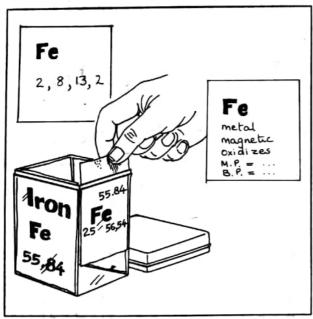
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<b>*</b> 5			Selentum 78.96	52 Tellurium 127.60	Polonium (209)	
<b>*</b>	Nitrogen 14.0067	Phosphorus 30.97376	33 Arwenic 75.9216	Sb Antimony 121.75	Bi Bismuth 208.9804	
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an gor to		18	Cu Copper 63.546	Ag Silver 107.868	79 Au Gold 196.9665	
Periodic Table of Element			Nickel Nickel 58.70	Pd Palladium 106.4	78 Pt Platinum 195.09	
Table of	6	T .	27 Cobalt 58.9332	45 Rh Rhodium 102.9055	77 Ir Iridium 192.22	
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*9-4-44		V B	Cr Chromium 51.996	42 MO Molybdenum 95.94	74 W Tungsten 183.65	106 Unhilbestum (263)
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35	Te di	·	Sc Scandium 44.959	Y Yttrium 86.9059	57° La Lanthanum 136.9055	Actinium 227.0278
:	Be Beryllum 9.01218	Mg Magnesium 24.305	Calchum 60.08	Strontium 67.62	Ba Bartum - 137.33	Ra Radium 6.941
Hydrogen		Na Sodium 22.98977	Totassium 39.0963	ST Rubidium 85.4678	Cesium 132.9054	67 Fr Francium (223)

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	140.12	140.9077	144.24	(145)	150.4	151.96	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967
	8	5	28	8	z	98	8	26	8	2	91	ē	102	103
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Series**	Thortum	Protectneum	Uranium	Neptunium	Plutonium	American	Curtum	Berkellum	Californium	Eineteinium	Fermium	Mendelevium	Nobelium	Lawrencium
	232,0381	231.0359	238.029	237.0482	(244)	(243)	(247)	(247)	(151)	(252)	(257)	(258)	(259)	(260)

## A Three-dimensional Model of the Periodic Table

Textbooks of chemistry give charts of the periodic table. These charts do not contain all the information required for the study of elements. Apart from these charts, you may have come across a huge periodic table chart in your laboratory which gives you more information. But it is difficult to handle this chart. Moreover, you cannot take it home.

If you feel like it, you can construct your own periodic table. You will need around 85 cubic transparent plastic boxes. Ignoring the tops and bottoms, a cubic plastic box has four transparent sides. Let us take an element

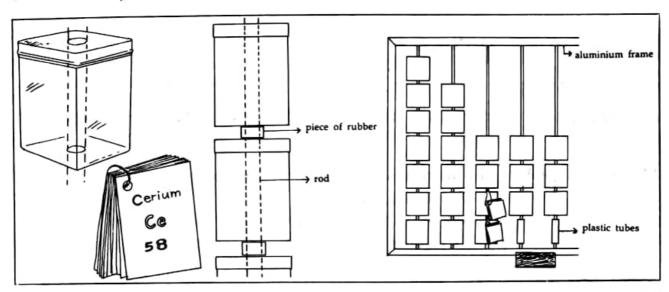


like iron. Using four differently coloured strips of paper cut to the size of the sides of the box, we can represent information about iron on these four sides. Face 1 would show the name, symbol and the atomic weight of the element. The second face would show its symbol along with the atomic number and mass numbers of major isotopes. The third face would show the electronic configuration, whereas the fourth face would show the properties of the element. The illustration shown here will tell you how to prepare a box

for any given element. All the required information about the elements is available in standard books on chemistry.

Prepare such a box for every element. In case of elements not known to Mendeleev, you can leave one surface, preferably the one showing electronic configuration, blank. (If you find it difficult to get transparent plastic boxes, use cardboard ones and paste the information on the sides.)

Now how will you assemble this periodic table? Drill a hole through the centre of the lid and the bottom of each box. Now you can pass a rod or wire through the box. Arrange the boxes in the columns to prepare the groups as shown in your periodic table charts. A simple aluminium or wooden frame can be used to support columns of boxes. Please remember that you are using cubic boxes. They need some space to rotate about the wire. If you pack your columns too close, you will not be able to rotate the boxes. (Photographs of such a model are given on the inner cover pages of this book.)



What is the use of such a periodic table? First, you can play with it! In any given column, you can rotate the boxes to show the same colour. For example, if you bring the surface showing properties in front, you can see the variations in different properties along the rows and columns. You will also notice that these variations are quite regular at both ends of the periodic table, but are rather fuzzy in the middle. If you choose to arrange the boxes to show the electronic configuration surface, you will be able to see a pattern in how the shells are filled. You will also see (most of) the gaps that Mendeleev left. It is worthwhile spending a vacation in making such a model. It would be very rewarding investment, and students who use this model will easily become familiar with the intricacies of the periodic table. You will enjoy constructing this model, especially if you make it with a group of friends.

One last suggestion. For the lanthanides and actinides you can prepare two bunches, each of 14 cards. Each card should include the name, the symbol and the atomic number of the corresponding element. You can tie these bunches as shown in the figure above. Remember, we have only suggested to you what can be shown on the four faces of the boxes. You may like to try other ways of choosing your information and displaying it.

APPENDIX C

## Table of Elements (14)

Element	Origin of the name	Discoverer, year of discovery and comments
Actinium (Ac)	Gr. aktis, aktinos, beam or ray	Andre Debierne, 1899 and F. Giesel, 1902
Aluminium (Al)	L. alumen, alum. Ancient Greeks and Romans used alum in medicine and dyeing	Wohler, 1827
Americium (Am)	The Americas	Seaborg, James, Morgan, and Ghiorso, 1944
Antimony (Sb)	Gr. anti + monosia, metal not found alone. It is found in over 100 mineral species. Sb is derived from Gr. Stibium	Earlier than the 17th century
Argon (Ar)	Gr. argos, inactive	Lord Rayleigh and Sir William Ramsay, 1894
Arsenic (As)	L. arsenicum, Gr. arsenikon, yellow orpiment, identified with arsenikos, male, from the belief that metals were of different sexes	Albertus Magnus, AD 1250; Schroeder, 1649
Astatine (At)	Gr. astatos, unstable. Longest lived isotope $^{211}$ At ( $t_{1/2} = 8.3 \text{ h}$ )	D. R. Corson, K. R. Mackensie, and E. Serge, 1940
Barium (Ba)	Gr. barys, heavy	Sir Humphrey Davy, 1808

Berkelium (Bk)	Berkeley, home of University of California	Thompson, Ghiorso, and Seaborg, December 1949
Beryllium (Be)	Gr. beryllos, beryl, a mineral	Vauquelin, 1798
Bismuth (Bi)	Ger. weisse masse, white mass, later Wismuth and Bisemutum	Claude Goeffroy the younger, 1753
Boron (B)	Ar. buraq, Pers. burah	Sir Humphrey Davy, and Gay-Lussac and Thenard, 1808
Bromine (Br)	Gr. bromos, stench	Baland, 1826
Cadmium (Ca)	L. cadmia, Gr. kadmeia—ancient name for calamine, zinc carbonate, discovered from an impurity in zinc carbonate	Stromeyer, 1817
Calcium (Ca)	L. calx, lime	Berzelius, Pontin and Davy, 1809
Californium (Cf)	State and University of California	Thompson, Street, Ghiorso, and Seaborg, 1950
Carbon (C)	L. carbo, charcoal	Prehistoric discovery
Cerium (Ce)	Named for the asteroid Ceres which was discovered in 1801	Klaproth, Berzelius and Hisinger, 1803.
Cesium (Cs)	L. caesius, sky blue	Bunsen and Kirchoff, 1860. After the removal of alkaline earths from
ada na arte na Arte na arte n	adia a victoria consideration de la considerat	
* ****	n natural di grana.	new blue lines were discovered

Chlorine (Cl)	Gr. chloros, greenish-yellow	Scheele, 1774
Chromium (Cr)	Gr. chroma, colour. It formed coloured compounds	Vauquelin, 1797
Cobalt (Co)	Kobald, from the German, goblin or evil spirit; cobalos, Greek, mine	Brandt, 1735
Copper (Cu)	L. cuprum, from the island of Cyprus	Known since prehistoric times
Curium (Cm)	Pierre and Marie Curie	Seaborg, James, and Ghiorso, 1944
Dysprosium (Dy)	Gr. dysprositos, hard to get at	Lecoq de Boisbaudran, 1886
Einsteinium (Es)	Albert Einstein	Ghiorso, December 1952
Element 104	Kurchatovium (Ku) in Kurchatov. Ghiorso and t the name of Rutherfording	at Dubna (USSR) named it honour of Igor Vasilerich he Berkeley group proposed um (Rf). IUPAC solved the milquadium (Unq) was given
Element 105	Hahnium (Ha) after the late	bubna and the Berkeley group he latter gave it the name e German scientist Otto Hahn. entium (Unp) (June 1967).
Element 106	Both Dubna and Berkeley-I	Livermore group have worked it Unnilhexium (Unh) (June
Element 107	1976, Soviet scientists discovery. But it has not	at Dubna announced the yet been confirmed.
Erbium (Er)	Ytterby, a town in Sweden	Urbain and James isolated it independently, 1905

Europium (Eu)	Europe	Boisbaudran, 1890. Demarcay isolated this earth in pure form, 1901
Fermium (Fm)	Enrico Fermi	Ghiorso, 1952
Flourine (F)	L. and F. fluere, flow, or flux	Isolated by Moissan in 1886. In 1529, Georgius Agricola described the use of flourspar as a flux
Francium (Fr)	France	Mlle. Marguerite Perey, 1939
Gadolinium (Gd)	gadolinite, a mineral named after Gadolin, a Finnish chemist	
Gallium (Ga)	L. Gallia, France; also from L. gallus, a translation of Lecoq, a cock	Lecoq de Boisbaudran, 1875
Gold (Au)	Sanskrit jual; Anglo-Saxon gold, Au (L. aurum, shining dawn)	Known and highly valued from the earliest times
Hafnium (Hf)	Hafnia, Latin name for Copenhagen	D. Coster and G. von Hevesey, 1923
Helium (He)	Gr. helios, the sun	In 1868, Janissen detected a new line in the solar spectrum during the solar eclipse. He believed it to exist only in the sun. Crookes found the same line during the spectroscopic examination of the residual gas from Hildebrand's experiment
Holmium (Ho)	L. Holmia, for Stockholm, Cleve's native city	Cleve

Hyrodgen (H)	Fr. hydro, water, and genes, forming	Cavendish, 1766
Indium (In)	Brilliant indigo line in its spectrum	Reich and Richter
Iodine (I)	Gr. iodes, violet coloured	Courtois, 1811
Iridium (Ir)	L. iris, rainbow; its salts are highly coloured	Tennant, 1803
Iron (Fe)	Anglo-Saxon iron, Fe (L. ferrum)	Known since prehistoric times. (Iron pillar dating about AD 400 stands in Delhi)
Krypton (Kr)	Gr. kryptos, hidden	Ramsay and Travers, 1898
Lanthanum (La)	Gr. lanthanein, to lie hidden	Mosander, 1839
Lawrencium (Lr)	Ernest O. Lawrence, inventor of the cyclotron	A. Ghiorso, T. Sikkeland A. E. Larsh, and R. M. Latimer, March 1961
Lead (Pb)	Anglo-Saxon lead, Pb (L. plumbum)	Known since prehistoric times
Lithium (Li)	Gr. líthos, stone found in igneous rocks	Arfvedson, 1817
Lutetium (Lu)	Lutetia, ancient name for Paris	Urbain, 1907
Magnesium (Mg)	Magnesia, district in Thessaly	Isolated by Davy, 1808
Manganese (Mn)	L. magnes, magnet, from magnetic properties of pyrolusite; It. manganese, corrupt form of magnesia. Both names are derived from Magnesia, an ancient city in Asia Minor	Scheele, Bergman, and Gahn, 1774

Mendelevium (Md)	Dmitri Mendeleev	Ghiorso, Harvey, Choppin, Thompson, and Seaborg, early 1955
Mercury (Hg)	Planet Mercury; Hg (hydragyrum, liquid silver)	Known since prehistoric times
Molybdenum (Mo)	Gr. molybdos, lead. The mineral molybdenite was thought to be the ore of lead	Scheele, 1778
Neodymium (Nd)	Gr. neos, new; didymos, twin—an inseparable twin brother of lanthanum	von Welshack, 1885
Neon (Ne)	Gr. neos, new	Ramsay and Travers, 1898
Neptunium (Np)	Planet Neptune	McMillan and Abelson, 1940
Nickel (Ni)	Ger. Nickel, Satan or 'Old Nick's' and from Kupfernickel meaning false copper	Cronstedt, 1751
Niobium (Nb)	Niobe, daughter of Tantalus	Hatchett, 1801
Nitrogen (N)	L. nitrium; Gr. nitron, native soda; genes, forming	Daniel Rutherford, 1772
Nobelium (No)	Alfred Nobel, inventor of dynamite	A. Ghiorso, T. Sikkeland, J.R. Walton, and G.T. Seaborg, April 1958
Osmium (Os)	Gr. osme, a smell	Tennant, 1803
Oxygen (O)	Gr. Oxys, sharp, acid, and genes, forming, acid former	Priestley

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Palladium (Pd)	Asteroid Pallas; Gr. Pallas, goddess of wisdom	Wollaston, 1803
Phosphorus (P)	Gr. phosphorus, light bearing; ancient name of the planet Venus when appearing before sunrise	Brand, 1669
Platinum (Pt)	Sp. platina, silver	Ulloa, 1735 and Wood, 1741
Plutonium (Pu)	Planet Pluto	
Polonium (Po)	Poland, native country of Marie Curie	Marie Curie, 1898
Potassium (K)	English potash, pot ashes L. kalium; Ar. Qali, alkali	Davy, 1807
Praseodymium (Pr)	Gr. prasios, green; didymos, twin	von Welsbach, 1885
Promethium (Pm)	Prometheus, who according to mythology, stole fire from heaven	Wu, Segre and Bethe, 1942
Protactinium (Pa)	Gr. protos, first. Protoactinium was shortened to Protactinium	K. Fajans and O.H. Gohring in 1913
Radium (Ra)	L. radius, ray	Pierre and Marie Curie, 1898
Radon (Rn)	From radium; called niton at first, L. nitens, shining	Dorn, 1900
Rhenium (Re)	L. Rhenus, Rhine	Noddack, Tacke and Berg, 1925
Rhodium (Rh)	Gr. Rhodon, rose	Wollaston, 1803

Rubidium (Rb)	L.rubidius, means deepest red	Bunsen and Kirchoff, 1861. They examined the line spectra of the residue from lepidolite after the removal of other alkali salts and discovered two dark red lines (at the red end of the spectrum)
Ruthenium (Ru)	L. Ruthenia, Russia	Klaus, 1844
Samarium (Sm)	Samarskite, a mineral	Lecoq de Boisbaudran, 1879
Scandium (Sc)	L. Scandia, Scandinavia	Nilson, 1876
Selenium (Se)	Gr. selene, moon	Berzelius 1871. He found it associated with Tellurium, named after the earth
Silicon (Si)	L. silex, silicis, flint	Berzelius, 1824; crystalline silicon discovered by Deville, 1854
Silver (Ag)	Anglo-Saxon seolfur, siolfur, Ag. (L. argentum)	Known since ancient times
Sodium (Na)	English soda; medieval Latin sodanum, headache remedy; Na (L. Natrium)	Davy, 1807
Strontium (Sr)	Strontian, town in Scotland	Davy, 1808. Adair Crawford, 1790
Sulphur (S)	Sanskrit, sulvere; L. sulphurium	Ancient times
Tantalum (Ta)	Tantalus, Greek mythological character, father of Niobe	Ekeberg, 1802
Technetium (Tc)	Gr. technetos, artificial, first element to be produced artificially	Perrier and Segre, 1937

Tellurium (Tl)	L. tellus, earth	Muller von Reienstein, 1782
Terbium (Tb)	Ytterby, village in Sweden	Mosander, 1843
Thallium (Tl)	Gr. thallos, a green shoot or twig; (due to beautiful green spectral line, which identified the element)	Crookes, 1861
Thorium (Th)	Thor, Scandinavian god of war	Berzelius, 1828
Thulium (Tm)	Thule, the earliest name of Scandinavia	Cleve, 1879
Tin (Sn)	Anglo-Saxon tin, Sn (L. stannum)	Ancient times
Titanium (Ti)	L. Titans, the first sons of the Earth, mythology	Gregor, 1791
Tungsten (W)	Swedish tungsten, heavy stone	Peter Woulfe, 1779 (mineral-wolframite) and Scheele, 1781 (Scheelite)
Uranium (U)	Planet Uranus	Klaproth, 1789
Vanadium (V)	Scandinavian goddess, Vanadis, because of its beautiful multicoloured compounds	del Rio, 1801
Xenon (Xe)	Gr. xenos, stranger	Ramsay and Travers, 1898
Ytterbium (Y)	Ytterby, village in Sweden near Vauxholm	Gadolin, 1794
Zinc (Zn)	Ger. zink, of obscure origin	Known since ancient times; zinc was used in the 13th century AD in India

Zirconium (Zr) Ar. zargun, gold colour Klaproth, 1789

Gr: Greek L: Latin Sp: Spanish Ger: German

Ar : Arabic F : French It : Italian

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