HOW DO WE KNOW?

THE STRUCTURE OF THE PERIODIC TABLE

BY ANDREW ROBINSON

The periodic table is familiar in classrooms all over the world, but it took a century of scientific endeavour to be fully realised

THE GREAT PHYSICIST Ernest Rutherford is famously reported to have said, "All science is either physics or stamp collecting", to the irritation of subsequent generations of scientists who were not physicists. Yet when Rutherford was awarded a Nobel prize in 1908 for a physics experiment, the prize was given for chemistry. Rutherford took it with good humour, referring to his "instant transmutation from physicist to chemist".

Rutherford played a key part in developing a periodic law governing the chemical elements in the 20th Century, and our understanding of elements today is down to both chemistry and physics. The law was discovered 145 years ago this month, in February 1869, by Dmitri Mendeleev and other chemists. Although he's regarded as a chemist, Mendeleev spent almost no time searching for the elements in his laboratory.

What constitutes a chemical element has long been debated, and is still unresolved to some extent. The concept of an element goes back to the ancient Greek philosophers. They recognised just four terrestrial elements: earth, water, air and fire. These corresponded with the shapes of the four Platonic solids known to mathematicians: the cube, the icosahedron, the octahedron and the tetrahedron. Thus, the liquidity of water was thought to parallel the relatively smooth shape of the 20-faced icosahedron, while the pain caused by touching fire was explained by the sharp corners of the tetrahedron. When a fifth Platonic solid, the 12-faced dodecahedron, was later discovered, Aristotle proposed the existence of a fifth element. It was 'quintessence', the celestial aether.

Of course, some of the 90 or so naturally occurring substances we recognise today as elements have been known since antiquity or even earlier – for example, carbon, copper, gold, iron, lead, mercury, silver, tin and sulphur. These substances were found in an uncombined form or were easily separable from the minerals in which they occurred. For many centuries, alchemists occupied themselves in attempting to transform the naturally occurring 'base' metals, such as iron and lead, into the 'noble' metals, gold and silver, without success. In the scornful words of the influential natural philosopher Francis Bacon, writing in the 1620s: "All the philosophy of nature which is now received is either the philosophy of the Grecians, or the other of the alchemists. The one never faileth to multiply words, and the other ever faileth to multiply gold."

MODERN MATTER

The modern concept of the chemical element began to emerge only in the late 18th Century with the work of the French chemist, Antoine-Laurent de Lavoisier. He is generally regarded as the founder of modern chemistry from the 1770s until his death under the guillotine in 1794. Using quantitative experiments, Lavoisier defined an element empirically as a material substance that was yet to be decomposed into any ➜

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There are currently 118 known elements, but not all of them occur naturally

> IN A NUTSHELL

Two millennia after the Ancient Greeks wrongly classified the four elements as fire, water, wind and earth, Dmitri Mendeleev uncovered underlying patterns in nature – leading to one of the most powerful tools in science.

more fundamental substances. In 1789, the year of the French Revolution, Lavoisier published his *Elementary Treatise On Chemistry*, in which he listed 33 simple substances or elements. Many of these are accepted as elements today – the gases hydrogen and oxygen and the metals known since antiquity plus manganese, molybdenum and tungsten, and the non-metals carbon, sulphur and phosphorus. But other supposed chemical elements in Lavoisier's list included lime and baryta, which are now known to be chemical compounds, and light and heat, which belong in physics, not chemistry. However, Lavoisier correctly rejected the ancient Greek elements of earth, water, fire and air, on the grounds that they had been shown to be composed of more fundamental substances.

The next step towards classifying the elements was taken by an English chemist, John Dalton, around 1803. Dalton assumed that each element consisted of a particular type of atom – an indivisible entity. Using Lavoisier's data, Dalton estimated the relative atomic weights (see 'Need to know', p105) of several important elements by analysing simple chemical compounds. Water appeared to be about one-eighth hydrogen and seven-eighths oxygen by weight. This led Dalton to assign an atomic weight of 1 to hydrogen and 7 to oxygen, by assuming water's molecular formula to be HO. Although Lavoisier's measured proportions were somewhat inaccurate, and Dalton's molecular formula in this particular case was erroneous (as everyone now knows), his approach was sound. The relative atomic weights of the elements would prove crucial, after further refinement, to the construction of periodic tables in the 1860s.

A German chemist, Johann Wolfgang Döbereiner, began the process. From 1817, over several years he noticed that triads of elements sharing similar chemical properties also shared a pattern in their atomic weights. For instance, the alkali metals lithium, sodium and potassium had the respective atomic weights 7, 23 and 39. Sodium's atomic weight must therefore lie midway between that of lithium and potassium. (7 + 39 = 46; 46 ÷ 2 = 23.) The same relationship held for the alkaline-earth metals calcium, strontium and barium, and for the halogens chlorine, bromine and iodine. Between 1827 and 1858, other chemists extended Döbereiner's observations beyond these triads by adding magnesium to the alkaline-earth metals and fluorine to the halogens. Oxygen, sulphur, selenium and tellurium were classified as a family; nitrogen, phosphorus, arsenic, antimony and bismuth as yet another family.

MULTIPLE APPROACHES

In 1858 an Italian chemist, Stanislao Cannizzaro, published a standardised list of atomic and molecular weights. He did so by reviving the 1811 hypothesis of his compatriot, chemist-cum-physicist Amedeo Avogadro, concerning gases. Avogadro, unlike Dalton, had guessed that gases such as hydrogen and oxygen were composed of molecules, which were themselves composed of atoms. This meant that the molecular weight of the gas must be different from the atomic weight of its constituent element. The molecular weight depends on how many atoms of the element are contained in the molecule: two atoms in the case of oxygen. Cannizzaro's analysis formed the basis for discussion at the first international congress of chemists, held in Karlsruhe, Germany, in 1860.

Among those attending were Dmitri Mendeleev from Russia, Julius Lothar Meyer from Germany and William Odling from Great Britain. All three chemists, along with two others, John Newlands and Gustavus Hinrichs and a French geologist, Alexandre-Émile Béguyer de Chancourtois, proposed different versions of the periodic table during the 1860s. They investigated patterns in atomic weights, chemical properties and, in the case of Hinrichs, atomic spectra of the 63 elements known at this time.

Mendeleev's proposal, which occurred to him while writing a Russian chemistry textbook, was the last of these six. It was published in draft form in 1869 and more fully in 1871, although it appears not to have been influenced by the five earlier proposals. All the proposals had considerable merit, but only Mendeleev's would become established. The main reason it succeeded was that in 1869-71 Mendeleev had made a number

THE KEY DISCOVERY

It was the genius of Dmitri Mendeleev that placed the elements in a logical, periodic table, arranging them by atomic weight and subsequently spotting similar chemical properties

THE PERIODIC TABLE struck Mendeleev while he was writing an immensely successful textbook. In January 1869, he completed volume one. However, it discussed only eight out of the 63 known elements. Volume two, he knew, required a less rambling structure to fit the publisher's format and deadline. So, on 17 February 1869, (1 March in the Gregorian calendar), he concentrated on shuffling the elements, both on paper and in his mind. Indeed he may have played a form of solitaire (patience) with 'element' cards. Virtually certain is that he used two classifying tools simultaneously. He wrote out the elements in rows by increasing atomic weight, thereby spotting periodic repetitions of chemical properties. And he listed several 'natural groups', like alkali metals and halogens, in columns, thereby spotting patterns of increasing atomic weight.

This generated what he called his 'first try' (see below). The missing element was Sc, scandium – unknown in 1869 but discovered in 1879, with an atomic weight of 45.

Dmitri Mendeleev may have arranged the elements like a game of solitaire to create his famous table

7 Li	9.4 Be	11 B	12 C	14 N	16 O	19 F
23 Na	24 Mg	27.4 Al	28 Si	31 P	32 S	35.5 Cl
39 K	40 Ca	?	50 Ti	51 V		

Dmitri Mendeleev's early periodic table, devised in 1869, categorised the known elements in order of atomic weight (small numbers). Scandium (bottom row) was discovered as the missing element in the table in 1879

CAST OF CHARACTERS

The greatest scientific minds of the past two centuries unlocked the order of the elements

John Dalton (1766-1844), the son of a poor country weaver and the father of the modern atomic theory, was a schoolmaster in Manchester. He controversially maintained that the chemical elements were composed of atoms, and in 1803 compiled a list of relative atomic weights covering some of the most important known elements.

Johann Wolfgang Döbereiner (1780-1849) was a German chemist who started as an apothecary's apprentice. He became a professor at the University of Jena, where his lectures were attended by his lifelong friend Goethe. In 1817, he spotted a pattern in the atomic weights of triads of elements with similar chemical properties.

Dmitri Mendeleev (1834-1907), the leading Russian scientist, was the youngest of 14 children. He lost both parents in his teens but managed to obtain some scientific training in St Petersburg and then went to Germany, before returning to Russia. By analysing atomic weights and chemical properties, he devised his periodic table in 1869.

Ernest Rutherford (1871-1937) is probably the greatest modern physicist after Einstein. Born in New Zealand, he carried out most of his research in Britain, at Manchester and Cambridge, where he directed the Cavendish Laboratory. This work included revealing the structure of the atomic nucleus, which led to the concept of atomic number.

Henry Moseley (1887-1915) was an English physicist. After training under Rutherford at Manchester, he returned to Oxford University in 1913 for research work. There he discovered the key relationship between an element's atomic number and its chemical behaviour. He was killed by a sniper's bullet at Gallipoli, during the First World War.

TIMELINE

They make up the Universe, but it's taken nearly a century to discover and categorise the elements

1817 In triads of chemically similar elements, such as chlorine, bromine (pictured) and iodine, Wolfgang Döbereiner observes the second element's atomic weight to lie midway between that of the first and third elements.

1858 Atomic weights are standardised by Stanislao Cannizzaro, using Amedeo Avogadro's 1811 hypothesis, that equal volumes of any gas at the same temperature and pressure contain equal numbers of molecules.

1869 After partially successful attempts by several chemists to detect periodicity in the atomic weights of the elements, Dmitri Mendeleev, while writing a textbook, introduces the basis of a successful periodic table.

1875 Gallium, the first of three hitherto unknown chemical elements predicted by Mendeleev from his periodic table, is discovered by Paul-Émile Lecoq de Boisbaudran. Scandium is discovered in 1879, germanium in 1886.

1911 After bombarding gold foil with alpha particles, Ernest Rutherford and collaborators establish the nuclear model of the atom. Antonius van den Broek theorises that an element's nuclear charge determines its atomic number.

1913 By examining elements' X-ray spectra, Henry Moseley demonstrates that nuclear charge and atomic number are connected; chemical properties – and hence periodicity – are determined by this number; and only around 90 elements occur naturally.

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of predictions of the existence of unknown elements. He labelled them with the Sanskrit word, *eka*, meaning 'one'. They included *eka*-aluminium, *eka*-boron and *eka*-silicon, which he predicted would have the atomic weights 68, 44 and 72, respectively. The first of them was discovered in 1875 and named gallium (atomic weight 69.7), the second in 1879 and named scandium (atomic weight 45.0), the third in 1886 and named germanium (atomic weight 72.6). Moreover, Mendeleev predicted almost all of the chemical properties of the new elements correctly.

Not all his predictions were so successful. Well before his death in 1907, new discoveries challenged his theory. In fact, current versions of the periodic table ignore three cardinal principles dear to Mendeleev: the valency, the indivisibility, and the immutability of the atom.

The valency is the number of chemical bonds an atom can form with other atoms. The noble (inert) gases helium, neon, argon, krypton, radon and xenon – discovered in the 1890s by the chemist William Ramsay and the physicist Lord Rayleigh – appeared totally unreactive, with a 'forbidden' valency of zero. Today, we know some do form a few chemical compounds. The discovery of the electron in 1897 by the physicist JJ Thomson disproved indivisibility – the atom plainly had an inner structure. And radioactivity, discovered by the physicist Henri Becquerel in 1896 and named by the physicists-cum-chemists Marie and Pierre Curie in 1898, showed that transmutation of elements does occur. Elements like uranium, polonium and radium all undergo radioactive decay.

BY THE NUMBERS

Most serious of all the objections, though, was Mendeleev's unyielding reliance on increasing atomic weight as the chief ordering principle of his periodic table. The higher the atomic weight of an element, the later should be its position in the periodic table, he maintained. Mendeleev himself was aware of this difficulty, because he allowed one or two exceptions to this rule – notably for tellurium, which he placed earlier than iodine despite an atomic weight of 127.6 for tellurium versus 126.9 for iodine. He justified this reversal on the grounds that the atomic weights for one or both of these elements had been incorrectly determined. But his reasoning turned out to be wrong. While tellurium does indeed have a higher atomic weight than iodine, its atomic number, 52, is now known to be smaller than the atomic number of iodine, 53.

Atomic number was a concept unknown to Mendeleev. In some 19th-Century periodic tables, elements were simply numbered according to increasing atomic weight. The concept owes its existence to physicists, notably the work of Rutherford and Henry Moseley in 1911-14. Rutherford discovered the atomic nucleus, with its positively charged protons, around which negatively charged electrons orbit in a kind of 'Solar System'. Moseley followed a suggestion by an economist and amateur physicist, Antonius van den Broek, that the number of an element should correspond to its nuclear charge, in other words to its number of protons. By measuring the wavelengths of characteristic X-ray spectral lines of many elements, Moseley showed that the wavelengths depended in a regular way on the element's atomic number.

It is atomic number, not atomic weight, which is the ordering principle of the many versions of the modern periodic table. The reason why atomic weight nevertheless remains a good guide to an element's properties is that increasing atomic weight generally parallels increasing atomic number, because atomic weight is determined by the protons and the neutrons in the nucleus. As the number of protons rises through the periodic table so, as a general rule, does the number of neutrons. Therefore rising atomic number and increasing atomic weight roughly correspond.

That said, the physics of the atom will never completely predict its chemical behaviour as an element. In the words of *The Periodic Table*, a celebrated collection of short stories by Primo Levi, the Italian-Jewish chemist who evaded being gassed at Auschwitz in 1944, 'one must distrust the almost-the-same'. Even potassium and sodium, nearest neighbours as alkali metals in the periodic table, can behave very differently under the same circumstances: one causing an explosion, the other not. Alluding to his own narrow escape from death in the Holocaust, Levi added: "The differences can be small, but they can lead to radically different consequences, like a railroad's switch points". It's an appropriate conclusion to the convoluted history of the most profound discovery in chemistry. ■

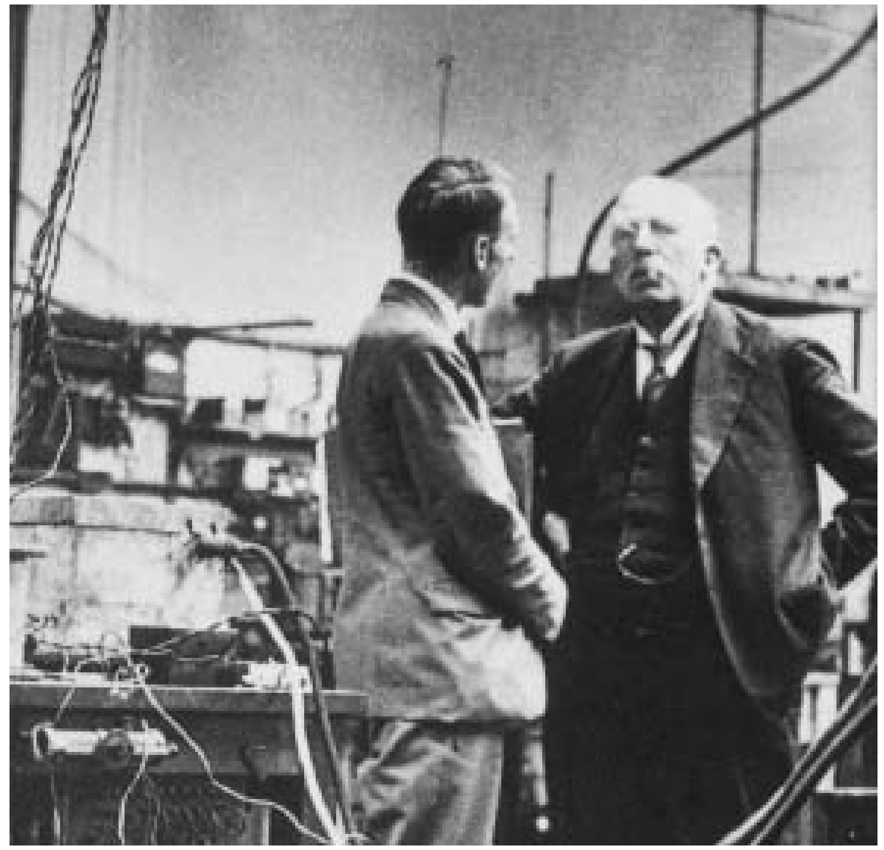
NEED TO KNOW

Terms you'll need to understand the periodic table

1 ATOMIC NUMBER
The atomic number of an element is the number of protons in its atomic nucleus. Oxygen's atomic number is 8, gold's 79. Many elements occur in more than one form, known as isotopes, with equal numbers of protons but different numbers of neutrons. Carbon has two stable isotopes, carbon-12 (the most common) and carbon-13, and one radioactive isotope, carbon-14.

2 ATOMIC WEIGHT
Also known as relative atomic mass, the atomic weight of an element is the ratio of the average mass of one atom of the element to one-twelfth the mass of an atom of carbon, which has an atomic weight of approximately 12. Oxygen's atomic weight is 16, gold's 197.

3 ELEMENT
A chemical element, such as oxygen or gold, is a substance that cannot be resolved into simpler substances by chemical means. The atoms of a given element all have the same atomic number. The atomic number of each element is different.



Ernest Rutherford (right) in his laboratory at Cambridge University was awarded the Nobel Prize in chemistry in 1908 for his work that helped shed light on patterns in the periodic table

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