Chemistry Background Book

The Periodic Table

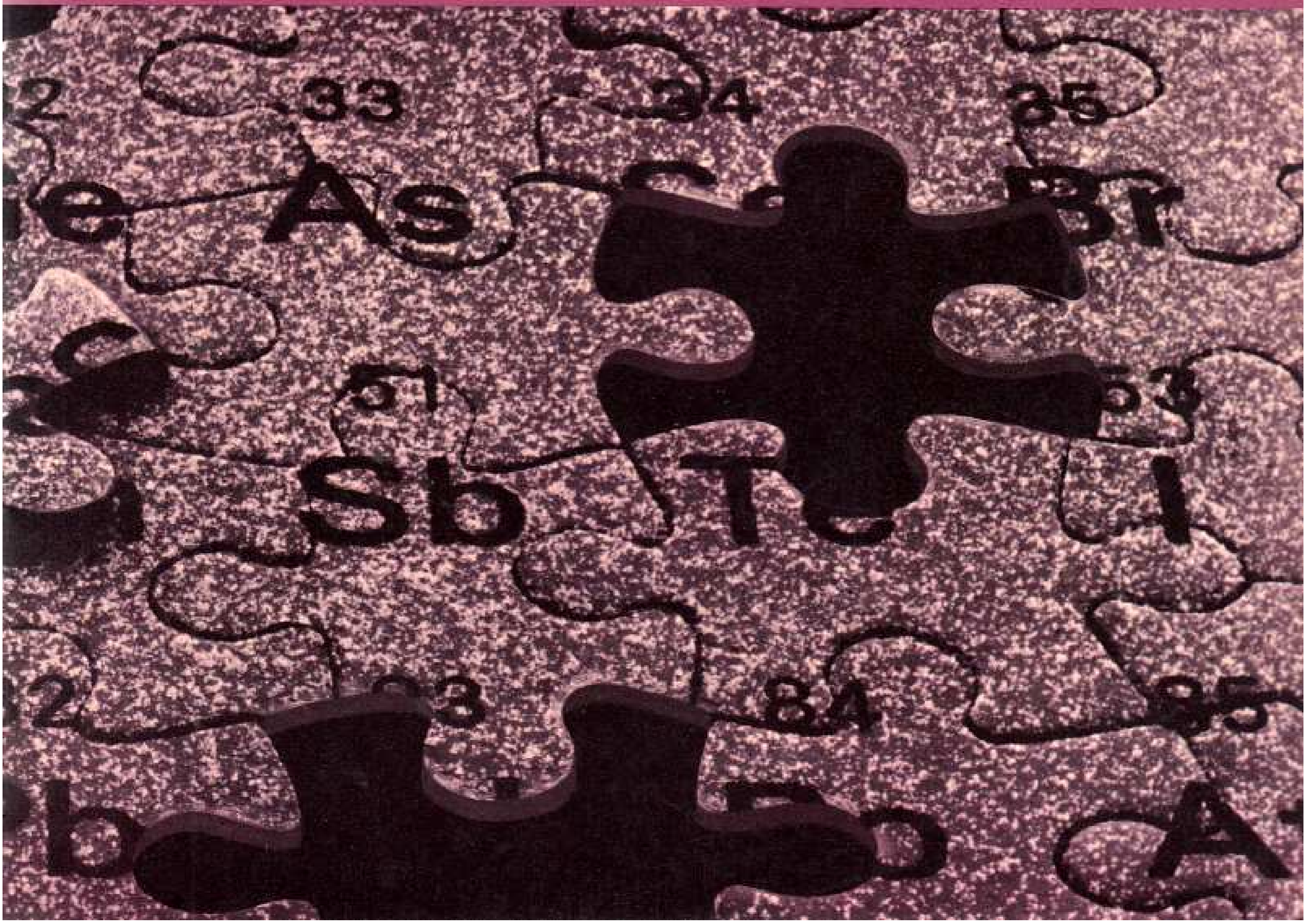


TABLEAU DES SUBSTANCES SIMPLES.

	Noms nouveaux.	Noms anciens correſpondans.
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofete. Baſe de la mofete.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobolt	Cobolt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'Epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

A page from Lavoisier's famous book *Traité Élémentaire de Chimie*, showing the way in which he grouped the chemical elements then known. Several of the substances he listed were not, in fact, elements. Can you identify these?
British Museum

part one Bringing order to the elements

The table of letters, the alphabet, is learned when we are very young. It is not memorized for its own sake, as a poem is, but as a pattern which enables us to learn about other things. Thousands of words can be made from its twenty-six letters. Moreover, when we look into a dictionary in order to find out how to spell 'biennial', for example, we automatically open the book nearly at the beginning. Wanting next to find the word 'propinquity', we skip a great chunk of the book with one turn. Because we have a pattern in our heads, we save time; we know where to look. Another pattern which we learn when young is the Multiplication Table; it orders our mathematical thinking. We can apply this knowledge to more complex problems.

The Periodic Table has something in common with these examples. It brings order to our knowledge of chemistry.

Its most valuable effect on science, however, was during its making. It forced men to look for elements. Boyle had introduced the idea of the chemical element in 1660. Davy pointed out that only a small number of the substances known in his day were in fact elements – the rest were combinations of these elements, or compounds. Chemists felt that some pattern might exist which would bring elements into some sort of order. They started searching for it. As the pattern began to form, certain substances seemed to be needed to complete it. They were looked for and discovered.

All this took a long time and was very difficult.

To appreciate some of the difficulties that the searchers had, let us take another example. You find a box filled with pieces of old jig-saw puzzle. You are curious to find out what the puzzle will look like when fitted together. Some of these pieces (compounds) are from another puzzle but you don't know this yet. Some other pieces (unknown elements) are not in the box, and must be found – but you won't try to do this until you realize they *are* missing. The picture on the box was lost long ago, so you don't know what the finished result should look like. A good Sunday afternoon's task.

Scientists have succeeded in solving a problem of this type, but immensely more complex. Elements as different from one another as iron and chlorine, or sodium and carbon, have been fitted into an orderly scheme.

Let us examine the earliest attempts to bring order to the knowledge which was being gathered by the scientists. Three names for a start:

Antoine Lavoisier and his 'Groups'

J. W. Döbereiner and his 'Triads'

John Newlands and his 'Octaves'

Order in Groups: Lavoisier – A French nobleman, Lavoisier had many scientific interests. In 1790 he was a member of the commission that introduced the metric system, but he is most famous for his explanation of burning which led to the downfall of the 'phlogiston theory'. In 1789 Lavoisier published one of the most influential books on chemistry ever written. It was called *Traité Élémentaire de Chimie* (*Elements of Chemistry*), and in it he gave a list of 'simple substances not decomposed by any known process of analysis', or, as we would say, a list of 'the elements'. He divided this list into several groups, based on the similar chemical behaviour of the elements in each group. As you can see from the accompanying illustration (photographed from his book), he put oxygen, nitrogen, hydrogen, light, and heat together in the first group. In the second, he put sulphur, phosphorus,

Antoine Lavoisier (1743–94), who first attempted to sort the elements into groups. His arrangement is shown inside the front cover.
Radio Times Hulton Picture Library

carbon, chlorine, and fluorine. He called these the 'acidifiable' elements, by which he meant those elements that formed an acid on combining with oxygen. In the third group, he put the metals: silver, arsenic, bismuth, cobalt, copper, tin, lead, tungsten, and zinc. Finally, in the fourth group, he put what he called the 'simple earthy salt-forming substances': lime (calcium oxide), baryta (barium oxide), magnesia (magnesium oxide), alumina (aluminium oxide), and silica (silicon dioxide). In Lavoisier's time, this last group was believed to be composed of elements because the substances had not then been broken down into anything simpler. We now know them to be compounds which are very difficult to decompose into their constituent elements.

Order in Threes: Döbereiner's Triads – Lavoisier's work was an important beginning; it implanted the idea of a relationship between the elements, but it didn't give much of a clue to the eventual pattern. The next step in piecing together the puzzle was taken in 1817 by a German scientist, J. W. Döbereiner, who was a professor at the University of Jena where Goethe, the German poet, attended his lectures.

Döbereiner realized that three recently isolated elements, calcium, strontium, and barium, all had properties that were strikingly similar. Perhaps you too have noticed elements which were similar, and thought that they might be chemically related? Calcium, strontium, and barium all occur naturally as carbonates and sulphates which do not dissolve in water and which do not decompose easily when heated. Their chlorides are all soluble in water and their oxides dissolve in water to produce a strongly alkaline solution. The three elements were also isolated in the same way: electrolysis of the molten chlorides by Davy in 1808.

Döbereiner noticed that the atomic weight of strontium (88) was almost midway between the atomic weights of calcium (40) and barium (137). He called this group of three elements a 'triad'. In later years, he noticed also that two other 'triads' of elements – chlorine, bromine, and iodine, and lithium, sodium, and potassium – repeated the same pattern. Not only were their properties similar but also the atomic weight of the middle one fell halfway between those of the other two. Döbereiner thought he had discovered the key to the jig-saw: the elements of nature fitted together in threes. His discovery became known as the 'Law of Triads'. But this grouping in threes was restricted to only a few elements. What of all the others? Döbereiner's observation that the link-up between the elements depended in some way upon their atomic weights provided the key.

Order in Eights: Newlands's Octaves – Before further progress could be made, it was necessary to find out the atomic weights of all the known elements with some degree of accuracy. In Döbereiner's time atomic weights were still largely a matter of guesswork, and it was not until 1857, after intensive work by other scientists, that an accurate method was found for determining them. Six years later John Newlands, a British chemist, found that when the elements were arranged in order of their atomic weights, with hydrogen (the lightest element) numbered 1, the second lightest (thought at the time to be lithium) numbered 2, the third numbered 3 and so on, then elements 1, 8 and 15 were similar, as were elements 2, 9 and 16 and so on. As Newlands wrote 'the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music'. This kind of repetition, with similar properties

J. W. Döbereiner (1780–1849), who grouped some of the elements in 'triads' (groups of three).

'periodically' recurring, is called periodic, and is the origin of the name 'periodic table'. Unfortunately, although the periodic relationship Newlands had found held good for the first sixteen elements, it did not work after the seventeenth. This made scientists rather reluctant to accept Newlands's ideas.

At the Chemical Society meeting where he put forward these ideas, one eminent scientist was so sceptical of their usefulness that he enquired 'whether Mr Newlands had ever examined the elements according to the order of their initial letters?' This is how Newlands worked out his 'Arrangement of Elements'.

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
Co,Ni	Cu	Zn	Y	In	As	Se
Br	Rb	Sr	Ce,La	Zr	Di,Mo	Ro, Ru
Pd	Ag	Cd	Sn	U	Sb	Te
I	Cs	Ba, V	Ta	W	Nb	Au
Pt, Ir	Os	Hg	Tl	Pb	Bi	Th

J. A. R. Newlands, who in 1863 proposed the 'Law of Octaves' whereby elements are arranged like the octaves in a musical scale.

Notice two striking errors. First, in each vertical row of similar elements, there are elements that just do not belong in that group – for example, the metals cobalt and nickel in between the two similar elements chlorine and bromine. This was the chief reason why the arrangement was not accepted. Second, the metal tellurium (Te) has been placed before iodine, though its atomic weight is greater. This was a bold step. By taking it, Newlands could put iodine in the same group as the similar element bromine. But, although it made for an orderly pattern of properties, it was obviously 'forcing the pieces to fit'. One often tries this in ordinary jig-saws; the pattern seems right but the pieces won't interlock.

Questions

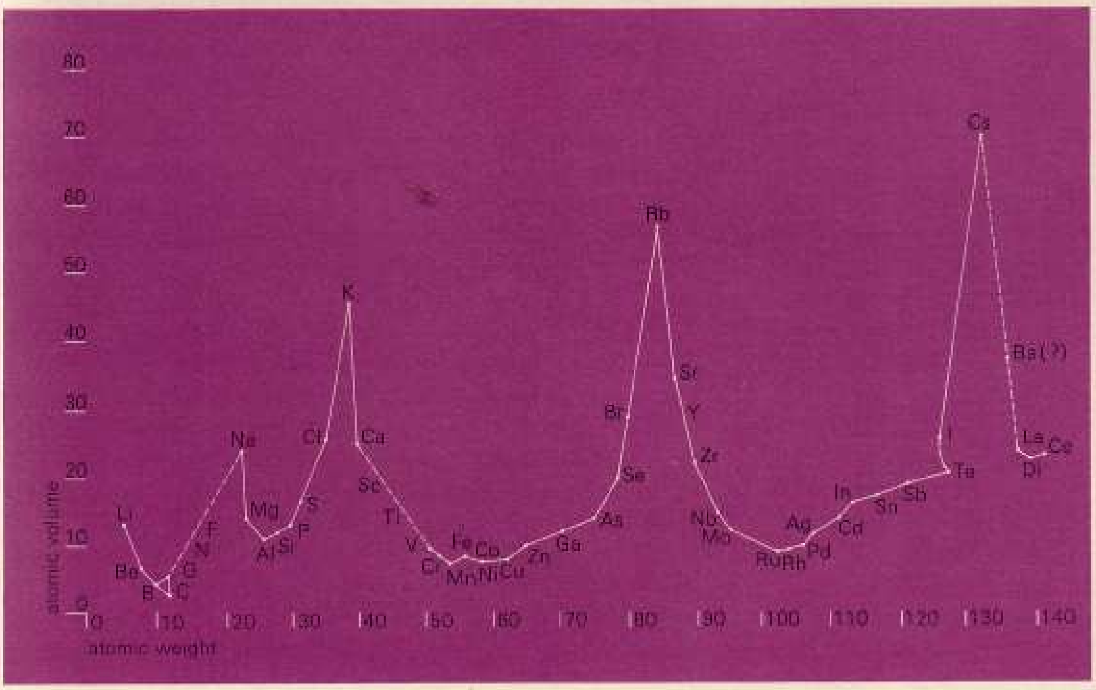
1. Given that the atomic weight of lithium is 6·94 and of potassium is 39·1, what would you suppose the atomic weight of sodium to be?
Check the answer in your *Book of Data*.

2. In Newlands's second group of elements (Li–Os – see above), which elements strike you as being out of place?

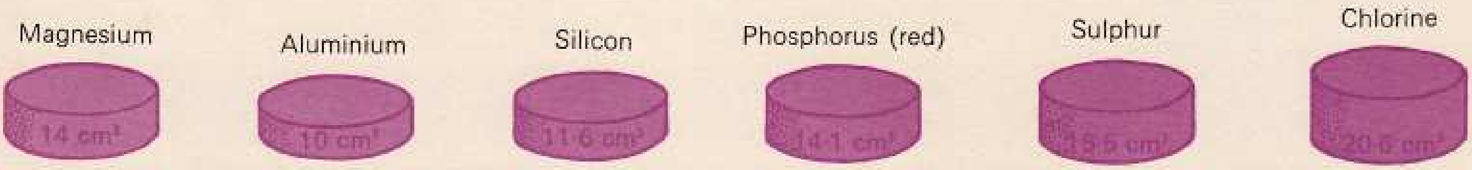
part two Further progress

Lothar Meyer (1830–95), who plotted atomic volume against atomic weight to give the curve shown in the accompanying graph.

Lothar Meyer's atomic volume curve, showing a periodic relationship of the elements based on atomic weight.



Gram-atomic volumes of the Lithium Group of metals and of the elements in the third period. Notice the pattern of volume change and see where these elements fit into Lothar Meyer's curve. (The drawings of the cylinders – each with a radius of 1cm – are half actual size.)



Meyer's Curves – Meanwhile, two other chemists had been grappling with the same problem that Newlands had attempted to solve. One, Lothar Meyer, was working in Germany; and the other, Dimitri Mendeleev, in Russia. In 1864 Lothar Meyer, then thirty-four years old and Professor of Chemistry at Tübingen, worked out the volume that one gram atom of an element would occupy if it were a solid. This he called the 'atomic volume' of the element. He plotted atomic volumes against atomic weights to give the curve shown in the accompanying graph. Look at lithium, sodium, and potassium. They lie on the highest points of the curve – as do rubidium and caesium, which are members of the same 'family' but are much rarer. (Find the positions of the other groups of elements that have been mentioned and see if they too occupy related positions.) From Lothar Meyer's curve it is possible to arrive at a periodic arrangement of the elements similar to that put forward by Mendeleev (as discussed below); indeed Meyer did produce such a table. But most of the credit for this arrangement of the elements goes to Mendeleev because he was a man bold enough to make some detailed predictions about elements which nobody had yet discovered.

Mendeleev's Table – Dimitri Mendeleev, who published his work in 1869, was Professor of Chemistry at St Petersburg (now Leningrad). He arranged the elements according to their atomic weights, much as Newlands had done but with two important differences: he left gaps for elements which, he said, had not yet been discovered; and he listed separately some 'odd' elements (for example, cobalt and nickel) whose properties did not fit in with those of the main groups. This regrouping helped to remove the obstacle to the use of Newlands's arrangement and, apart from the fact that it contained only about sixty elements, Mendeleev's periodic table is in principle much the same as that which we use today (see p. 6). In other words, the outline of the jig-saw was complete, although a number of the pieces were still missing.

Perhaps the most important feature of Mendeleev's work was that he left gaps in his table where he thought the 'missing' elements should be. This was important because, if a theoretical idea in science is to be really useful, it should not only explain the known facts but also enable new things to be predicted from it. In this way the theory can be tested by seeing whether or not the predictions prove to be correct, and also the theory can lead to scientific advance from following up the new ideas. Both Newlands and Lothar Meyer failed to provide a basis for prediction in their work. But with Mendeleev – and this drew attention to his table in the first place – not only were elements discovered which fitted the gaps in the table that he had left for them, but also their properties agreed remarkably well with those that Mendeleev had said they should have.

Take one example. When Mendeleev was arranging his table, he left a gap for an element between silicon and tin. He predicted that the atomic weight of this element would be 72 and its density 5·5 – basing his predictions on the properties of other known elements which surrounded the gap. Fifteen years later the element was discovered. It had an atomic weight of 72·6 and a density of 5·47. It was given the name germanium. Mendeleev made other predictions about it too. To see how close his calculations were, look at the table on page 8.

3	4																
Li	Be																
11	12																
Na	Mg																
19	20	21															
K	Ca	Sc															
37	38	39															
Rb	Sr	Y															
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70
Cs	Ba	La	*Ce*	*Pr*	*Nd*	*Pm*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Er*	*Tm*	*Yb*
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102
Fr	Ra	Ac	*Th*	*Pa*	*U*	*Np*	*Pu*	*Am*	*Cm*	*Bk*	*Cf*	*Es*	*Fm*	*Md*	*No*

Periodic Table

There are hundreds of different versions of the periodic table. Nearly all of them are divided into the same groups and periods, but they are laid out differently to emphasize particular relationships between elements. Here is the version with which you are probably familiar.

										1 H	2 He				
										5 B	6 C	7 N	8 O	9 F	10 Ne
										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
71 *Lu*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
103 *Lw*															

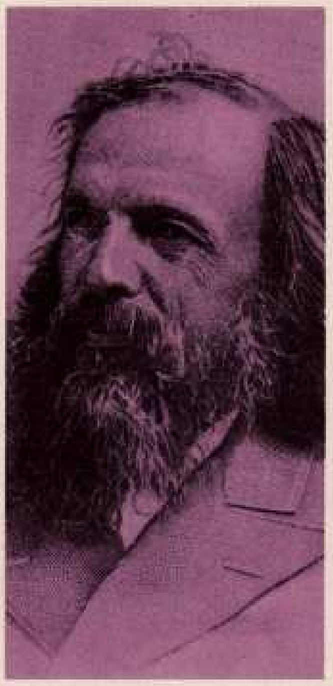
Some Properties of Germanium

Mendeleev's Predictions	*Observed Properties*
Will be a light grey metal	Is a dark grey metal
Will combine with two atoms of oxygen to form a white powder (the oxide) with a high melting point	Combines with two atoms of oxygen to form a white powder (the oxide) with a melting point above 1,000°C.
The oxide will have a specific gravity of 4·7	Specific gravity of the oxide is 4·703
The chloride will have a boiling point less than 100°C.	The chloride boils at 86·5°C.
The specific gravity of the chloride will be 1·9	The specific gravity of the chloride is 1·887

This confirmation of Mendeleev's predictions was the strongest possible proof that his ideas were correct. Nevertheless his ideas still needed modifying. Like Newlands before him, Mendeleev had placed tellurium (atomic weight 127·6) in front of iodine (atomic weight 126·9). It was the same problem of 'forcing the piece with the right pattern' to fit. He justified this by arguing that a more accurate determination of their atomic weights would show the atomic weight of tellurium to be less than that of iodine. Chemists very soon set about redetermining these values, but merely succeeded in confirming the original ones. It was some years before a satisfactory explanation was forthcoming.

Question

The elements on Lothar Meyer's atomic volume curve can be equally well arranged in the form of a table of elements. The position of the elements in the table depends upon the position of the elements on the curve. See if you can work out the table.



D. I. Mendeleev (1839–1907), who was the first to produce a periodic table similar to those in use today.
Radio Times
Hulton Picture Library

A crystal of the metal, germanium, the properties of which Mendeleev predicted so accurately.
Standard Telephones and Cables Ltd

part three The final solution

Moseley and Atomic Numbers – Up to 1900 the only definite idea that people had about atoms was that of their weights. But during the first years of the present century a great deal was found out about atomic structure (as described in a Background Book called *Inside the Atom*). Among other things, it was discovered that each atom had a central core (or nucleus) of positive electrical charge. This discovery was made by Lord Rutherford who, at the time, was in charge of the Physics Department at Manchester University. Working under him there was a young research student called Henry Moseley. On investigating the X-ray spectra of various atoms, Moseley found that the amount of positive charge carried by an atomic nucleus was a definite, and different, amount for each element – in the same way that atomic weight is different for each element. This amount of positive charge was called the atomic number of the element. Hydrogen had an atomic number of 1, helium of 2, lithium of 3, and so on – the atomic number of each element is shown in the periodic table on page 11. Moseley also found that, if elements were arranged in order of their atomic numbers, they fell into nearly the same periodic pattern as they did when they were arranged in order of their atomic weights. Nearly but not quite. Tellurium came before iodine, as Newlands had felt it should come, without any forcing. Thus a problem that had been baffling chemists for a long time had at last been solved.

The idea of atomic numbers also helped to clear up several other small irregularities in Mendeleev's table and, ever since Moseley's work in 1913, atomic number and not atomic weight has been the basis for arranging the elements. After Moseley – he was killed at Gallipoli in the first World War at the age of twenty-eight – a few elements still remained to be discovered; their absence was even more obvious when the atomic number arrangement of the elements was being used instead of the atomic weight. Chemists set to work to find them, and now all the elements that are discoverable in nature have, we believe, been discovered. In a sense the jig-saw is complete – but *not* the periodic table. Elements are still being added to the table, but these elements are being made in the laboratory and are not, as far as we know, to be found in nature.

Questions

1. Would you suppose that atomic number and atomic weight were in any way related? If so, what kind of relationship do you suppose it would be?

2. It might be possible to group the elements according to their colours. Would this make a sensible pattern, and if not why not?

H. J. G. Moseley (1887–1915), whose work on atomic numbers led to the modern periodic table.
The Royal Society

part four Use of the Periodic Table

When the periodic table was being built up, it was obviously useful in pointing to 'missing' elements. Mendeleev's predictions about the elements needed to fill the gaps in his table, and the kind of properties that they should have, led to many of these elements being discovered far sooner than they would otherwise have been. Moseley's work, too, led to further discovery of elements. But now that the gaps have been filled, what use is the periodic table? Its most important use at the present time is what it has always been – to order a confused heap of factual information into a simple pattern of related facts which the human mind is able to comprehend. Without the order that the periodic table provides, the study of chemistry would often be chaotic. Let us look more closely at what this 'order' is.

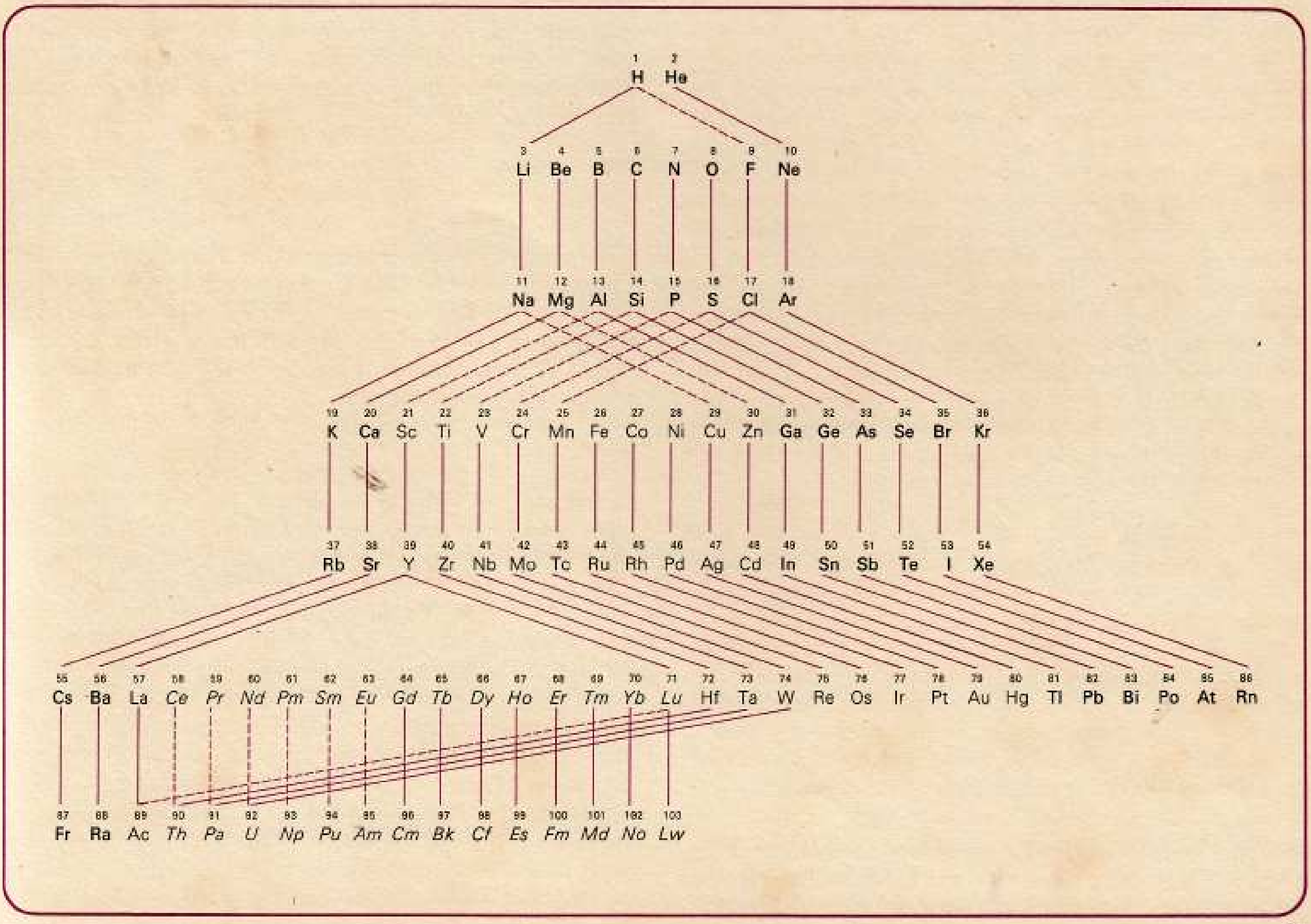
The elements in the periodic table are related to each other in two ways: *vertically* in rows that are called 'groups'; and *horizontally* in rows that are called 'periods'.

Groups – The groups consist of families of elements that have similar properties. For example, the Lithium Group (see periodic table) consists of the alkali metals. These do not behave in a way that we usually associate with metals. Compared with most other metals, they have low melting and boiling points (see *Book of Data*). They all react spontaneously with water to form very strong alkalis – hence their name, alkali metals. Chemical reactivity is the most apparent characteristic of this family, and that is why we never meet with them in the metallic state except sometimes in the laboratory.

Lithium, the lightest solid element, reacts quietly and steadily with water; sodium reacts more violently and melts with the heat of the reaction; and potassium actually catches fire. As we proceed down the group, so the reaction becomes more vigorous. We should expect caesium to react explosively – and this is what happens. Similar comparisons can be made with the reactions of the alkali metals with other chemicals. The resemblance is most obvious between those members of the family that are listed next to each other and least obvious between those that are listed farthest apart. Sometimes irregularities creep into the pattern. For example, the melting points of the chlorides of the alkali metals decrease from sodium to caesium but that of lithium (which we would expect to be the highest) is the lowest of all. This fact was so unexpected that it led chemists to try to discover the reason why, and they found it was to do with the very small size of the lithium atom. Highlighting such irregularities is another useful job of the periodic table. Without the table, a lot of irregularities would not have been noticed and many interesting investigations would not have been started.

Moving across the periodic table, we meet with groups of metals, many of which are familiar. It is a useful exercise to study some of the members in these groups and to see if you can pick out any family resemblances. (What about magnesium and calcium in the Beryllium Group, nickel and platinum in the Nickel Group or silver and gold in the Copper Group?) Eventually we arrive at the Carbon Group, where the first member, carbon, is obviously a non-metal and the last member, lead, is obviously a metal. Those elements in between (silicon, germanium, and tin) show a gradual transition from the non-metallic to the metallic state. We now use germanium, a half-metal, as a semi-conductor in transistor sets. In the Fluorine Group, the family of halogens, all the elements are non-metals, although iodine, as its lustrous crystals suggest, has some metallic characteristics. As you may have noticed, the non-metals in the periodic table (there aren't

Another well-known version of the periodic table. Full lines indicate a pronounced resemblance between elements; dotted lines indicate some resemblance.



many of them but they are important) occupy the top right-hand corner of the table. The inert gases, forming a separate group on the extreme right, terminate the horizontal periods and so constitute a kind of dividing line between one period and another.

Periods – The periods, which run horizontally across the table, vary a great deal in length. In the second and third (which we shall look at in more detail), there are eight in each. The fourth and fifth are longer. They each consist of eighteen elements, including many well-known metals. Longest of all is the sixth period with thirty-two elements. To list all thirty-two along the same line would make for a cumbersome chart, and for convenience a metallic series of elements called the 'rare earths' is often listed separately below. (The rare earth elements, as their name suggests, are found in only very small quantities, and for a long time they proved difficult to separate from their ores. However, thanks to modern separation techniques, especially ion exchange, some of them are coming into prominence.) The seventh period, in which all the elements are radioactive, is incomplete. It, too, is expected to contain thirty-two elements, but so far there are only seventeen, most of which have been made in the laboratory. In brief, the structure of the periods is 2, 8, 8, 18, 18, 32, 32, which is a good deal more complicated than the regular 8, 8, 8, 8 . . . as Newlands imagined it to be. Yet you may be able to see a pattern even here.

$$2=2\times1$$

$$8=2\times(1+3)$$

$$8=2\times(1+3)$$

$$18=2\times(1+3+5)$$

$$18=2\times(1+3+5)$$

$$32=2\times(1+3+5+7)$$

Each step is made up of twice the sum of odd numbers and, as you will learn later, reflects the way in which the electrons (negative charge) are held by the nucleus (positive charge).

The periods exhibit a less obvious relationship between the elements than the groups. Here the elements are rather next-door neighbours than families. By way of example let us take a closer look at the second and third periods. These consist of seven elements each, eight counting the inert gases. The second extends from lithium to fluorine, and the third from sodium to chlorine. The lefthand elements in each period – lithium and sodium – are metals and the righthand elements – fluorine and chlorine – are non-metals. Those in between represent a gradual transition from metal to non-metal, with the second period containing in it more non-metals than any other. An interesting pattern emerges if we look at the compounds these elements form with hydrogen. The numbers beneath the elements show the maximum number of hydrogen atoms they combine with.

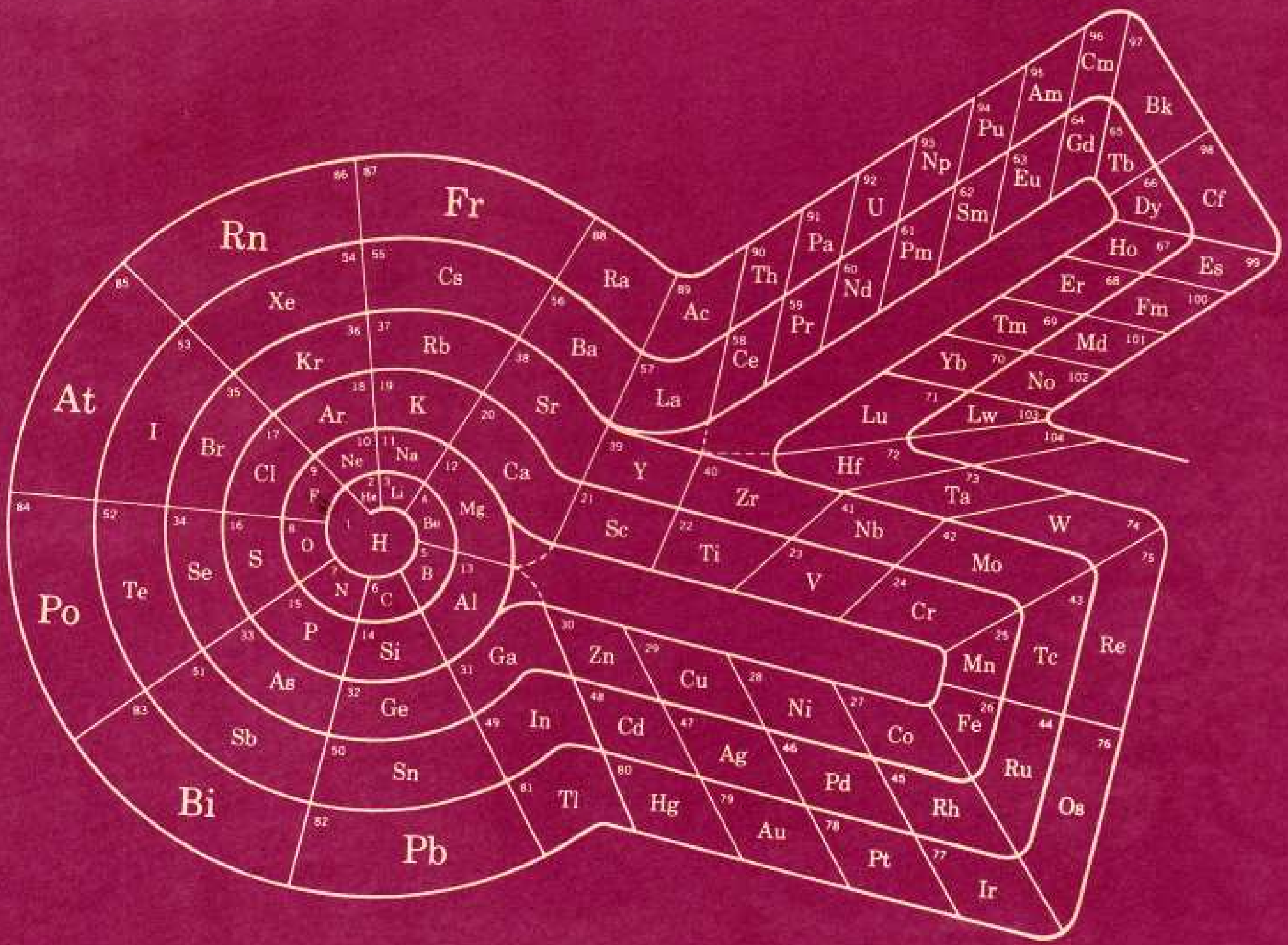
Lithium Sodium	Beryllium Magnesium	Boron Aluminium	Carbon Silicon	Nitrogen Phosphorus	Oxygen Sulphur	Fluorine Chlorine
1	2	3	4	3	2	1

Compounds with oxygen exhibit a very different pattern, but a pattern nevertheless. Why are there regularities of this kind? In probing to find out, people are led to a much deeper understanding of chemistry. As with irregularities, it is unlikely that these patterns of regularity would be noticed if it were not for the periodic table.

Question

It is interesting to see what properties of elements are related in a periodic way to their atomic numbers. A useful method of showing this is to plot on a graph the property against the atomic numbers – similar to the method used by Lothar Meyer when he plotted atomic volume against atomic weight (see page 4). Try plotting melting points, boiling points and latent heats of the elements (from your *Book of Data*) against atomic number, and examine carefully the curves that you get. Then plot some other properties of the elements against atomic number and see if you can make sense of your results.

An unusual shape for the periodic table – without an obvious break between the periods.



Chemistry Background Books
General editor H P H Oliver Author of this book N Coats
Art editor Ivan Dodd
Published for the Nuffield Foundation by Longmans/Penguin Books
Longmans Green and Co Ltd 48 Grosvenor Street London W1
Penguin Books Ltd Harmondsworth Middlesex England

First published 1966
Reprinted 1967
Made and printed in Great Britain by The Curwen Press Limited

CBB04312