I.V. Petryanov
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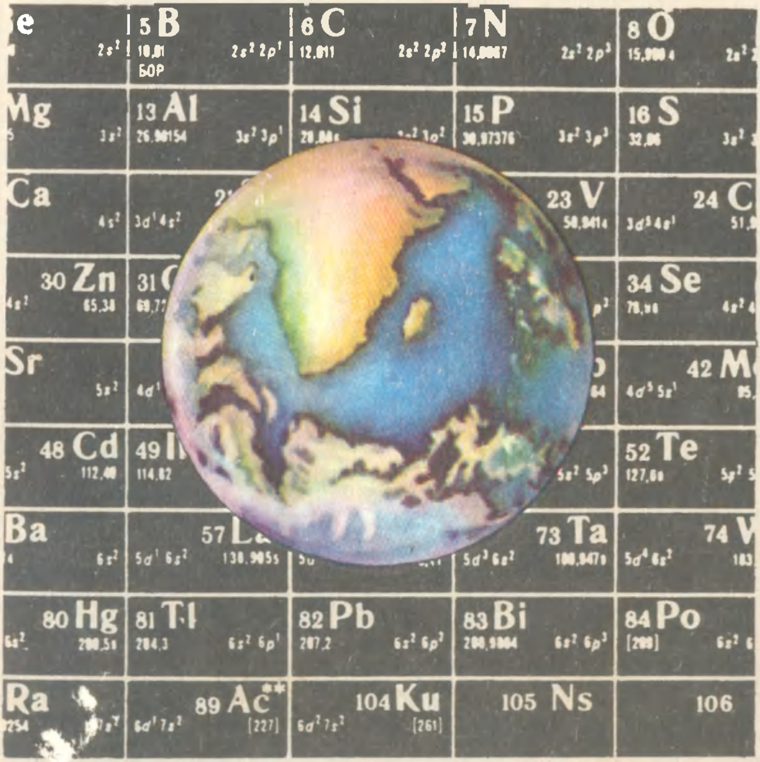
ELEMENTARY ORDER



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From Scientists

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ELEMENTARY ORDER:

Mendeleev's Periodic System

Translated from the Russian by
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Contents

D. I. Mendeleev
(photo, 1869).

> ...The aforesaid is a far from full account of what has been seen so far in the boundless region of chemical evolvements by means of the periodic law telescope and, the more so, it is not all that there is yet to be seen....
>
> *D. Mendeleev*

How the Elements Were Reduced to Order

Many are the feats in the history of human knowledge, but few can compare with that of Dmitri Ivanovich Mendeleev. The importance of Mendeleev's bold scientific breakthrough not only remains undiminished in the course of time, but continues to grow. Nobody can tell whether the content of one of science's greatest generalizations, the periodic law of the elements, will ever be completely exhausted.

History is strict, and perhaps overparticular, in picking out and in grading all that has been discovered and created by man. The astoundingly clear-cut features of Mendeleev's table in our time conceal the colossal work done by him in analyzing all that had been discovered previously concerning the transformations of matter. This work became the foundation that made feasible Mendeleev's remarkable intuitive guess about the existence of a new law, the law of periodicity of the properties of chemical elements.

Laws of nature, discovered by man, differ in the volume of knowledge they enable us to acquire, and as to the fields of learning they are valid in. This makes it difficult to compare them with one another. But all of nature's laws are comparable in their most vital aspect – the possibility they provide for predicting new phenomena and foreseeing the hitherto unknown. In this respect, the periodic law has no equal in the history of science.

Mendeleev paved the road to modern and even future chemistry by indicating the rational way to search for the elements. On the basis of his periodic law scientists have predicted the existence of previously unknown chemical elements and described their properties.

No such triumphant success had ever been achieved in the century-old history of chemistry. A new basic law of nature had been discovered. The chemistry of separate, unrelated substances gave way to an orderly table, uniting all the chemical elements into a single system. But Mendeleev confronted science with an even more grandiose problem: to account for the mutual relations between all the elements, and between their physical and chemical properties.

Mendeleev's periodic law had a tremendous influence on the progress of research in atomic structure and in the nature of matter. In turn, the advances in atomic physics, the development of new investigation techniques, and the evolution of quantum mechanics extended and deepened the essence of the periodic law.

The discovery of the periodic law is the supreme landmark in the annals of chemistry. Historians of science usually differentiate two periods in the development of chemical knowledge: *before* and *after* Mendeleev's law.

The state-of-the-art before Mendeleev. There were 63 known elements at this time. Their properties had been only poorly investigated; even the atomic weights had been incorrectly or inaccurately determined. Are 63 elements sufficient or too few for the job Mendeleev undertook? If we recall that today 106 elements are known, then 63 would not seem to be very many. But they were quite sufficient to note some regularity in the variation of their properties. If only 30 or 40 elements had been known it would have hardly been possible to make some discovery. A definite minimum of known elements were required. This is why we can rightfully call Mendeleev's discovery a timely one.

But were there no scientists before Mendeleev that had tried to reduce all the known elements to a definite order, to classify them and to arrange them into some kind of system?

Many tried. We cannot contend that their attempts were of no avail; they did reveal some grains of truth. In 1829, for instance, the German chemist Johann Wolfgang Döbereiner grouped elements with similar chemical properties into sets of three: lithium, sodium and potassium; chlorine, bromine and iodine; etc. He called these groups triads. Subsequently, the whole set of such elements were named natural groups.

The eminent Swiss-born Russian chemist, Germain Henri Hess, became interested in 1849 in the classification of the elements. In his textbook "Foundations of Pure Chemistry" he described four groups of nonmetallic elements with similar chemical properties:

iodine	tellurium	carbon	nitrogen
bromine	selenium	boron	phosphorus
chlorine	sulphur	silicon	arsenic
fluorine	oxygen		

Hess wrote: "This classification is still very far from a natural one, but it does unite elements and groups that are quite similar, and when more comprehensive information becomes available, the classification can be improved".

One of the attempts to classify the elements was made in 1862 by the French geologist Alexandre Émile Beguyer de Chancourtois. He presented his system in the form of a helix on the surface of a cylinder. Plotted on each turn of the helix were 16 elements. Similar elements were arranged one under the other along generatrices of the cylinder. But none of the scientists of his time paid any attention to Beguyer de Chancourtois's arrangement.

In 1866 the English chemist John Alexander Reina Newlands proposed the so-called law of octaves. He contended that everything in the world complies with a general harmony, which should be the same for both chemistry and music. Hence the properties of chemical elements, arranged in the order of increasing atomic weight, should repeat after each seven elements, in the same way as in the musical scale similar notes are found in octaves following each seven successive notes. But, according to the law of octaves, such entirely unlike elements as carbon and mercury were supposed to be similar.

When Newlands reported on his work at a meeting of the London Chemical Society, one of those present asked with great sarcasm whether the learned speaker had tried to arrange the elements in alphabetical order, and whether this had led to the discovery of some law.

Closer than others to the truth, very likely, were the English chemist William Odling and the German chemist Julius Lothar Meyer. In 1864 Meyer proposed a table in which all the known chemical elements were divided into six groups in accordance with their valencies. In appearance, Meyer's table was somewhat like the future table proposed by Mendeleev. But neither Meyer's nor any other of the previous classifications contained the one basic idea: the general and fundamental law of the variation in the properties of chemical elements. They only displayed a semblance of order in the world of elements. The same shortcoming was inherent in Odling's table as well.

Mendeleev's forerunners, who only observed particular features of the fundamental law of the world of chemical elements, could not, for various reasons, rise to the supreme generalization and perceive the existence of basic order in this world.

Why was it Dmitri Ivanovich Mendeleev that succeeded in discovering the periodic law of the elements? How was it done?

"A Trial System of the Elements". On February 17, 1869, while preparing for a business trip, Professor Dmitri Ivanovich Mendeleev of the University of St. Petersburg, jotted down the first draft of a table of chemical elements on the back of the envelope of a letter he had received from a chemical plant, asking him to come and unravel some production problem they had. In this tentative table, Mendeleev arranged the elements in the order of increasing atomic weights and then noted the periodic repetition of their properties. On that day he postponed his trip to the plant to do more work on his table. First he wrote down all the elements then known with their most important chemical and physical properties on separate cards. Arranging the cards in various ways, taking into consideration the atomic weights of the elements, their properties and the properties of the compounds they form, Mendeleev compiled his first version of a system of chemical elements. He called it "A Trial System of the Elements, Based on Their Atomic Weight and Chemical Similarity". On March 1, 1869, Mendeleev sent his "Trial System", printed in the form of a table, to various Russian and foreign scientists.

This first draft of the table is very crude and imperfect; it is far from the modern form of the periodic system. But it was the earliest graphic illustration of the law discovered by Mendeleev: "Elements arranged according to the magnitudes of their atomic weight display distinct periodicity of their properties". This formulation is taken from Mendeleev's paper "Relationship Between the Properties and Atomic Weight of Elements". This paper was the result of Mendeleev's reasoning when working on his "Trial System...".

Not once in this paper does Mendeleev use the term "periodic law". Like all great scientists he is unassuming and careful in his final conclusions. The fact that he had actually discovered a basic law of nature was clear to him from the very beginning. But he felt that much still remained to be done before the observed regularity could be called a law and be recognized by other scientists as one.

For two and a half years, up to December 1871, Mendeleev continued to work on his discovery.

The first report on the discovery was made March 6, 1869 at a session of the Russian Chemical Society. Mendeleev did not attend the session. In place of the absent author, his paper was read by the chemist N. A. Menshutkin. The following formal entry was made in the proceedings of the Russian Chemical Society concerning the session held on March 6, 1869: "N. Menshutkin made a report on behalf of D. Mendeleev on 'A Trial System of the Elements, Based on Their Atomic Weight and Chemical Similarity'. In the absence of D. Mendeleev, the discussion of this problem is postponed until the next session".

These formal unimaginative proceedings became a historical document of immense consequence, signifying mankind's first information on a new law of nature. But many scientists, contemporaries of Mendeleev, hearing of and becoming acquainted with this system of the elements for the first time, could not understand it.

What was the decisive step? Mendeleev singled out three circumstances that, in his opinion, facilitated the discovery of the periodic law.

In the first place, the atomic weights of most of the known chemical elements had been determined more or less accurately.

Secondly, a clear-cut concept had been formed concerning the groups of elements having similar chemical properties (natural groups).

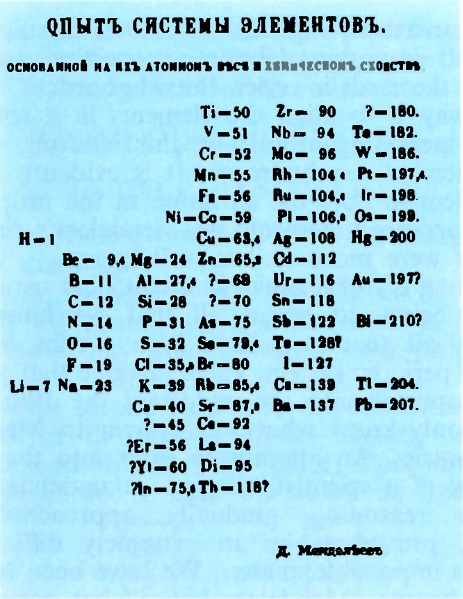
In the third place, the chemistry of many rare elements had been investigated by 1869. Without this knowledge it would have been very difficult to reach any definite conclusions.

Finally, the decisive step toward the discovery of the law was made when Mendeleev compared *all* the elements with one another on the basis of their atomic weights. His predecessors had compared with one another only elements that were similar, i.e. the elements of the natural groups. These groups turned out to be unrelated. Mendeleev united them logically in the design of his table.

How was the periodic law discovered? Historians of science sometimes indulge in an argument as to what idea was unfolded first in Mendeleev's mind, the concept of the periodic law or the periodic system of elements?

This, in our opinion, is a pointless discussion. The system of elements is a regularity expressed in the form of a table. But to grasp the essence of the law it was necessary first to arrange all the known chemical elements into a definite system, i.e. into a table. Therefore, it is quite impossible to separate the system from the law.

The following quotation demonstrates Mendeleev's own account of the creative process that led to the discovery of the periodic law. "...Unintentionally, the idea occurred that there must be some relation between the mass and chemical properties. And since the mass of substances is finally expressed, though not absolutely but only relatively, in the form of the weights of atoms, it is necessary to look for a functional correspondence between the individual properties and their atomic weights. We cannot find anything, however, be it mushrooms or some relationship, unless we look and try. Hence, I began to sort out the elements, writing their names on separate cards, together with their atomic weights, basic features, elements similar to them an



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti-50	Zr-90	?-180.
			V-51	Nb-94	Ta-182.
			Cr-52	Mo-96	W-186.
			Mn-55	Rh-104,4	Pt-197,4.
			Fe-56	Ru-104,4	Ir-198.
			Ni-Co-59	Pl-106,6	Os-199.
H-1			Cu-63,4	Ag-108	Hg-200
	Be-9,4	Mg-24	Zn-65,2	Cd-112	
	B-11	Al-27,4	?-68	Ur-116	Au-197?
	C-12	Si-28	?-70	Sn-118	
	N-14	P-31	As-75	Sb-122	Bi-210?
	O-16	S-32	Se-79,4	Te-128?	
	F-19	Cl-35,5	Br-80	I-127	
Li-7	Na-23	K-39	Rb-85,4	Cs-133	Tl-204.
		Ca-40	Sr-87,6	Ba-137	Pb-207.
		?-45	Ce-92		
		?Er-56	La-94		
		?Yt-60	Di-95		
		?In-75,6	Th-118?		

Д. Менделѣевъ

“My first ideas on periodicity,” wrote Mendeleev, “were expounded in a leaflet that was sent by me on March 1, 1869 to many scientists.” This is the very first table of the periodic system of the elements. Remarkable is the fact that it already has gaps with question marks for then unknown elements.

elements with atomic weights close to their weights. This quickly led to the conclusion that the properties of elements are a periodic function of their atomic weights. Having doubts about certain obscure points, I never for a minute doubted the generality of the conclusion I had arrived at, because it was impossible to regard this phenomenon as being mere chance.”

It would seem that everything concerning the discovery was quite simple. As a matter of fact, there is nothing unusual about writing the symbols for the elements on cards, together with their atomic weights and most important (basic) properties, and then arranging the cards in order. But what order? The most obvious way is to align the elements in a row in the order of increasing atomic weights, starting with the lightest element, i.e. hydrogen. It is evidently no difficult problem to note the variation in the properties of correctly arranged elements. In Mendeleev's time these properties were more or less well known.

What then is to Mendeleev's credit? Let us agree, for the time being, to forget all that we know about chemistry, all that you have been taught in school about the periodic system. Then, imagine that you have been transported into the middle of the 19th century and can only know what was known to Mendeleev's contemporaries. An attempt to enter into the creative laboratory of a scientist, to gain an understanding of how his reasoning gradually approached some discovery, proves to be an extremely difficult, and sometimes impossible, matter. We have been fortunate, however, because Mendeleev himself has come to our aid, leaving an account of how he began to arrange and combine his cards. We shall attempt, step by step, to follow the course taken by this great scientist. We cannot guarantee complete accuracy, but matters, evidently, took place as follows.

First we shall consider the sequence of the elements in the order of increasing atomic weights.

Hydrogen (H) has the lowest atomic weight; it equals 1. The next in order at that time was lithium (Li). Its atomic weight is about 7. But there was no single opinion as to the next element. The point is that there was some doubt about the chemical formula for beryllium oxide. Some chemists thought it should be BeO, whereas others preferred Be_2O_3. In the first case the atomic weight of beryllium would be 9 (rounded off), and in the second, 14. Hence, its place in the row was uncertain. If we leave Be alone for the time being, the further arrangement of the elements should be:

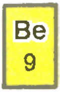
B(11) C(12) N(14) O(16) F(19) Na(23)

Mg(24) Al(27) Si(28) P(31) S(32) Cl(35)

Here the atomic weights have been rounded off to whole numbers.

How did Mendeleev arrange his cards with the elements? Of course, on his first card he had also written the name, atomic weight and properties of hydrogen.

He put the second card with the atomic weight and properties of the metal lithium directly under the hydrogen card. In the third place, alongside lithium, Mendeleev placed a card on which he had written:



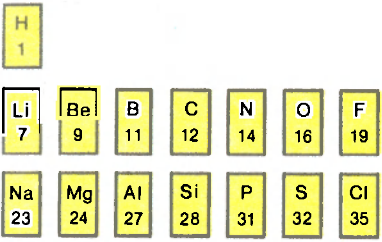
This was a bold maneuver because, of the several values of possible atomic weights of beryllium, Mendeleev chose one quite definitely. What made him do this? Simply, because he had taken into account the features of beryllium's chemical properties. They constitute a smooth transition from the properties of lithium to those of boron.

Mendeleev put the boron card in the fourth place. The fifth place was occupied by carbon. Nitrogen was the sixth, and it was followed by oxygen and fluorine.

The ninth card, belonging to sodium, was placed under the second, on which, as we already know, the chemical characteristics of lithium had been written.

The following two places were taken by magnesium and aluminum. Under the carbon card he put silicon, under nitrogen he put phosphorus, under oxygen he put sulphur, and under fluorine he put chlorine.

At this point, Mendeleev had arranged his cards at the beginning of his table as follows:



H 1						
Li 7	Be 9	B 11	C 12	N 14	O 16	F 19
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35

Thus the vertical columns consisted of chemically similar elements. The metal lithium resembles the metal sodium: both are soft, light in weight, can be cut with a knife, and react violently with water, forming alkalis. Beryllium and magnesium also resemble each other. Fluorine has much in common with chlorine; they form like compounds with various metals. And every chemist knows that the properties of oxygen and sulphur are similar to one another.

In this arrangement, the periodicity of properties of the elements is quite clearly revealed. Elements with like properties correctly succeed one another in these first two short periods of Mendeleev's table.

How, exactly, were these periods constructed by Mendeleev?

He was, perhaps, not quite accurate when he contended that he had arranged the elements in the order of their atomic weights.

If he had actually put the elements in the order of increasing atomic weights, using the values known to science at that time, it would have been impossible to perceive any periodic law, even in the first rows of his table. More probable is the opposite: on the basis of the periodic law, Mendeleev established the correct atomic weight of beryllium.

Subsequent investigations confirmed this prediction.

If we proceed from the atomic weights known in the middle of the 19th century, the row of elements following chlorine should have been:

K 39	Ca 40	V 51	Cr 52	Ti 52	Mn 55	Fe 56	Co 59
Ni 59	Cu 63	Zn 65	As 75	Se 78	Br 80		

The mystery of the empty space. But, in continuing his table, Mendeleev arranged his cards quite differently. Under the sodium card he put the card for potassium, which resembles sodium closely, and potassium became the beginning of a new row. This put calcium under magnesium, which it resembles.

The next in the order of increasing atomic weight should have been vanadium, but its card was put aside for the time being. Instead, Mendeleev put an empty card (!) next to calcium. From the point of view of a chemist of that time, this was an incomprehensible and entirely unjustified action.

It could be expected that the empty card would be followed by the vanadium card. But, instead of vanadium, Mendeleev assigned the next place to titanium. Moreover, Mendeleev, without conducting any investigations himself and contrary to what was known about titanium by all the world's chemists, dared to change the atomic weight of vanadium from 52 to 48 (!). He finally placed the card for vanadium next after titanium, which was then followed by chromium and manganese.

According to what principle did Mendeleev arrange his cards? In this row of the table, he again put an element contrary to the order of increasing atomic weights as known at that time.

Before placing the titanium card into the table, Mendeleev, in essence, predicted its true atomic weight, as he had done for beryllium.

This period of Mendeleev's table is a long one. Manganese is followed by iron (Fe) – 56, cobalt (Co) – 59, nickel (Ni) – 59, and then copper (Cu) – 63 and zinc (Zn) – 65. But following zinc, Mendeleev again left two gaps, one after the other.

Next followed cards with the well-known elements arsenic, selenium and bromine, concluding the long period. Here the cards of arsenic, selenium and bromine were found to be under the like elements, phosphorus, sulphur and chlorine, at the end of the preceding short period.

What we have looked into makes it quite evident that everything connected with the construction of the

H 1									
Li 7	Be 9	B 11	C 12	N 14	O 16	F 19			
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35			
K 39	Ca 40	?	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 59
Cu 63	Zn 65	?	?	As 75	Se 78	Br 80			

table was not as simple as Mendeleev would have us think, judging from the quotation given above. Facts alone, known to chemists before Mendeleev, were insufficient to reveal one of nature's greatest laws, the periodic law of the elements.

If all the elements known up to 1869 are arranged in order of their atomic weights, without correcting the atomic weights of certain elements, seemingly arbitrarily, and without leaving empty spaces, it will be extremely difficult, or even impossible, to perceive the existence of any periodic regularity.

It was insufficient to have a detailed knowledge, however complete, of all the chemical information that had accumulated over the centuries. An unerring intuition, as well as scientific boldness, are required, once you have realized the existence of a periodic relationship, to change the old and to predict the new.

The paramount prediction. What do the empty spaces, or gaps, in Mendeleev's table signify?

Maybe they are deficiencies in nature and that is why chemists had not found elements to fit the empty rectangles in the table? Or maybe they are deficiencies in mankind's knowledge of nature? Does an element exist in nature whose atomic weight, for instance, is greater than that of calcium and less than that of titanium, and whose chemical properties resemble those of boron and aluminum?

Mendeleev had no doubts whatsoever. He was sure that each space in his table corresponds to a definite chemical element that must certainly exist.

The locations of the cards on which the names of chemical elements had been written, spaces in the periodic table in which the symbols of the elements and their atomic weights appear, were of most profound significance to Mendeleev. They determined the nature of each element, its physical and chemical properties, and the properties of its compounds.

A long paper by Mendeleev was published in 1871 in the Journal of the Russian Chemical Society. It was called “The Natural System of the Elements and Its Use to Indicate the Properties of Undiscovered Elements”. It is doubtful whether any other paper resembling this one had ever been published in world scientific literature. In the paper, Mendeleev described three chemical elements that had never been seen by anybody. Moreover, he described them in much more detail than could be expected even from some investigator that had held their compounds in his hands and had devoted to them long years of research in the laboratory.

“I have decided to do this so that sometime in the future, when one of these bodies I have predicted is discovered, I will have the opportunity to make sure myself and to convince other chemists of the validity of the assumptions on which my proposed system is based”, wrote Mendeleev in this paper.

In what way does the periodic law enable one to describe the unknown? How does a space in the table determine the properties of the corresponding element? This can best be done, following Mendeleev’s example, by comparing the properties of an empty space (gap) with those of its neighbours. Let us separate out of the table the part containing the empty spaces and their surrounding elements.

The gap between calcium and titanium is at the beginning of the fourth period. The two empty spaces located next to zinc (Zn) and arsenic (As) are at the end of the fourth period.

The hypothetical element that was meant to occupy the first gap was called *eka-boron* by Mendeleev. In the table it follows calcium. The element that should occupy the empty space next to zinc was called *eka-aluminum* by Mendeleev, and he called the adjacent element *eka-silicon.*

	II	III	IV	V
2	Be 9	B 11	C 12	N 14
3	Mg 24	Al 27	Si 28	P 31
4	Ca 40	?	Ti 48	V 51
	Zn 65	?	?	As 75
5	Sr 88	Y 89	Zr 91	Nb 94
	Cd 112	In 114	Sn 119	Sb 120

The empty space for eka-boron is between calcium (atomic weight 40) and titanium (atomic weight 48). Consequently, the atomic weight of eka-boron should be close to the mean value:

$$\frac{40+48}{2}=44.$$

With oxygen eka-boron should form an oxide similar in composition to the oxides of boron and aluminum: X_2O_3. Eka-boron should be a light metal because it is located between two light metals: calcium and titanium. The relative densities (or specific gravities) of eka-boron's neighbours enable its relative density to be assessed. That of calcium is 1.5 and for titanium it is 4.5. Hence, the relative density of eka-boron should be approximately

$$\frac{1.5+4.5}{2}=3.0.$$

Eka-boron should have colourless salts, because its neighbours form colourless compounds. The metal (eka-boron) is not volatile because its neighbours do not have this property either. Its principal properties should be weak, i.e. it should form only weak acids and alkalis, because the corresponding properties of titanium are also weak. In this way one can predict the chemical properties of a new element, unknown to and unseen by anyone.

Let us attempt to describe the properties of one more element, whose empty space is next to zinc and which Mendeleev named eka-aluminum.

Mendeleev left two gaps between zinc and arsenic. The atomic weight of arsenic is 75, that of zinc 65. We readily see that eka-aluminum should have an atomic weight of about 70. It is located in the third column, next to the metal zinc. This column contains aluminum, also a metal, and eka-aluminum should resemble it. This indicates that eka-aluminum should also be a metal.

Then we determine its density from that of its closest neighbours, taking into account, however, that next to eka-aluminum there is another gap for eka-silicon. The relative density of eka-aluminum should be close to 6.0.

At high temperatures compounds of aluminium and chlorine are volatile. Hence, the chlorides of eka-aluminum should also be volatile.

Mendeleev ends his description of the properties of eka-aluminum with the following words: “We can expect it to be discovered by spectroscopic investigations, by a method similar to the discovery of indium and thallium, which are further on in the table...”.

Mendeleev thus not only described what was yet unknown, but also predicted how it would be detected.

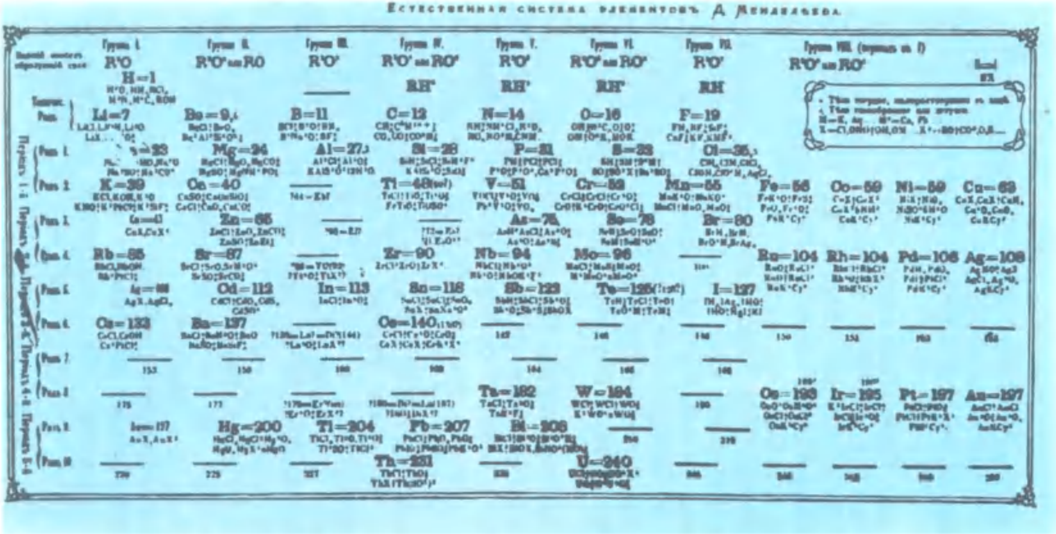
A concise account of the most important events following the discovery of the periodic law. What happened in the two and a half years after Mendeleev's discovery?

In September 1869, Mendeleev showed that the atomic volumes of chemical elements are periodic functions of their atomic weights. In October, he discovered the same relationship for the highest valency of elements in salt-forming oxides.

In the summer of 1870, Mendeleev found it necessary to change the incorrectly determined atomic weights of indium, cerium, yttrium, thorium and uranium, and, consequently, to change their places in the system of elements. Hence, uranium turned out to be the last element of the natural row, with the heaviest atomic weight.

On December 11, Mendeleev completed his paper called "The Natural System of the Elements and its Use to Indicate the Properties of Undiscovered Elements". Here he first called his system a natural one and first employed the concept of the "periodic law". In April 1871, Mendeleev first called his system a periodic one: "... it would be more proper to call my system a periodic one because it follows from the periodic law...". In July 1871, Mendeleev finished writing his main paper devoted to the periodic law. It was called "Periodic Order of the Chemical Elements". After many years, Mendeleev, in recalling this paper, said: "This is the best summary of my views and ideas on the periodicity of the elements...".

In this paper Mendeleev first gave the canonical formulation of the periodic law, which existed up to its physical substantiation: "The properties of elements and, consequently, the properties of the simple or complex bodies they form, are a periodic function of their atomic weights".



This table was inserted by Mendeleev into one of the first editions of his textbook “Fundamentals of Chemistry” (1871). It still has many gaps. Gallium, scandium and germanium had not yet been discovered, and the table has no zero group. Spaces have been left in the table for the unknown analogues of manganese, iodine, tellurium, cesium, barium and tantalum. The whole series of long dashes corresponds to the then hypothetical rare-earth elements (between barium and tantalum, i. e. between Ba and Ta). The majority of the elements predicted by Mendeleev were actually discovered. Note how much this table has

How Mendeleev's predictions came true. Less than six years passed up to the time of news that spread all over the world of science. In 1875 a young French spectroscopist, Paul Emile Lecoq de Boisbaudran, separated a new element out of a mineral mined in the Pyrenees. Lecoq de Boisbaudran was put on its trail by a faint violet line in the spectrum of the mineral; this line could not be identified as belonging to any known element. He named the new element gallium in honour of his native land which had once been called Gaul. Gallium is a very rare metal and Lecoq de Boisbaudran had much difficulty in preparing an amount slightly larger than a pin head. But he turned out to be very adept in his profession and he contrived to conduct many interesting experiments with this tiny amount. In detail he described the density of gallium, its melting point, its compound with oxygen and even its salts.

You can imagine Lecoq de Boisbaudran's surprise when, through the Academy of Sciences in Paris, he received a letter with a Russian stamp. In the letter he was informed that everything was quite correct in his description of gallium, except for its specific gravity: gallium is 5.9 times as heavy as water, rather that 4.7 times as maintained by him.

Could it be possible that someone else had discovered gallium before him? Lecoq de Boisbaudran determined the density of gallium again, after purifying the metal more carefully. He found that he was mistaken and that the author of the letter, who was, of course, Mendeleev, was right: the relative density of gallium is 5.9, instead of 4.7.

Another four years later, in 1879, the Swedish chemist, Lars Fredrick Nilson, discovered a new element in the rare mineral gadolinite. He called it scandium (for Scandinavia). When its properties were investigated, it became absolutely obvious that it was nothing but the long well-known eka-boron that had been predicted by Mendeleev.

More time passed, and 17 years after Mendeleev had made his predictions, the German chemist, Clemens Alexander Winkler, discovered a new element and called it germanium (for Germany).

This time it was unnecessary for Mendeleev to point out that this newly discovered element had been predicted by him beforehand. Winkler reported that germanium completely corresponds to Mendeleev's eka-silicon. Winkler wrote: "One is not likely to find a more striking proof of the validity of the idea of periodicity than in this newly discovered element. This is no simple confirmation of a bold theory; here we see an obvious broadening of chemical horizons, a mighty advance in our knowledge".

Winkler was not looking for germanium on the basis of its features predicted in Mendeleev's paper. He ran across it by chance. It turned out that the still undiscovered elements had already been taken into account; that there were just as many as the empty spaces in Mendeleev's periodic table. The properties and features were known, more or less, and it could be predicted beforehand in what minerals to look for them, what chemical methods were required to extract them from these minerals in which they were concealed.

The existence in nature of over ten new, previously unknown elements was predicted by Mendeleev himself. He predicted correct atomic weights of dozens of elements. All subsequent searches for new elements in nature were conducted by investigators with the aid of the periodic law and the periodic system. Not only did they serve to help scientists in their search for truth, but also facilitated the correction of errors and prevented misconceptions.

The Arduous Road Travelled by the Periodic Law

Mendeleev's predictions came true in brilliant fashion. Three new elements, gallium, scandium and germanium, were discovered. The beryllium riddle that had long puzzled scientists was solved at last. Its atomic weight was finally determined accurately and its place alongside of lithium was confirmed for all time. By the nineties, according to Mendeleev, "periodic order has become consolidated". Chemistry textbooks in various countries began, with no more doubt, to include Mendeleev's periodic system.

This great discovery was universally recognized.

But the system of elements still retained too many puzzles, too much that was still incomprehensible and obscure. Like a chemistry sphinx, it asked scientists riddle after riddle that could not be answered.

How many elements should there be in the periodic table? Should there be any elements lighter than hydrogen and heavier than uranium, or any between hydrogen and lithium? Why were there still gaps in the table corresponding to elements predicted by Mendeleev? What about the mysterious domain of rare earths, located in the middle of the table? How many should there be? Each year the discovery of several new rare-earth elements was announced and, after a short time, it became clear that the investigators had simply made a mistake.

You can see how many question marks the periodic system confronted scientists with.

But there were no answers.

The reason was that the basic principle had not yet been cleared up. Scientists did not know what fundamental physical cause made the properties of the elements vary periodically. There were only vague guesses that the properties of the elements may be connected in some way with the structure of their atoms. But nobody had any reliable knowledge on atomic structure.

Even the atomic weight, this, it would seem, firm support of the periodic law, sometimes miscarried. For example, the atomic weight of tellurium is greater than that of iodine. But, on the basis of its chemical nature, tellurium had to be put ahead of iodine. The same anomaly was found for cobalt and nickel. Chemists asked in vain why this was so; no answer was forthcoming.

At times, the destinies of great discoveries are ill-starred. They encounter crucial ordeals that can sometimes even cast into doubt the very validity of the discovery.

This, precisely, is what happened to the periodic system of the elements.

The periodic system undergoes a severe trial.

Without more ado, we disclose that this trial was associated with a large set of gaseous chemical elements that were named the inert, or noble, gases.

The first of these was helium. Almost all chemical handbooks and encyclopedias give the date for the discovery of helium as 1868 and attribute it to the French astronomer Pierre Jules Cesar Janssen and the English astrophysicist Sir Joseph Norman Lockyer. They sometimes add that a special medal was struck to commemorate the discovery of helium.

But, as indicated by investigations of historians of science, all of this is not quite accurate.

Janssen took part in an expedition to observe a total solar eclipse in India in August of 1868. His main contribution to science is that he found a way to observe solar protuberances after the eclipse had ended. Previously they were observed only during an eclipse.

Lockyer also observed protuberances, but without any relation to solar eclipses, and without leaving his native British Isles, in the middle of October of the same year. Both scientists sent accounts of their observations to the Academy of Sciences in Paris, but, since London is much closer to Paris than Calcutta, the letters arrived on almost the same day and were read at a session on October 26. There was nothing in either letter about any new element that was supposedly present in the sun. And the medal mentioned above was struck to commemorate the development of a new method of observing protuberances, these immense outbursts of solar matter.

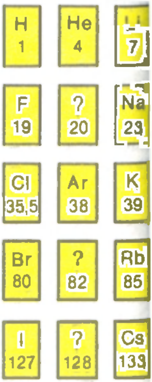
Various scientists, including Janssen and Lockyer, began to examine the spectra of protuberances in detail. Soon reports appeared mentioning the fact that the spectra contain a line that cannot be attributed to any element that exists on the earth. In January 1869, the Italian astronomer Pietro Angelo Secchi designated the line by the symbol D_3. Under this designation it has been recorded in the history of science as the "birth certificate" of the discovery of helium. The name helium (from the Greek *helios*, meaning the sun) was proposed by the English chemist Sir Edward Frankland. The first public announcement of the discovery of the new solar element was made on August 3, 1871 at the annual meeting of British scientists by the Scottish mathematician and physicist William Thomson (first Baron Kelvin).

The aforegoing is the true history of the detection of helium in the sun. For a long time it remained a hypothetical element. Nobody had any idea of what this chemical element was like, or what its properties were. Some scientists completely denied the existence of helium, contending that the line D_3 belongs to some ordinary element under conditions of high temperatures.

Helium was found on earth only in 1895, and its discovery was also preceded by a series of interesting events.

At the beginning of the nineties, the eminent English physicist John William Strutt (third Baron Rayleigh) noted an incomprehensible phenomenon: the density of pure nitrogen, extracted from air, was found by him to be greater than that of the same nitrogen obtained by chemical means from any nitrogen-containing compound. The difference was quite small, thousandths of a gram, but it was independent of the conditions of the experiment.

Rayleigh turned to his friend, Sir William Ramsay, the Scottish chemist, with the proposal to apply their united efforts to solve this puzzle. Rayleigh and Ramsay employed different methods of investigation, but reached the same conclusion: each litre of air contains about 10 cm^3 of some impurity. On April 29, 1894, Ramsay wrote a letter to his wife in which he said that it was quite probable that the nitrogen contains some



This is the way Ramsay predicted the existence of the noble (inert) gases on the basis of the periodic system. Essentially, this was done in exactly the same way as Mendeleev predicted gallium, germanium and scandium. The question marks were soon replaced by the newly discovered elements: neon, krypton and xenon. The atomic weights given on the cards are only approximate.

inert gas that had escaped their attention and that they may possibly discover a new element. This is the first mention of the word "inert"; the impurity could not be made to react chemically with any known reactive.

Rayleigh and Ramsay called the new gas argon, from the Greek word meaning "inert". Its chemical properties were extraordinary, primarily because they simply did not exist. Many scientists refused to regard argon as a new element. Even Mendeleev contended that argon has the chemical formula N_3, i.e. it is an allotropic form of nitrogen N_2. (In the same way as in the case of oxygen O_2 and ozone O_3.) Moreover, the atomic weight of argon was found to be greater than that of potassium, so that there was no place for this "workless one" (the Greek word argon is made up of the parts *a-*, without + *ergon*, work) in the periodic table.

These were the troubled times in which terrestrial helium claimed its right to existence. On February 1, 1895, the Hawaiian-born American geochemist William Francis Hillebrand informed Ramsay that the uranium ore cleveite evolves a chemically inactive gas when it is heated. The spectrum of this gas resembles that of nitrogen, but contains certain new lines. Ramsay repeated the experiments of his American colleague. He accumulated sufficient gas and, on March 14, conducted a spectroscopic analysis. The spectrum displayed a shining bright line, not to be found in nitrogen and argon spectra. The idea came to Ramsay that he had come across another unknown gas, which he made haste to name "krypton". He asked the English physicist and chemist Sir William Crookes, who was well known for his work in spectroscopy, to confirm his conclusions. On March 24 Ramsay received the following telegram from Crookes: "KRYPTON IS HELIUM. COME AND SEE IT".

This is how terrestrial helium was discovered. Soon it was also found in air. It turned out to be an inert gas, lighter than argon. After the problem with argon, helium posed another problem for the periodic system. Arguments became more and more heated. Pessimistic opinions were heard from time to time, pointing out the imperfections of the periodic system.

The discoverer of inert gases, Ramsay (and he was supported by other scientists) maintained a sensible view of the matter. He considered it feasible to find the proper places in the table for the inert gases, for instance, by putting them into a special group. By this time, a machine for efficiently liquefying air had been developed, and Ramsay with his assistant, the English chemist Morris William Travers, were engaged in fractionating atmospheric air (separating it into fractions), hoping to find new inert gases. Ramsay presented a paper in 1897 called "An Undiscovered Gas". Some years later he wrote in a book on noble and radioactive gases that he had, by the example of D. Mendeleev, described, as far as possible, the expected and assumed relations of the gaseous element, which should fill the gap between helium and argon.

This gap was destined to be filled by neon (from the Greek for "new"), discovered in May 1898. Then, in a short time, Ramsay and Travers found two more inert gases in the earth's atmosphere: krypton ("hidden") and xenon ("strange").

The problem of incorporating the inert gases into the periodic system was solved in 1900. In March 1900, Mendeleev and Ramsay, the two persons most interested in a proper solution of the problem, met and agreed that all the inert gases should be accommodated in the system between the halogens and alkali metals. This should be done in a way for them to form an independent zero group (or column). The first version of Mendeleev's table with a zero group was independently published in March of 1900 by the Belgian Leo Errera.

The discovery of the inert gases is a genuine scientific feat. They belong to the rarest stable elements existing on earth. Ramsay once said that there is less xenon in the air than gold in sea water. As a matter of fact, there is one part by volume of helium to 245 000 parts of atmospheric air, one part of neon to 81 000 000 parts, one part of argon to 106 parts, one part of krypton to 20 000 000 parts and one part of xenon to 170 000 000 parts. The most abundant is argon and small wonder that it was the first to be discovered. Actually, the argon first discovered was a mixture of all the inert gases.

We add that the discovery of the inert gases is said to be one of the four great discoveries at the end of the nineteenth century that led to a revolution in natural science (the others are the discoveries of the electron, X-rays and radioactivity).

A brief but vital interlude. The history of science is interspersed with no small number of curious and amazing coincidences. An especially interesting one is that exactly 27 years, day for day, after Mendeleev jotted down his first draft of "A Trial System of the Elements ...", on March 1, 1896, the French physicist Antoine Henri Becquerel discovered the phenomenon of radioactivity. It consists in the emission, by uranium minerals, of invisible rays, which are capable of passing through opaque bodies and affecting photographic plates.

It was soon found that the property of emitting rays belongs to the uranium in the mineral; the same property was found to be possessed by thorium. A large group of researchers began to investigate this new phenomenon. Among them were the French physicists and chemists Marie Sklodowska Curie and Pierre Curie, and the New Zealand-born English physicist Sir Ernest Rutherford (first Baron Rutherford of Nelson). Their researches laid the foundations for the theory of radioactivity.

From that time, two great discoveries of the nineteenth century, the periodic law and radioactivity, began to develop simultaneously, frequently coming into contact with each other. Astounding hypotheses and discoveries, advanced and made at these points of contact, have had immense influence on mankind's knowledge of the structure and properties of matter.

Still another trial of the periodic system. It all began with Marie Curie's discovery that certain uranium minerals display much stronger radioactivity than uranium itself. This led to the supposition that this radioactivity should be attributed to new, yet unknown radioactive elements. The Curie family, Pierre and Marie, began to search for them. They managed to procure several tons of the waste left when uranium ore undergoes an extraction process. They worked on this mountain of material for months. This unparalleled, truly heroic labour yielded splendid results. In July 1898 they announced the discovery of polonium (named after Mme. Curie's native Poland), and in December, of radium (from the Latin *radius*, meaning "a ray"), two new radioactive elements. A year later the French chemist Andre Louis Debierne, a collaborator of Mme. Curie, discovered actinium, still another radioactive substance.

It was not by chance that we used the word "substance". The discoveries of new elements enumerated above were unusual. When, for instance, Lecoq de Boisbaudran discovered gallium, he soon had at his disposal such amounts of its compounds that they could be weighed by rough scales.

The discoveries of polonium, radium and actinium were made indirectly. As a result of prolonged chemical manipulations, the discoverer managed to concentrate a substance with high radioactivity. After measuring this radioactivity, the discoverer arrived at the conclusion that something new seemed to have been found. But there was no unambiguous answer to the question as to whether the substance is a compound of a single radioactive element or of several. Moreover, the elements were available in only vanishingly small quantities.

To investigate them the chemists had to change their customary techniques. They had to learn to work with amounts of radioactive elements weighing negligible fractions of a milligram. They could only assess the course of the chemical operations by measuring the intensity of radioactive emission. Thus a new branch of science, radiochemistry, was founded.

Only brilliant intuition and their extraordinary capability as experimenters enabled Marie and Pierre Curie to infer that polonium should be an analogue of tellurium, and radium an analogue of barium. The proof of this required several years of painstaking and diverse investigations. What a great amount of labour was required, for example, to correctly determine the atomic weight of radium. Mendeleev had foreseen spaces in the periodic table for these two new elements. Radium took the place of eka-barium, whereas polonium had been predicted under the name dvitellurium.

Actinium, on the other hand, could not find itself a definite residence in the table for a long time, because it had turned out to be a capricious and somewhat insidious element.

But Mendeleev, as you already know, had left several empty spaces at the end of the sixth and beginning of the seventh period: five between bismuth and thorium and one between thorium and uranium. Thus, there was plenty of spaces for the three new elements.

The turn of the century brought a surprise packet: three radioactive substances, all gaseous. If samples containing radium, thorium or actinium are put into a closed vessel and then, after a certain length of time, the air is pumped out of the vessel, the radioactive strangers are pumped out together with the air. They were called emanations (from the Latin word *emanare* meaning "to flow out"): radium emanation, thorium emanation and actinium emanation. Later, their names were shortened to radon, thoron and actinon.

What are they: three new independent radioactive elements, differing in the same way as thorium and uranium, or as polonium and radium do? And, strictly speaking, where do they come from, from where do they flow out, these three puzzling emanations?

The answers that were found by scientists to these questions had a truly historical significance, both for the further destiny of the periodic law, and for all of the subsequent development of radioactivity theory.

Radon, thoron and actinon could not be distinguished from one another by chemical means, i.e. it was as if they all had one and the same face. Consequently, it

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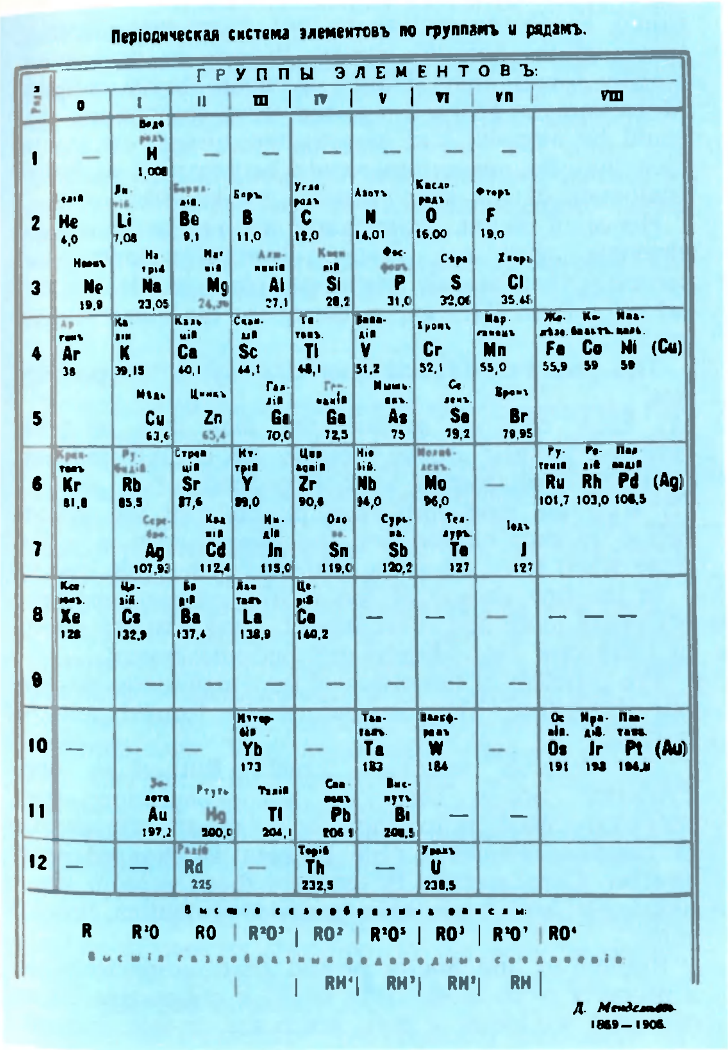
This table of the periodic system was given in the eighth edition of "Fundamentals of Chemistry", published in 1906, and was the last during Mendeleev's lifetime. It has substantially less gaps. Gallium, scandium and germanium, predicted by Mendeleev, have already occupied their lawful spaces. Radium, also predicted by Mendeleev, has also been discovered. It was described by him under the name of eka-barium. Also among the discovered elements are the noble gases, which have found themselves accommodation in a new zero group. The rare earths have, up to this time, been insufficiently investigated, and their position in the table is still uncertain.



Періодическая система элементовъ по группамъ и рядамъ.

Ряды	ГРУППЫ ЭЛЕМЕНТОВЪ:								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Водородъ **H** 1,008	—	—	—	—	—	—	
2	Гелій **He** 4,0	Литій **Li** 7,03	Бериллій. **Be** 9,1	Боръ **B** 11,0	Углеродъ **C** 12,0	Азотъ **N** 14,01	Кислородъ **O** 16,00	Фторъ **F** 19,0	
3	Неонъ **Ne** 19,9	Натрій **Na** 23,05	Магній **Mg** 24,36	Алюминій **Al** 27,1	Кремній **Si** 28,2	Фосфоръ **P** 31,0	Сѣра **S** 32,06	Хлоръ **Cl** 35,45	
4	Аргонъ **Ar** 38	Калій **K** 39,15	Кальцій **Ca** 40,1	Скандій **Sc** 44,1	Титанъ. **Ti** 48,1	Ванадій **V** 51,2	Хромъ **Cr** 52,1	Марганецъ **Mn** 55,0	Желѣзо. Кобальтъ. Никкель. **Fe** **Co** **Ni** **(Cu)** 55,9 59 59
5		Мѣдь **Cu** 63,6	Цинкъ **Zn** 65,4	Галлій **Ga** 70,0	Германій **Ge** 72,5	Мышьякъ. **As** 75	Селенъ. **Se** 79,2	Бромъ **Br** 79,95	
6	Криптонъ **Kr** 81,8	Рубидій. **Rb** 85,5	Стронцій **Sr** 87,6	Иттрій **Y** 89,0	Цирконій **Zr** 90,6	Ніобій. **Nb** 94,0	Молибденъ. **Mo** 96,0	—	Рутеній Родій Палладій **Ru** **Rh** **Pd** **(Ag)** 101,7 103,0 106,5
7		Серебро. **Ag** 107,93	Кадмій **Cd** 112,4	Индій **Jn** 115,0	Олово. **Sn** 119,0	Сурьма. **Sb** 120,2	Теллуръ. **Te** 127	Іодъ **J** 127	
8	Ксенонъ. **Xe** 128	Цезій. **Cs** 132,9	Барій **Ba** 137,4	Лантанъ **La** 138,9	Церій **Ce** 140,2	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербій **Yb** 173	—	Танталъ. **Ta** 183	Вольфрамъ **W** 184	—	Осмій. Иридій. Платина. **Os** **Jr** **Pt** **(Au)** 191 193 194,8
11		Золото **Au** 197,2	Ртуть **Hg** 200,0	Таллій **Tl** 204,1	Свинецъ **Pb** 206,9	Висмутъ **Bi** 208,5	—	—	
12	—	—	Радій **Rd** 225	—	Торій **Th** 232,5	—	Уранъ **U** 238,5		
Высшіе солеобразные окислы:	R	R^2O	RO	R^2O^3	RO^2	R^2O^5	RO^3	R^2O^7	RO^4
Высшія газообразныя водородныя соединенія					RH^4	RH^3	RH^2	RH	

Д. Менделеевъ
1869—1906.

would hardly be proper to put them into different spaces of the periodic system, though, as was subsequently found, they differed in their atomic weights. Moreover, the properties of the three emanations that could be assessed and investigated turned out to be such that the emanations could be regarded as heavy analogues of the inert gases, i.e. like "eka-xenons".

Hence, if radon, thoron and actinon are chemical elements, they are, firstly, chemically inert, and secondly, there is only one empty place in Mendeleev's table for them. This gap is meant for the heaviest inert gas.

This puts two difficult questions before the periodic law.

(1) How can we explain the fact that elements differing in their atomic weights are entirely indistinguishable with respect to their properties?

(2) With the most important principle of the system being "to each element its own place", what is to be done when three elements contend for a single space?

In the first decade of our century, these questions, becoming more and more urgent, hung like the sword of Damocles over Mendeleev's periodic system.

The problem of the origin of the emanations was no less disturbing. They seemed to be formed out of nothing.

The English scientists Ernest Rutherford and Frederick Soddy came to the conclusion that radioactive decay is accompanied by the transformation of chemical elements. One element is changed into another. Consequently, the concept that the atom is an indivisible and immutable particle of matter lay in ruins.

Rutherford and Soddy proved that radioactivity is a property of an atom. In its decay a radioactive atom can emit two kinds of rays, which are, in fact, streams of material particles denoted by the Greek letters α and β. The α particles turned out to be positive doubly charged helium ions, and the β particles are simply electrons. Since the α particles have quite a large mass (the atomic weight of helium being approximately 4), a loss of one such particle cannot but affect the radioactive atom. It can no longer continue to exist as such and is transformed into a lighter element having an atomic weight less by 4 units.

The emanations were formed in exactly this way. The process by means of which radon is "born" is:

$$\frac{-\mathrm{He}}{\mathrm{Ra} \rightarrow \mathrm{Rn}}.$$

This chain of transformation of the elements, the first to be investigated, was used by Rutherford and Soddy in proposing their theory of radioactive decay in 1902. The theory was based on the hypothesis that the elements can be transformed. A year later Soddy and Ramsay proved that helium was present, along with radon, above a sample of radium.

This is how the origin of emanations became known. A conjecture began to loom vaguely: all radioactive elements are related in some way to one another. True, there were precarious grounds for supposing that there may be three independent series of radioactive transformations. They begin with uranium, actinium and thorium, respectively, and all end with nonradioactive lead. Intermediate substances, however, were insufficient to justify more rigorous conclusions. But they turned up before long.

Ten, twenty, thirty new radioactive substances were found by scientists in the next few years. This was like a volley of canister shot fired at the periodic system, which, in the face of menacing facts, did not seem to be a well-defended target.

These "radioelements" (we enclosed this word in quotation marks because scientists were lost in conjectures: were these genuine chemical elements or some kind of intermediate form of matter?) appeared in such great quantities that it would be senseless to think up special names for them. A different system of nomenclature was used. There were *X* products: uranium-*X* and thorium-*X*; there were radium-*A*, radium-*B* and radium-*C*; there were radioactinium and radiothorium. The convenience of this system of nomenclature was in the fact that it enabled one to determine at once the definite series of radioactive transformations to which some "radioelement" belongs.

Gradually all the "radioelements" found themselves places in one or another radioactive family, or series: thorium, uranium or actinium. These series turned out to be distinctive classifications of the "radioelements".

But how were these families, or series, to be combined with Mendeleev's periodic system?

Chemists already knew of several examples of complete chemical indistinguishability of "radioelements". Several sets of "radioelements", appreciably differing in their atomic weights, differed in no way with respect to their properties, with the exception of radioactive ones. This was one extremity. Another consisted in the fact that there were quite a few cases in which the " radioelements" had the same atomic weights, but nothing in common when it came to properties.

These two extremities had to be coordinated in some manner with the periodic law and periodic system or....

Or acknowledge that "all these facts have made a wide breach in the principle taken by Mendeleev as the basis for his system," as contended by the famous French chemist Georges Urbain.

Or accept the fact that the periodic system, strictly speaking, cannot accommodate all the known elements, as contended by the no less famous British chemist Sir William Augustus Tilden.

Such was the formidable trial confronting the periodic system.

Now we shall see how the system stood this test.

The structure of the atom. When in 1897 the English physicist Sir Joseph John Thomson and the German geophysicist Johann Emil Wiechert independently discovered the electron, scientists in various countries made haste to incorporate it into their ideas on the structure of the atom. But this led to certain seemingly insurmountable inferences. The electron has a negative charge, whereas the atom as a whole is a neutral particle of matter. What does this mean, and what is the structure of the positive "counterbalance" to the negative electrons?

This carrier of the positive charge turned out to be the vulnerable point in the atomic models that were proposed in the first decade of our century.

At that time Rutherford was busily and persistently studying the nature and behaviour of α particles in his laboratory. He was the first to prove that an α particle is a doubly charged helium ion.

Of keenest interest to Rutherford was the behaviour of α particles in collisions with various materials, for instance, with thin metal sheets or foil.

In 1909, Rutherford's assistants, Hans Wilhelm Geiger and Ernest Marsden (later Sir Ernest), observed an amazing phenomenon. They had been bombarding gold foil with α particles. The great majority of the particles behaved as could be expected on the basis of theory: they were scattered at definite angles. But some recoiled backward as if they had met with a massive obstacle.

Geiger and Marsden considered that this circumstance was simply an error in observation. But the more their efforts in trying to eliminate the error, the more surely they became convinced that any error was out of the question.

Rutherford was astounded no less than his assistants. Many years later he recalled: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you had fired a 15-inch shell at a piece of tissue-paper and it came back and hit you".

If a positively charged particle, colliding with "something" bounces back like a tennis ball does after hitting a wall, the "something" should have a high positive charge, in the first place, and be of great mass, in the second. That is (and this was Rutherford's bold conjecture), it cannot be anything but the nucleus of an atom.

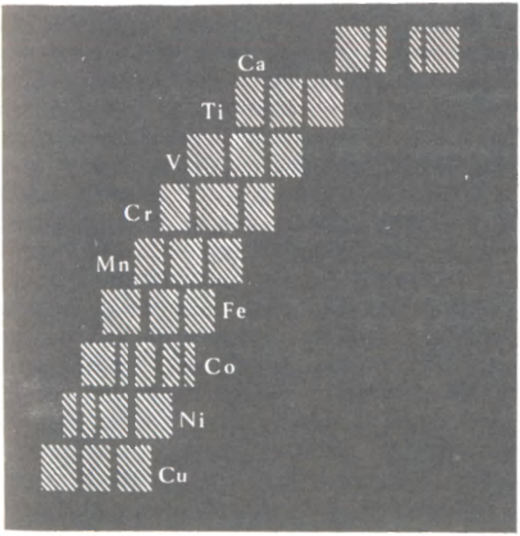
Thus the nuclear, or planetary, model of the atom was evolved. At its centre it had a massive positively charged nucleus surrounded by electrons travelling along orbits like planets around the sun. In May 1911, Rutherford published a paper in which this idea was clearly deduced.

To what numerically were the charges of atomic nuclei of various elements equal? Experiments and calculations indicated that for the light elements it was equal to approximately one half of the atomic weight. This ratio proved to be invalid for elements in the middle and at the end of the periodic system.

A little-known Dutch doctor of law and physicist Antonius Johannes van den Broek proposed, in 1913, that the charge of the atomic nucleus of any element is equal, numerically, to the number of the element in the periodic system.

Through the entire history of the periodic law, this intuitive guess was one of the most ingenuous and one of the most vital for its subsequent development. It was almost immediately proved experimentally. This proof was found by the young English physicist Henry Gwyn-Jeffreys Moseley, who was killed in the prime of life and talent on a battlefield of World War I in 1915. In investigating the X-ray spectra of the elements Moseley showed in 1913 that the wavelength of characteristic X-ray radiation varies regularly in going over from one element to the next, i.e. it depends upon the atomic number of the element.

It was possible to calculate the atomic number by measuring the wavelength. This number was found to



This document is also of great significance in the history of periodicity theory. The photograph clearly shows how regularly the lines of the X-ray spectra are displaced in going over from one element to the next.

really equal the positive charge of the atomic nucleus of the element.

All of these discoveries signified that the periodic law had been physically substantiated on a new and higher level of knowledge. This altered the formulation of the law: the properties of elements and their compounds are a periodic function of the magnitudes of the nuclear charges of their atoms.

Not the magnitudes of the atomic weights, which, though they increased in passing from element to element, did so without complying with any clear-cut law, but the integral values of nuclear charges became the basis of the periodic law. These integral values varied by exactly one unit in going from one element to the next.

Consequently, it could now be asserted with complete assurance that the periodic system, beginning with hydrogen (atomic number $Z = 1$) and ending (in Moseley's time) with uranium ($Z = 92$) consisted of exactly 92 elements, no more and no less.

Also consequently, physicists and chemists could now definitely tell how many elements had not yet been discovered. These elements had the atomic numbers 43 and 75 (analogues of manganese, which had been predicted by Mendeleev), 61 (a mysterious rare-earth element whose place was between neodymium and samarium) and 72 (an analogue of zirconium, which also had been predicted by Mendeleev).

We have not yet mentioned three elements with the atomic numbers 85, 87 and 91. They all belong to the "radioactive region" of the periodic system. In discussing this region, we dwelt on the fact that riddles had accumulated there that the periodic system could not solve.

As a matter of fact, how can we reconcile the structure of the system with the unexpected abundance of "radioelements"? How can we accommodate these elements in a limited number of spaces? And finally, just what are these "radioelements"?

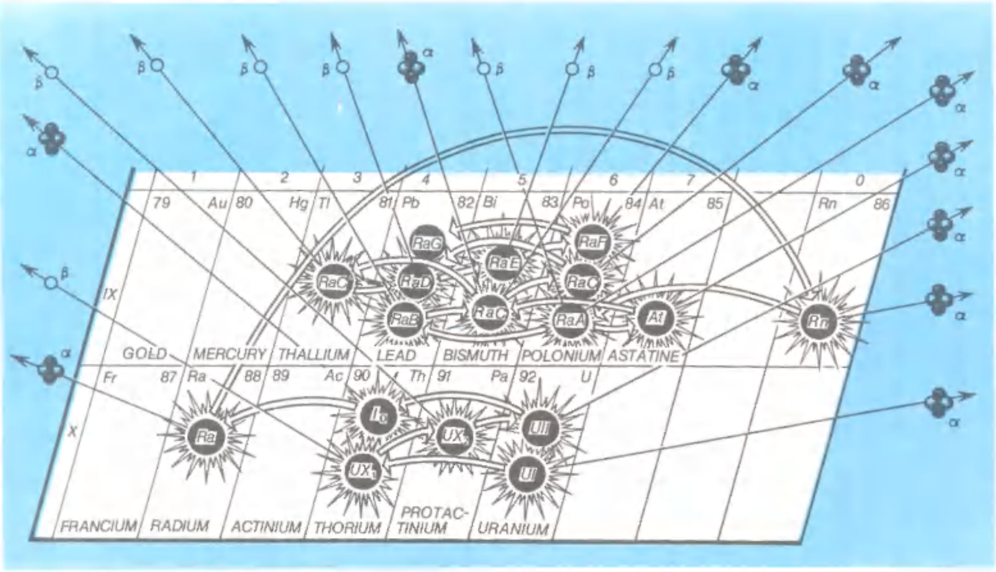
Radioactive displacement law and isotopes. By 1913, scientists were quite sure of the following.

All "radioelements" are grouped in three families, or series: the thorium series (with thorium as the parent element and with the atomic weights of all the included radioelements complying with the formula $4n$), the uranium series (with uranium as the parent and with the atomic weight formula $4n+2$), and the actinium series (actinium and $4n+3$). In the formulas n is a whole number. There was, of course, some lack of coordination in particulars, but, as a whole, scientists knew for sure that the gradual transmutation of radioactive elements into stable lead occurs as a result of α and β transformations.

Physicists and chemists also knew how the chemical nature of an element is altered when it undergoes an α or β decay.

In an α decay, the atom loses two positive charges and four units of mass. Back in 1910 Soddy was able to come up with the proposal that the element formed as a result of an α decay is displaced two groups (columns) to the left in the periodic system with respect to the initial space. Radium (second group), for example, is transformed into radon (zero group).

The β decays are a more complicated matter. The mass of the atom, as is known, does not actually change (it was already known that the mass of the electron is about 1/1840 of the mass of the hydrogen atom). But the positive charge of the atom should increase by one unit, because the electron carries away one unit of negative charge. Until scientists could acquire a clear concept of what a positive charge corresponds to, they



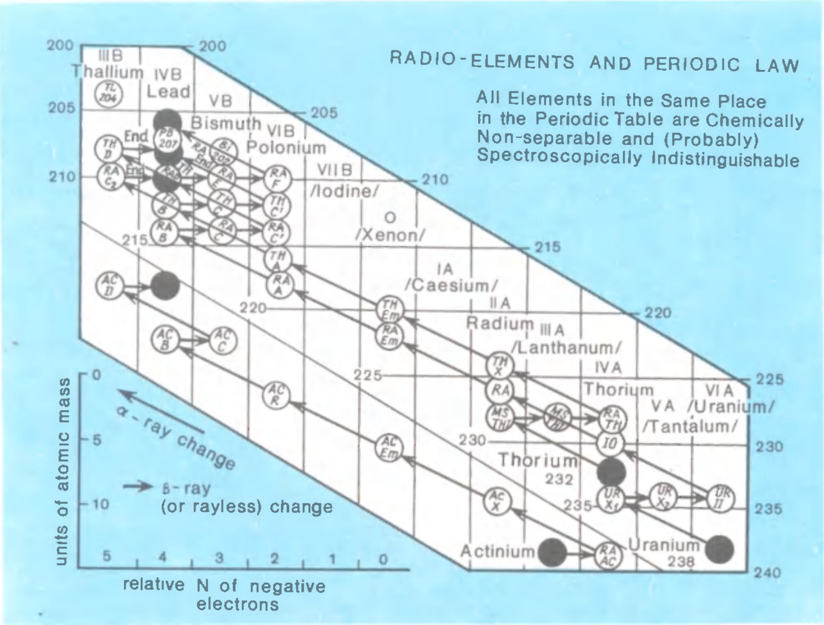
It is necessary to follow closely the travels of the descendants of a uranium atom along the periodic system. Their charge changes with each beta decay, and their mass as well with each alpha decay. What determines the chemical properties of the obtained nucleus? These obsolete names (UI, UX_1, etc.) are no longer used. It is accepted practice today to call the isotopes simply by the names of the corresponding elements, adding the mass number at the upper left. Instead of UI we write ^{238}U; instead of UX_1, ^{234}Th. Try to compile a table of the isotopes formed in the decay of uranium-238 could only indirectly determine to which place an element is moved as a result of a β decay. It turned out to be one space to the right in the periodic system.

All of these observations were generalized at the beginning of 1913 by Soddy and the Polish chemist and educator Kasimir Fajans, who formulated the law of radioactive displacement: in an α decay, the radioactive element is transformed into an element two spaces to the left of the initial element in the periodic system, whereas in a β decay, one space to the right.

But physicists and chemists knew other facts as well. It was known, for instance, that there were three "radioelements" having the properties of thorium, but different atomic weights, and that they could not be separated from one another by any chemical means. There were also three kinds of polonium and three kinds of radon. And finally there were known to be seven kinds of lead, of which three were stable (they concluded radioactive series) and four were radioactive (formed as a result of consecutive α and β decays within a series).

For a long time chemists had been disturbed by the vague idea that the atoms of the same element may be nonhomogeneous. This was suggested, for instance, by the German chemist Friedrich August Kekulé von Stradonitz (who proposed the structural formula for benzene) and the famous Russian chemist Alexander Mikhailovich Butlerov (who developed the theory of the structure of organic compounds). The idea was most clearly formulated by Crookes who held that each element has varieties that differ in their atomic weights. But this idea never went beyond the guessing stage because, at that time, it could neither be confirmed nor rejected by experimental methods.

Only in 1913 (see how fruitful this year was in discoveries!) was Soddy able finally to endow the guess



This diagram was given by F. Soddy in his paper on the law of radioactive displacements. It shows the intimate relationship that exists between the radioactive families and the structure of the periodic system.

with the required material essence. He proposed that "radioelements" with identical chemical properties be regarded as varieties of one and the same radioactive element. For example, the three emanations should be regarded as three varieties of a single chemical element with the properties of an inert gas.

Soddy called these varieties isotopes. The word "isotope" is derived from the Greek words *isos* (equal, or identical) and *topos* (place).

In this way, isotopes were found to be varieties of a single chemical element occupying a single space in the periodic system. According to Soddy, isotopes had atomic nuclei with the same charge but different atomic weights.

It was soon found that isotopism is inherent, not only in the "radioactive region" of the periodic system, and that many stable elements also have isotopes. The first stable isotopes were found to belong to neon. This discovery was made by J. J. Thomson and his co-worker, the English physicist and chemist Francis William Aston.

To account for the true cause of isotopism we shall have to get somewhat ahead of our story. The elementary particle called the neutron (because it has no charge) was discovered in 1932. Scientists proposed and substantiated the proton-neutron model of the nucleus. The number of protons in the atomic nucleus of a given element is rigorously constant. It determines the magnitude of its positive charge and is equal to the atomic number of the element. But the number of neutrons can vary in quite wide limits. Hence, isotopism is associated with the structure of the nucleus. Isotopes of an element have different numbers of neutrons, whereas the number of protons is always the same.

In this manner the periodic system overcame this redoubtable obstacle as well.

The new meaning and significance of the atomic weight (atomic mass). Mendeleev contended that the chemical properties of elements are determined by their atomic weights. This turned out to be wrong. Its place in the periodic system and, consequently, all the chemistry of an element is determined, not by its atomic weight (or, more exactly, its atomic mass), but by its atomic number, i.e. the charge of its nucleus.

Does this imply that the atomic weight has entirely lost its significance and is used today only for calculations when analyzing the chemical composition of some substance?

By no means! In any publication of the periodic system of the elements, the value of its atomic weight is given immediately under the symbol of each element.

It should be pointed out, however, that physicists considered it more correct to use the term “relative atomic mass” or, for short, “atomic mass”. Though it is inaccessible for direct perception and has not so far been actually seen, the atom can now be “weighed” to an exceptionally high degree of accuracy.

This has been achieved because the meaning of the atomic mass has immeasurably increased today in physics. The mass of the atom has become the basic quantity in calculations concerning nuclear power engineering and nuclear chemistry. Without knowing exact values of the atomic masses, one cannot establish the mechanism of nuclear reactions or calculate the amount of energy to be produced.

The following values indicate to what accuracy the masses of atoms have been measured today:

^{1}H – 1.00782522
^{2}D – 2.01410219
^{4}He – 4.00260361
^{14}N – 14.00307438
^{16}O – 15.99491494

The error in the measurement of atomic masses, not exceeding the last significant digit, is only one thousand millionth of the measured value. True, in their everyday work, chemists manage with two, and sometimes three, places following the decimal point.

When isotopes were discovered, the reason why atomic masses are, as a rule, fractional numbers was cleared up. Elements having several isotopes contain them in different amounts. Their different content is taken into account in calculating atomic masses.

Two concepts must not be confused: the mass number and the atomic mass of an isotope. The mass number is the sum of the number of protons and the number of neutrons in the atomic nucleus of a given isotope. It is always a whole number. In dealing with radioactive elements, the periodic table has the mass number of the most long-lived isotope (i.e. the one having the longest half-life) written under the chemical symbol instead of the atomic mass. The atomic mass of an isotope is the actual mass of an atom of the isotope, directly measured in an experiment using a mass spectrometer. It is never equal to the sum of the masses of the protons, neutrons and electrons that make up the atom. The bonding energy of these particles in the atom contributes a substantial correction. The atomic mass of an isotope is never expressed by a whole number.

In discussing the atomic mass, we ask you to keep in mind the following relationship:

$$\frac{1}{12}[{}^{12}_{6}\mathrm{C}] = 1.$$

It has the following history.

In compiling the very first version of his system of elements, Mendeleev took the atomic mass of hydrogen equal to unity. Then he compared all the atomic masses of the other elements with that of hydrogen.

It was decided at the International Organization of Chemists in 1860 to accept hydrogen as the basis for the scale of atomic weights. For almost half a century the lightest element, hydrogen, held this honourable post. In 1906 the chemists transferred to the oxygen scale; the basis for the scale of atomic weights being 1/16 of the atomic weight of oxygen. This was, of course, more convenient because oxygen forms compounds with almost all the elements.

When it was found that three different isotopes of oxygen exist in nature and that their content in natural oxygen is not constant, the physicists established for themselves a "physical" scale of atomic weights. They agreed to take as their unit 1/16 of the mass of the most abundant light isotope of oxygen and to take its atomic weight equal to exactly 16. This eliminated the error due to the inconstant isotope composition of oxygen of various origins.

With the modern high precision of measurement, such "dual power" began to be the cause of many misunderstandings and errors. Moreover, it became clear that the isotope ^{16}O does not justify the hope placed on it and cannot ensure the required accuracy. It turned out to be an inconvenient standard for atomic masses.

In the years 1958-1961, for this reason, scientists reconsidered this question that is so exceptionally vital for all of natural science: what should be employed as the basis for a modern scale of precise atomic masses? Of all the elements, only two, fluorine and carbon, could lay claim to the honourable role of a basic constant for physics and chemistry.

Fluorine has only a single isotope and its atomic mass, therefore, is a constant value. Carbon has two stable isotopes, but its compounds with hydrogen are very convenient for directly comparing the atomic masses of various isotopes of almost all the elements.

Since both the "fluorine" and "carbon" scales for atomic mass each had important and valuable advantages, it was agreed to conduct a world-wide referendum among physicists and chemists to find out which scale they preferred. Soviet physicists also participated in this referendum. Carbon was the winner. It was decided to accept as the basis of the new unified scale of atomic mass the atom of the most abundant carbon isotope ^{12}C and to assume that

$$\frac{1}{12}[{}^{12}_{6}C] = 1.$$

Only after the discovery of isotopism did it become clear why in the pairs of adjacent elements: argon-potassium, cobalt-nickel and tellurium-iodine, the atomic masses of the preceding elements are greater than those of the subsequent ones. It was found that the isotopes of argon, cobalt and tellurium with the highest atomic masses are also the most abundant. On the contrary, potassium, nickel and iodine are not notable for a high content of their heavier isotopes. But we already know that the atomic mass of an element is affected by the content of its isotopes in per cent. Hence, the first elements in the pairs Ar-K, Co-Ni and Te-I have the higher atomic masses.

But the abundance of isotopes in nature is such that the atomic masses of the elements, with the exception of the three cases mentioned above, increases with the charge of the atomic nuclei. Why this is so and not otherwise is an extremely complicated question. Some comprehension can be gained by resorting to the data of nuclear physics, as well as those of astrophysics that study the processes in which chemical elements originate as the result of nuclear reactions in the stars.

The Periodic Law is the Law of Atomic Structure

In his time Mendeleev wrote with a certain feeling of disappointment: "...we do not know the cause of periodicity". He did not live to see the unravelling of this mystery.

When it had been proved that the atomic number of an element is numerically equal to the charge of its atomic nucleus, the physical essence of the periodic law became clear.

But why do the properties of chemical elements vary periodically as their nuclear charge increases? Why does the system of elements have the structure it has and not some other one; why do its periods contain a strictly definite number of elements? So far, there had been no answers to these questions.

The mystery of the periodic system of elements was finally solved when the extremely complex structure of the atom became clear, together with the structure of its outer electron shells and the motion of the electrons about the positively charged nucleus in which almost all of the atomic mass is concentrated.

All the physical and chemical properties of matter are determined by atomic structure. The periodic law, discovered by Mendeleev, is a universal law of nature because it is based on the law of atomic structure.

How did physicists and chemists get to know the structure of the atom? The planetary model of the atom, proposed by Rutherford, soon won general acknowledgement. It is true, however, that scientists had no more or less clear idea of the number of particles making up the nucleus of the atom, and how (and how many) electrons are arranged in its orbits.

We shall discuss the atomic nucleus further on. As concerns electrons.... Did the investigators really have any reliable way available of knowing how atomic electrons conduct themselves?

As it turned out, they did. The study of spectra became the means of unlocking the mystery of electronic distribution. It was as if the atom itself revealed its structure in astonishing and colourful language, the language of spectral lines of light emitted by the atom. Each spectral line is evidence that an electron has changed its position with respect to the atomic nucleus. By examining the spectra of various elements, scientists observed in the spectra important regularities, similarities and differences.

It was precisely this investigation of spectra, both optical and X-ray, that enabled the arrangement of the electrons about the atomic nucleus to be established in more or less detail.

The most significant conclusion was that the electrons are distributed among definite shells, and that each shell should contain a strictly definite number of electrons. To denote these shells, scientists used the capital letters K, L, M, N, O, P, Q, etc. In this way, the shell closest to the nucleus was named the K-shell, the next the L-shell, etc.

Another essential feature was the possibility of determining the maximum number of electrons that could be accommodated in each shell. It was found that this is determined by the formula $2n^2$, where n is the shell number.

The capacities of the various electron shells are as follows.

	K	L	M	N	O	P	Q
n	1	2	3	4	5	6	7
$2n^2$	2	8	18	32	50	72	98

Finally, the third remarkable result led to the conclusion that within each shell not all the electrons are the same, and that they can be united into definite groups. With such information about atoms at our disposal, we shall now make an attempt to explain the structure of the periodic system.

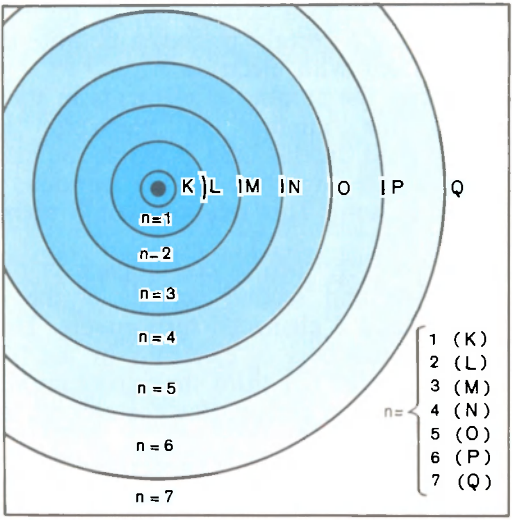
The most important factor in the structure of the periodic system. It would seem that most important is the fact that the periodic system represents the periodic variation in the properties of chemical elements with the increase in the nuclear charge (Z) of their atoms and unites elements of like properties within the framework of definite groups.

All of the halogens, for instance, fluorine, chlorine, bromine, iodine and astatine, are arranged in the VII group (column). But we see that in the same group, in the form of a parallel vertical column, three more elements, manganese, technetium and rhenium, are arranged. They also resemble one another. But why did they get into the same group with the halogens? This is an interesting and important question and, at the proper time, it will be answered.

For the time being, we point out that each group of the periodic table is divided into two subshells, or subgroups: the main subgroup (*a*) and auxiliary subgroup (*b*). In our example, the halogens constitute the *a*-subgroup and manganese and its analogues, the *b*-subgroup.

Nevertheless, all of this is still not the most important factor in clearing up the structure of the periodic system as it was developed by Mendeleev.

Perhaps the most important is the concept of periods. As a matter of fact, the system is said to be periodic because it is a set of periods. Each period contains a strictly definite number of elements, beginning with an alkali metal and ending with an inert gas. Only the first period is an exception because it



A diagram showing the consecutive arrangement of the electron shells in an atom. The shell number is equal to the principal quantum number *n*; the energies of the electrons are proportional to the value of *n*.

begins with gaseous hydrogen. All of this is exceptionally important, but still not the most important of all factors.

Moseley's law enables us to uniquely determine the number of elements in each period of the system:

Period number	1	2	3	4	5	6	7
Number of elements	2	8	8	18	18	32	32

Among the numbers of chemical elements in the periods, there is not a single one that has not been previously encountered in the system of electron distribution among the specific electron shells. But this coincidence can lead to a conclusion: in the atoms of the elements along a certain period, a definite electron shell is being filled with electrons.

In other words, the number of elements in the period is equal to the number of electrons in the corresponding shell. In this case it would be extremely simple to relate the structure of the periodic system with that of the atom. This relation would seem to be amazingly obvious.

In reality, however, such a coincidence is observed only for the first and second periods of the system. They contain 2 and 8 elements, respectively. These are the same as the numbers of electrons in the first and second electron shells. The third shell accommodates 18 electrons, but the third period, like the second, is made up of only 8 elements.

Thus, the attractive equality: capacity of a period = = capacity of the corresponding electron shell is complied with, as the mathematicians would say, under very restricted conditions.

It follows that the periodic system is constructed according to a more complicated law than the system of consecutive electron shells.

We have come, evidently, to the point when we can finally state that the most important factor is that the capacity of the periods, beginning with the second, is repeated pairwise. Only the first period, consisting of hydrogen and helium, remains in isolation.

To clear up the structure of the periodic system it was necessary to establish the reason for the repetition of the periods. This was to be done on the basis of the data already available to science on atomic structure.

Electron shells are filled stepwise. Science is obliged, primarily, to the famous Danish physicist Niels Henrik David Bohr for establishing the real relationship between the structure of the atom and that of the periodic system. He was the first to explain the true causes of the periodic variations in the properties of the elements.

Bohr began by imparting a vital capacity to Rutherford's atomic model. According to all classical laws, the electron, in revolving about the nucleus, should gradually lose its velocity. At some definite instant it should stop and fall into the nucleus. This means that if the "planetary" atom could exist, then only for a negligible length of time. But there were atoms high and low, and they displayed no tendency to collapse.

Niels Bohr eliminated this contradiction by assuming that the electrons revolve about the nucleus along definite, rather than any, orbits, and lose no energy when in these orbits. Only when they transfer from orbit to orbit do the electrons emit or absorb quanta of energy, as the physicists say. Their calling cards are the lines of the spectrum. Such "allowed" orbits are said to be quantum orbits, and Bohr became known as the founder of the quantum theory of the atom (not to be confused with the quantum-mechanical theory, which is to be discussed later on). On the basis of this theory, Bohr undertook to explain the structure of the periodic system.

In an atom of hydrogen or helium, filling takes place in the *K*-shell which can accommodate two electrons. In helium this shell is already full; that is why helium is an inert gas, by virtue of the stability of its filled shell. By this time (at the beginning of the twenties), scientists had already understood that the chemical properties of elements are evidently determined by the number and arrangement of the electrons in the outer shells.

The second period of the system, from lithium to neon, consists of 8 elements, and 8 electrons can be accommodated in the *L*-shell. The eight-electron outer shell (like the two-electron one of helium) is an extremely stable formation. Therefore, neon is also an inert gas. In entering a chemical reaction, the atoms of the pertinent elements should either lose or gain electrons. Neither is of advantage to the neon atom.

The third period also consists of 8 elements, from sodium to argon. But there should be as many as 18 electrons in the third, or *M*-shell. Eight vacancies are filled in the atoms of the third-period elements. Argon, for the reason we already know (8 electrons in the outer shell) is still another inert gas. So far ten places for electrons of the *M*-shell remain free. In what elements does the filling of the free places continue?

Argon is followed by potassium and calcium. Maybe they are ones in which this filling takes place? Hardly. These two are typical alkali and alkaline-earth metals and, as indicated by our experience with the preceding, second and third, periods (with the pairs lithium and beryllium, and sodium and magnesium), the filling of the new *N*-shell should begin with potassium. This is the starting point of a new (the fourth) period of the system. By now you have evidently understood one simple principle: each period (excepting the first) begins with an alkali and an alkaline-earth metal, and that the filling of a new shell begins in the atoms of these elements.

Altogether, the fourth period consists of 18 elements. Hence, 10 electrons from the *M*-shell and 8 from the *N*-shell are distributed in some way in their atoms. The strict sequence of this distribution was still unknown by Bohr.

To make up for it, however, he did establish a fundamental principle: the filling of the electron shells in the atoms of chemical elements, beginning with the third, or *M*-shell, does not proceed consecutively until each shell is gradually filled to its full capacity (i.e. as in the K- and L-shells), but stepwise. In other words, the building up of the electron shells is temporarily interrupted because electrons belonging to other shells begin to appear in the atoms.

To obtain an understanding of Bohr's theory, we must first become acquainted with the peculiar atomic alphabet. Only with its aid can we give a graphical account of the inmost mysteries of atoms.

Four letters of the atomic alphabet. These letters, n, l, m_l and m_s, are not quite ordinary and are called quantum numbers by the atomic physicists. Historically, they were introduced gradually and their appearance is associated with the study of atomic spectra.

Physicists found that the state of any electron in an atom can be written by means of a special code, representing a combination of four quantum numbers. These are in no way abstract quantities used to write down electron states. On the contrary, they are of real physical significance.

You have already met the number n several pages earlier. It is part of the formula ($2n^2$) for finding the number of electrons that a shell can accommodate. Thus n is the number of the electron shell. In other words, it determines whether the electron belongs to a given electron shell.

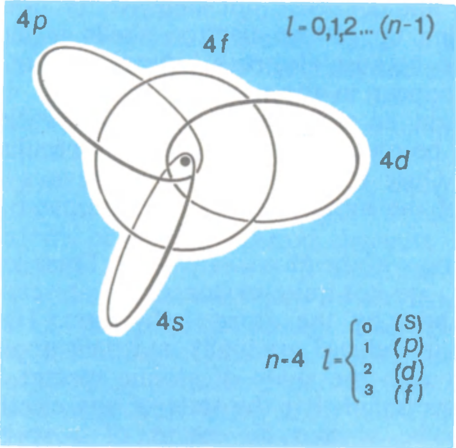
Known as the principal quantum number, n assumes only integral values:

$$1, 2, 3, 4, 5, 6, 7, \ldots,$$

corresponding to the shells

$$K, L, M, N, O, P, Q.$$

For example, when it is said that an electron is characterized by the value $n = 4$, it means that it belongs to the N-shell. Since n is included in the formula



The orbital quantum number l determines the possible types of orbits for a given value of n. The diagram shows all the types of electron orbits of only one N-shell of the atom. You, yourself, can draw such a diagram for any other shell. It is necessary only to bear in mind that the ratio l of the semiaxes of the ellipses should be equal to $\frac{l+1}{n}$.

for the energy of an electron, it is said that the principal quantum number determines the total store of energy of an electron in an atom.

Another "letter" of our atomic alphabet, the orbital, or subordinate, quantum number, is denoted by l. It was introduced to stress the inequivalence of all the electrons belonging to a given shell.

It was found that each shell is divided into subshells and that the amount of subshells is equal to the number of the shell. As you can readily see, the K-shell ($n = 1$) consists of one subshell, the L-shell ($n = 2$) of two, the M-shell ($n = 3$) of three, etc.

Each subshell of a given shell is characterized by a definite value of l. The orbital quantum number also has whole number values, but they begin with zero, i.e. 0, 1, 2, 3, ... Hence, l is always less than n. It can be readily understood that at $n = 1$, $l = 0$; at $n = 2$, $l = 0$ and 1; at $n = 3$, $l = 0$, 1 and 2, etc. Consequently, l varies from 0 to $n - 1$.

Permitted a manner of speaking, we could say that the number has a geometric image as well. The orbits of electrons belonging to one or another shell can be elliptical as well as circular.

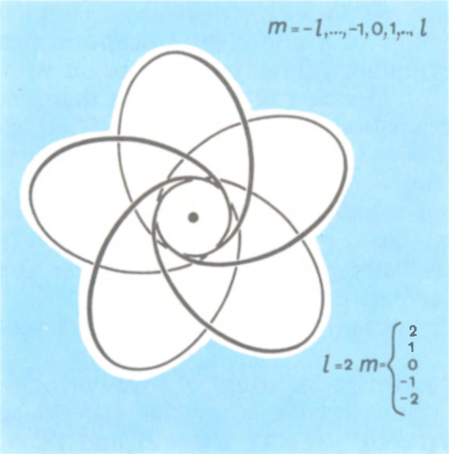
The different values of l specify the different types of orbits.

Physicists are great lovers of tradition and prefer to designate the electron subshells by the old letter symbols $s\,(l = 0)$, $p\,(l = 1)$, $d\,(l = 2)$ and $f\,(l = 3)$. These are the first letters of German words characterizing the features of series of spectral lines due to electron transitions: sharp, principal, diffuse and fundamental.

Now we can write in concise form the electron subshells in the electron shells.

Shells	Subshells
K $(n = 1)$	$1s$ $(l = 0)$
L $(n = 2)$	$2s$ $(l = 0)$; $2p$ $(l = 1)$
M $(n = 3)$	$3s$ $(l = 0)$; $3p$ $(l = 1)$; $3d$ $(l = 2)$
N $(n = 4)$	$4s$ $(l = 0)$; $4p$ $(l = 1)$; $4d$ $(l = 2)$; $4f$ $(l = 3)$
etc.	

We point out that the numbers preceding the letter symbols for the subshells are the principal quantum numbers. Two quantum numbers, the principal one n and orbital one l, are quite sufficient to offer an explanation of special features in the structure of the periodic system of the elements in the language of atomic theory. This can be done if we know how many



There can be five orbits of only a single type *d* in only a single electron shell. Try to determine in which shells such orbits are feasible. It is more correct to imagine that all these orbits are differently oriented in space.

electrons are accommodated by the various electron subshells.

We can determine this “how many” with the aid of the third and fourth quantum numbers, m_l and m_s, called the magnetic and spin magnetic quantum numbers.

We mentioned above that the quantum number l determines the type of electron orbit. The magnetic quantum number m_l is closely related to l and determines the direction of the arrangement of these orbits in space, on the one hand, and their number that is possible for the given l value, on the other hand. It follows from certain laws of atomic theory that for a given l the quantum number m_l takes on $2l+1$ integral values: from $-l$ to $+l$, including zero.

For $l = 3$, for instance, we have the following sequence of values for m_l: -3, -2, -1, 0, $+1$, $+2$, $+3$, i.e. seven values in all.

Why is m_l called the magnetic quantum number? Each electron rotating in orbit about the nucleus is, in essence, a turn of a coil carrying an electric current. This sets up a magnetic field. Hence, each orbit in an atom can be regarded as a plane magnetic shell. When an external magnetic field is applied, each electron orbit interacts with this field and tends to take on a definite orientation in the atom.

It is found that the number of electrons in each orbit is determined by the value of the spin magnetic quantum number m_s.

The behaviour of atoms in strong nonuniform magnetic fields showed that each electron in the atom conducts itself like a small, or elementary, magnet. This indicates that the electron revolves about its own axis like a planet in orbit about the sun. This property of the electron is called spin. This revolution of the electron, i.e. its spin, is constant and quite extraordinary. It can neither be accelerated, nor slowed down, nor stopped. It is the same for all the electrons in the world.

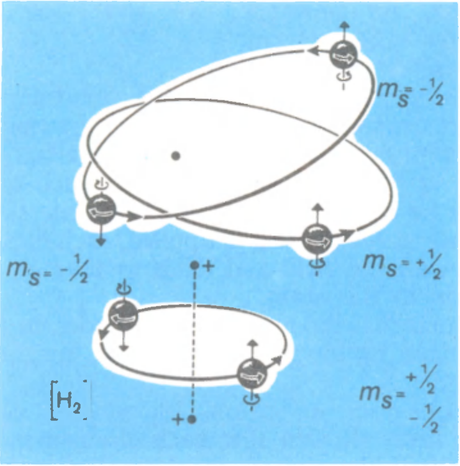
Though spin is a general property of all electrons, it is also the reason for the difference between the electrons in an atom.

Two electrons, rotating in the same orbit about the nucleus, have the same spin value, but they can differ in the direction of spin about their axes. This reverses the sign of the angular momentum and that of the spin.

Quantum calculations lead to two possible values of the spin quantum numbers that an electron in orbit can have:

$$s = +{}^1/_2 \quad \text{and} \quad s = -{}^1/_2.$$

There can be no other values. Therefore, only one or



In each orbit there may be either two paired electrons or a single unpaired one. The unpaired electron is of vital importance to the chemical characteristics of an element. It determines the formation of a molecule.

two electrons can rotate in each orbit. There cannot be any more.

Finally, we have the right to state that each electron subshell can accommodate a maximum of $2(2l+1)$ electrons, namely:

the *s*-subshell has $2(2 \times 0+1)=2$ electrons,
the *p*-subshell has $2(2 \times 1+1)=6$ electrons,
the *d*-subshell has $2(2 \times 2+1)=10$ electrons, and
the *f*-subshell has $2(2 \times 3+1)=14$ electrons.

From this we can obtain by simple addition the capacity of the successive shells.

Now we are capable of answering the question: what is the basic law of atomic structure?

How strikingly simple is this basic law to which the initially infinite complexity of atomic structure is reduced. All the capricious behaviour of the electrons in the outer shell of the atom, which governs all of its properties, can be expressed with rare simplicity: *no two electrons can be identical in an atom.*

The meaning of this law now becomes clear to us. Each electron in an atom should have a different set of values of their four quantum numbers: n, l, m_l and m_s. This law is known in science as the Pauli exclusion principle, after the Austrian-born Swiss theoretical physicist Wolfgang Pauli.

If we know the total number of electrons in a given atom, which equals its atomic number in Mendeleev's system, we can ourselves "construct" the atom; we can ourselves calculate the structure of its outer electron shell, determining the number and kind of electrons it contains. Let us now see how this is done in practice.

Architecture of the periodic system. Previously, in discussing the contribution made by Bohr in supplying an explanation of periodicity, we failed to mention one of his significant conclusions: *as Z increases, similar types of electronic configurations of the atoms are periodically repeated.* In essence, this is also a statement of the periodic law, but as applied to the process of distributing the electrons among the shells and subshells.

Knowing the law of atomic structure, we now can ourselves design the periodic system and offer an explanation for the reason why it is constructed in precisely that way. All that still is required is one slight terminological elucidation: elements in whose atoms *s*-, *p*-, *d*- and *f*-subshells are being built up are to be called *s*-, *p*-, *d*- and *f*-elements, respectively.

We must also keep in mind the fact that the formula for an atom, according to a strange tradition, is customarily written in somewhat uncommon form. But it is one we can readily get accustomed to. Physicists indicate the principal quantum number by the corresponding digit and the orbital quantum number by a letter. The number of electrons is given as a superscript to the right. An atom of hydrogen, for example, has only one electron, and its formula, therefore, is of simplest form: $1s$.

Thus, let us begin.

The first period contains the $1s$-elements hydrogen and helium. Since there can never be more than two s-elements, the first period can be schematically written as follows:

$$\boxed{1s^2}$$

Recalling, or rereading, what has been discussed in the preceding pages, you can readily reason out that the second period can be represented in the form:

$$\boxed{2s^2}\boxed{2p^6}$$

i.e. it contains elements in whose atoms the $2s$- and $2p$-subshells are being filled. The third period (in which the $3s$- and $3p$-subshells are built up) will then be:

$$\boxed{3s^2}\boxed{3p^6}$$

It is now obvious that similar types of electron configurations are repeated. Similar, but not identical, because, for instance, $1s^2$ is not the same as $2s^2$, and $2s^2$ is not $3s^2$.

Some prompting will be required in representing the structure of the fourth period. At the beginning of this period we have two 4*s*-elements, i.e. the filling of the *N*-shell ($n = 4$) begins before we have completely built up the *M*-shell. This shell, as we already know, has 10 more vacant places and is filled in the ten subsequent elements (3*d*-elements). When the filling of the *M*-shell is completed, the filling of the *N*-shell is resumed (with six 4*p*-electrons). Consequently, the structure of the fourth period is represented by:

$4s^2$	$3d^{10}$	$4p^6$

The fifth period, consisting of the same number (18) of elements as the fourth (18), is written in a similar way:

$5s^2$	$4d^{10}$	$5p^6$

The sixth period contains 32 elements (along with the *s*-, *p*- and *d*-elements, a new kind, the 4*f*-elements, have been added). Schematically, this period is represented by the following:

$6s^2$	$4f^{14}$	$5d^{10}$	$6p^6$

Finally, the next and seventh period is:

$7s^2$	$5f^{14}$	$6d^{10}$	$7p^6$

It should be kept in mind, however, that not all the elements of the seventh period are known. A modern version of Mendeleev's periodic table is given on p. 72. Its structure fully complies with the constructing procedure we have just been engaged in.

We have come to the point where we can now ask

MENDELEEV'S PERIODIC TABLE OF THE ELEMENTS

Periods	A I B	A II B	A III B	A IV B	A V B	A VI B	A VII B	A VIII B		
1	H						1 H 1.0079 $1s^1$ Hydrogen	2 He 4.00260 $1s^2$ Helium		
2	3 Li 6.94 $2s^1$ Lithium	4 Be 9.01218 $2s^2$ Beryllium	5 B 10.81 $2s^2 2p^1$ Boron	6 C 12.011 $2s^2 2p^2$ Carbon	7 N 14.0067 $2s^2 2p^3$ Nitrogen	8 O 15.999_4 $2s^2 2p^4$ Oxygen	9 F 18.99840 $2s^2 2p^5$ Fluorine	10 Ne 20.17_9 $2s^2 2p^6$ Neon		
3	11 Na 22.98977 $3s^1$ Sodium	12 Mg 24.305 $3s^2$ Magnesium	13 Al 26.98154 $3s^2 3p^1$ Aluminium	14 Si 28.08_6 $3s^2 3p^2$ Silicon	15 P 30.9737 $3s^2 3p^3$ Phosphorus	16 S 32.06 $3s^2 3p^4$ Sulphur	17 Cl 35.453 $3s^2 3p^5$ Chlorine	18 Ar 39.94_8 $3s^2 3p^6$ Argon		
4	19 K 39.09_8 $4s^1$ Potassium	20 Ca 40.08 $4s^2$ Calcium	21 Sc 44.9559 $3d^1 4s^2$ Scandium	22 Ti 47.90 $3d^2 4s^2$ Titanium	23 V 50.941 $3d^3 4s^2$ Vanadium	24 Cr 51.996 $3d^5 4s^1$ Chromium	25 Mn 54.9380 $3d^5 4s^2$ Manganese	26 Fe 55.84_7 $3d^6 4s^2$ Iron	27 Co 58.9332 $3d^7 4s^2$ Cobalt	28 Ni 58.70 $3d^8 4s^2$ Nickel
	29 Cu 63.54_6 $3d^{10} 4s^1$ Copper	30 Zn 65.38 $3d^{10} 4s^2$ Zinc	31 Ga 69.72 $4s^2 4p^1$ Gallium	32 Ge 72.5_9 $4s^2 4p^2$ Germanium	33 As 74.9216 $4s^2 4p^3$ Arsenic	34 Se 78.9_6 $4s^2 4p^4$ Selenium	35 Br 79.904 $4s^2 4p^5$ Bromine	36 Kr 83.80 $4s^2 4p^6$ Krypton		
5	37 Rb 85.467_8 $5s^1$ Rubidium	38 Sr 87.62 $5s^2$ Strontium	39 Y 88.9059 $4d^1 5s^2$ Yttrium	40 Zr 91.22 $4d^2 5s^2$ Zirconium	41 Nb 92.9064 $4d^4 5s^1$ Niobium	42 Mo 95.94 $4d^5 5s^1$ Molybdenum	43 Tc 98.9062 $4d^5 5s^2$ Technetium	44 Ru 101.0_7 $4d^7 5s^1$ Ruthenium	45 Rh 102.9055 $4d^8 5s^1$ Rhodium	46 Pd 106.4 $4d^{10} 5s^0$ Palladium
	47 Ag 107.868 $4d^{10} 5s^1$ Silver	48 Cd 112.40 $4d^{10} 5s^2$ Cadmium	49 In 114.82 $5s^2 5p^1$ Indium	50 Sn 118.6_9 $5s^2 5p^2$ Tin	51 Sb 121.7_5 $5s^2 5p^3$ Antimony	52 Te 127.6_0 $5s^2 5p^4$ Tellurium	53 I 126.9045 $5s^2 5p^5$ Iodine	54 Xe 131.30 $5s^2 5p^6$ Xenon		
6	55 Cs 132.9054 $6s^1$ Cesium	56 Ba 137.3_4 $6s^2$ Barium	57 La * 138.905_5 $5d^1 6s^2$ Lanthanum	72 Hf 178.4_9 $5d^2 6s^2$ Hafnium	73 Ta 180.947_9 $5d^3 6s^2$ Tantalum	74 W 183.8_5 $5d^4 6s^2$ Tungsten	75 Re 186.207 $5d^5 6s^2$ Rhenium	76 Os 190.2 $5d^6 6s^2$ Osmium	77 Ir 192.2_2 $5d^7 6s^2$ Iridium	78 Pt 195.0_9 $5d^9 6s^1$ Platinum
	79 Au 196.9665 $5d^{10} 6s^1$ Gold	80 Hg 200.5_9 $5d^{10} 6s^2$ Mercury	81 Tl 204.3_7 $6s^2 6p^1$ Thallium	82 Pb 207.2 $6s^2 6p^2$ Lead	83 Bi 208.9804 $6s^2 6p^3$ Bismuth	84 Po [209] $6s^2 6p^4$ Polonium	85 At [210] $6s^2 6p^5$ Astatine	86 Rn [222] $6s^2 6p^6$ Radon		
7	87 Fr [223] $7s^1$ Francium	88 Ra 226.0254 $7s^2$ Radium	89 Ac ** [227] $6d^1 7s^2$ Actinium	104 Ku [261] $6d^2 7s^2$ Kurchatovium	105 Ns [260] $6d^3 7s^2$ (Nilsborium)	106	107			

* LANTHANIDES

58 Ce 140.12 $6s^2$ $5d^1$ $4f^1$ Cerium	59 Pr 140.907 $4f^3 6s^2$ Praseodymium	60 Nd 144.2_4 $4f^4 6s^2$ Neodymium	61 Pm [145] $4f^5 6s^2$ Promethium	62 Sm 150.4 $4f^6 6s^2$ Samarium	63 Eu 151.96 $4f^7 6s^2$ Europium	64 Gd 157.2_5 $6s^2$ $5d^1 4f^7$ Gadolinium	65 Tb 158.9254 $4f^9 6s^2$ Terbium	66 Dy 162.5_0 $4f^{10} 6s^2$ Dysprosium	67 Ho 164.9304 $4f^{11} 6s^2$ Holmium	68 Er 167.2_6 $4f^{12} 6s^2$ Erbium	69 Tm 168.9342 $4f^{13} 6s^2$ Thulium	70 Yb 173.0_4 $4f^{14} 6s^2$ Ytterbium	71 Lu 174.97 $6s^2$ $5d^1 4f^{14}$ Lutetium

** ACTINIDES

90 Th 232.0381 $6d^2 7s^2$ Thorium	91 Pa 231.0359 $7s^2$ $6d^1 5f^2$ Protactinium	92 U 238.02 $7s^2$ $6d^1$ $5f^3$ Uranium	93 Np 237.0482 $7s^2$ $6d^1$ $5f^4$ Neptunium	94 Pu [244] $5f^6 7s^2$ Plutonium	95 Am [243] $5f^7 7s^2$ Americium	96 Cm [247] $7s^2$ $6d^1 5f^7$ Curium	97 Bk [247] $7s^2$ $6d^1 5f^8$ Berkelium	98 Cf [251] $5f^{10} 7s^2$ Californium	99 Es [254] $5f^{11} 7s^2$ Einsteinium	100 Fm [257] $5f^{12} 7s^2$ Fermium	101 Md [258] $5f^{13} 7s^2$ Mendelevium	102 (No) [255] $5f^{14} 7s^2$ (Nobelium)	103 (Lr) [256] $5f^{14} 6d^1 7s^2$ (Lawrencium)

ourselves: is this stepwise filling of the shells simply a device that physicists and chemists resorted to to explain in some way the phenomenon of periodicity, or is it a rigid physical law?

It is, of course, a law! Each electron, in its turn, that is included in an electron shell, is characterized by a definite amount of energy (or, as they say, occupies a definite energy level). First the sequence of these levels is such that it corresponds to a monotonic filling of the electron shells. But this monotony vanishes when the 3*p*-subshell has been filled. Instead of proceeding to fill the levels of the 3*d*-subshell, the electrons find it more favourable (from the energy standpoint) to first populate the levels of the 4*s*-subshell. It is this energy "seesaw" of "favourable-unfavourable" that clears up the stepwise filling of the electron shells. The next question posed is: why are periods of similar structure repeated in pairs?

We previously defined a period as being a set of elements beginning with an alkali metal and ending with an inert gas. But now, after mastering the language of electron configurations, we can state that the atom of any alkali metal (as well as the hydrogen atom) has an outer shell of the following structure:

$$\boxed{n\,s^1}$$

whereas that of an inert gas has

$$\boxed{n\,p^6}$$

Here *n* is the principal quantum number; it is also the number of the outer electron shell and it is also the number of the period, because each period begins with an atom in which a new electron shell appears.

We grant you the opportunity of formulating a definition of a period in the periodic system (keeping in mind the specific feature of the first period, which consists of only *s*-elements).

If we accept the fact that the configurations of the outer electron shells of the atoms of the bounding elements (initial and final) in a period are like ns^1 and np^6, then the similarly arranged periods (second and third, fourth and fifth, and sixth and seventh) will be repeated pairwise and consist of the same number of elements. This is so because no other distribution of the elements among the periods is possible.

Once again we underline the genius of D. I. Mendeleev as an "architect" in the structure of matter. Though he knew nothing about atomic structure, he was able to create a table of the chemical elements of astonishingly ordered design.

This design was so successful that it proved relatively simple to solve the mystery of electron shell structure on the basis of the laws of the chemical behaviour of the elements, revealed by the periodic table.

The periodic system and a lesson in chemistry. Approaching the problem rigorously and in a perhaps overparticular manner, we can pose the question: just what kind of periodic system have we been discussing?

It is a periodic system of the atoms. We considered the sequence with which the electron shells and subshells are filled, and how similar electron configurations are repeated. The elements, with the exceptional diversity and uniqueness of their properties, were only implied, but were not actually present. This comprises one of the many marvellous features of the periodic law. The more knowledge of it we gain, the more profound its content turns out to be.

After clearing up the laws of atomic structure, physicists and chemists were able to reveal the reasons for the periodicity in the variation of the properties of chemical elements and to account for the structure of the periodic system. But when we tried, on the basis of physical concepts, to explain why one or another element possesses certain definite properties, ideas of atomic structure often proved insufficient. As to its intrinsic substance, the periodic system of the elements is much deeper and much broader than the periodic system of the atoms.

We now turn our attention to hydrogen, the first chemical element. The electron structure of its atom is represented by 1*s*. It would seem that its place is in the group of alkali metals, in the 1*a*-subgroup. But the properties of hydrogen are such that it is difficult to choose a single, quite definite place for it. Sometimes it is actually put into the first group, implying kinship with the alkali metals. Like them hydrogen has a single electron in its outer shell, and it can display positive valency equal to unity. Finally, it can replace certain metals in their salts. But these are the only properties that are common to the other elements of the first group. Hydrogen is, after all, a nonmetal and a gas, whereas all the others are typical metallic elements.

Yet hydrogen has much in common with the halogens, elements of the seventh group. Like those of the halogens, molecules of hydrogen consist of two atoms. Both halogens and hydrogen are typical nonmetals. Like the halogens, hydrogen can also display negative valency, combining with metals to form distinctive substances called metal hydrides. But this resemblance is also too distant to regard hydrogen as a blood relation of the halogens.

Hence, as we see, hydrogen seems to combine the features of the elements of the first and seventh groups.

Such "two-facedness" of hydrogen is due to the structure of its atom. Any element, in giving up valence electrons, keeps intact one or several lower shells. Hydrogen, when it parts with its single valence electron, appears before us in the form of a "bare" atomic nucleus, the proton. Therefore, the chemistry of hydrogen is to some degree the unique chemistry of an elementary particle. It is the first element of the periodic system and our first evidence of how much richer its chemical potentialities are than could be supposed from its atomic structure.

Once Mendeleev stated that the elements of the second and third periods were typical. He reasoned that their distinctive chemical features determine, as it were, all the subsequent structure of the system. As a matter of fact, an understanding of the behaviour of the typical elements is quite sufficient to clarify, to a considerable extent, the chemical aspect of Mendeleev's table.

In "electron" language, the elements lithium and beryllium, which begin the second period, are 2*s*-elements. Both are metals; lithium readily parts with its outer electron; beryllium, much less willingly. In the atom of its neighbour boron, filling of the 2*p*-subshell begins, and the element itself turns out to be a nonmetal. Carbon, nitrogen, oxygen, fluorine and neon all display only nonmetallic properties.

One of the main rules of chemical interaction states: the atoms of an element can give up electrons from their outer shells or, on the contrary, they can gain electrons. This process of losing and acquiring electrons has a very definite purpose. Each atom wants, as it were, to become like the atom of the nearest inert gas, because the atoms of inert gases are extremely stable formations. For the elements of the second period, such paragons are helium and neon.

This is why, for instance, oxygen and fluorine are found to be the strongest oxidizers, having no equal in their chemically aggressive behaviour. To reach the eight-electron outer shell of neon, they require only a few more electrons, and they greedily "plunder" atoms of other elements to acquire them.

We mention another amazing feature of the second period. Three of its elements, carbon, nitrogen and oxygen, are, together with hydrogen, component parts of organic matter. They are, so to speak, especially responsible for all life on the earth. Why? This, very likely, is a question whose answer will require the efforts and research of more than one generation of future chemists.

In the third period, almost all is the same as the second. There are the 3*s*-elements, sodium and magnesium, and the 3*p*-elements, from aluminum through argon. Almost all, but not all. Sodium is a great deal more chemically active than its second-group predecessor, lithium. The same can be said for magnesium and beryllium. Aluminum, in contrast to boron, is a typical metal. Silicon, the base material of all ores and minerals, the "cement" that holds together the earth's crust, harbours certain prototypes of metallic properties. Phosphorus and sulfur are solids, not gases like their analogues, nitrogen and oxygen, of the second period. Chlorine, like fluorine, is a gas, also a chemical "aggressor", but one less fierce than fluorine. Of the whole set only argon differs in no way externally from neon.

What do we note when we compare the elements of the second and third periods? We observe a quite definite regular variation in properties along the groups and along the periods, vertically and horizontally. The basic features of these variations are retained farther on as well, in the subsequent periods.

These variations consist in the following.

The chemical activity increases as we move downwards in the subgroups of the alkali and alkaline-earth metals (if francium, for instance, could ever be obtained in metallic form, it would turn out to be the most active of all metals). This, consequently, is a special feature of the *s*-elements.

As to the *p*-elements, their metallic properties increase as we move downward. This is true even for the halogens: astatine, the heaviest of them, resembles a metal in many aspects. As we move from the left to the right (along a period), properties change appreciably from element to element. Carbon, for example, does not noticeably resemble boron, and gaseous nitrogen has nothing in common with carbon.

Have you noticed that so far we have been dealing with only the *s*- and *p*-elements? These elements are located in the main, *a*-subgroups of the periodic system. They have one common property: in their atoms, with the increase of Z, the outer electron shell is being filled (with the value of the principal quantum number n being equal to the period number).

Since the chemical properties of the elements depend to a great extent on the number of outer electrons, these properties appreciably change in going from element to element.

What kind of elements belong to the *b*-subgroups? We shall have to wait a little for the answer. First we wish to tell about one rather surprising phenomenon: it seems that inert gases can also combine to form chemical compounds.

How inert gases ceased to be inert. Take a look at the periodic system illustrated on page 72. You can see that all the groups, from the first through the eighth, contain elements of the *a*-subgroups. The main subgroup in the eighth group comprises the inert, or noble, or inactive, gases. They are: helium, neon, argon, krypton, xenon and radon.

A moment, please. Recall that when we told about the meeting between Ramsay and Mendeleev in 1900, we mentioned that they had come to the conclusion that it is most expedient to put the inert gases into a special zero group. The reason was that these gases displayed no capacity for participating in chemical interactions.

Where then is their rightful location: in the VIII*a*-subgroup or in a special zero group? Behind this “or” there is some highly interesting chemical history, to which we shall devote the next few pages.

Why are they inert? The French chemist Ferdinand Frederic Henri Moissan isolated fluorine gas and saw for himself what incomparable chemical activity this lightest of the halogen family is capable of. Moissan was the first to try to attack argon with fluorine, but with no result whatsoever. Chemists tried in a great variety of ways to obtain compounds of inert gases with other elements, but all in vain. It became a universally held opinion that helium and its fellow gases have no chemical properties whatsoever.

Their inertness could be explained only on the basis of the theory of atomic structure. The outer shell of inert gas atoms, beginning with neon, contains eight electrons (two in the outer shell of the helium atom). This electron octet is, in general, a sufficiently firm formation. For this reason, the scientists contended, the atoms of inert gases have no tendency to either acquire or to give up electrons. But there can be no chemical interaction without electron exchange. The first conception of the mechanism of chemical bonding, ionic and covalent, was based on the idea that atoms, when they take part in chemical interaction, tend to attain the outer electron configuration of the nearest inert gas in the system.

We draw your attention to one quite frequently encountered error. In characterizing inert gases, it is often said that they have a completely filled outer electron shell. On the whole, this statement is not true. Only in the atoms of helium and neon are the outer shells (the *K*- and *L*-shells, respectively) fully completed. In the atoms of all the subsequent inert gases, the outer shells (*M*, *N*, *O* and *P*) are by no means filled with electrons to their full capacity. By this essential feature helium and neon differ from their heavier analogues.

It would seem now that all is clear; that all the i's have been properly dotted and all the t's have been properly crossed. The inertness of six gaseous elements of the periodic system became an indisputable fact based on the postulates of Bohr's theory of the atom. But, speaking of history, it proves of interest to take into account the evidence of the contemporaries of some event. Arnold Sommerfeld, the famous German physicist that made a weighty contribution to periodic system theory, wrote: "When we called the eight-electron shell of the noble gases an especially stable configuration, that was by no means a theoretical explanation; it was only an expression of empirical facts".

Sommerfeld wrote this in 1924. Obviously, he had some doubts about the "especial stability" of the outer electron shell in the atoms of inert gases.

We should add, however, that many chemists displayed great interest in inert gases during the first half of the twentieth century, not excluding them at all from their spheres of activity.

The founding of inert-gas chemistry. Such enthusiasts in the field of chemistry were able to observe a peculiar phenomenon. During the crystallization of certain compounds, heavy inert gases could penetrate into the crystal lattice and could get stuck there. Xenon, for example, could be retained in the ice crystals when water is frozen. With water this xenon formed an unusual compound that could be written as $Xe \cdot 6H_2O$. This compound cannot, of course, be called a truly chemical one, because the outer electron shell of the atoms of the intruding inert gas remained intact. Such compounds are said to be clathrate ones, or simply clathrates. A great number of clathrates are known today, including ones formed by inert gases. A great deal of the work in obtaining such clathrates and in their investigation was done by the prominent Soviet chemist Boris Aleksandrovich Nikitin.

The hint suggested by Sommerfeld so long ago had its repercussions in the thirties. Thanks to quantum mechanics (which we shall discuss on page 97), theoretical chemistry made substantial advances in those years. Theoretical chemists calculated the electron-binding energy in atoms and compared the changes in the ionization potentials and the ionic radii of various elements. The capacity of atoms to participate in chemical interaction was finally expressed quantitatively. Chemistry was transformed more and more into an exact science.

Certain calculations definitely indicated that the "electron octets" in the atoms of heavy inert gases are not so unapproachable as they were thought to be. As far back as 1933, the world-famous American chemist, Linus Carl Pauling, contended that krypton and xenon can form chemical compounds with fluorine. In any case, theory does not exclude such a possibility. But almost three decades passed before Pauling's statement was confirmed. The reason was the almost unshakable belief in the exceptional stability of the outer shell of the atoms of inert gases. In addition, the techniques of experimental research on free fluorine were not sufficiently advanced.

Many years ago Moissan guessed by intuition that the unassailable "electron bastions" of inert-gas atoms would be overwhelmed by fluorine. For a long time nobody succeeded in preparing compounds of fluorine and oxygen: oxygen fluorides. Most of them were obtained only after World War II. As a rule, oxygen fluorides have low stability and belong, so to speak, to the more exotic chemical substances that are of more interest to theoreticians than to applied chemistry. But certain of these compounds have found application in chemical synthesis. One of these is oxygen difluoride (O_2F_2).

This difluoride enabled the synthesis of interesting chemical compounds that contain the molecular ion of oxygen (O_2^+). Such compounds are said to be dioxygenyl. One of them was prepared in 1961 by the young Canadian chemist, Neil Bartlett. The chemical formula of this compound could be written as: $O_2^+[PtF_6]^-$. Here oxygen appears in the quite unusual role (for oxygen) of a cation.

It is not this circumstance, however, that is of most interest to us. Bartlett calculated that the energy required to detach an electron from a molecule of oxygen is equal to 12.20 eV. This, according to atomic energy measures, is an impressive but not too great a value. It is only slightly more than that required to detach one electron from an atom of xenon (12.13 eV). A comparison of these energy values is what suggested to Bartlett the idea of attempting to combine xenon with platinum hexafluoride.

In the spring of 1962, this Canadian chemist reported that he had succeeded in preparing the world's first chemical compounds of xenon: $Xe(PtF_6)$ and $Xe(PtF_6)_2$. This is the event that announced the founding of chemistry of the noble gases. It was an event that occurred quite unexpectedly.

Bartlett's feat started off a genuine chain reaction in the synthesis of chemical compounds of the inert gases. One of the more humorously inclined contemporaries called the situation in chemistry "a nightmare of xenon fluorides". In the same year (1962), xenon difluoride, tetrafluoride and hexafluoride were obtained, and their synthesis proved, essentially, to be a relatively simple chemical operation. The compounds themselves showed no change, not only at room temperature, but even when slightly heated. In a word, they could be said to be stable.

The next year the chemists launched an attack on krypton, but here their success was much more meager. Krypton forms only one compound with fluorine: the difluoride KrF_2, and it is by no means distinguished for its stability.

From the theoretical viewpoint, the highest capacity for participating in chemical interaction should be possessed by the heaviest inert gas, radioactive radon, because it has the lowest ionization potential (10.75 eV) of all the inert gases. But it is difficult to deal with precisely because it is radioactive. It is inconvenient in experiments owing to the short half-lives of its isotopes and the strong radiation, which leads to the breaking of chemical bonds. Nevertheless, a stable compound (in the chemical sense), radon difluoride, has been prepared.

Inert-gas chemistry today. The term "inert-gas chemistry", so unusual a quarter of a century ago, does not lead now to even a vestige of astonishment. The investigation of the chemical compounds of inert gases has become an important field of inorganic chemistry.

In a more rigorous approach, the aforegoing primarily pertains to the chemistry of xenon. The xenon compounds that have been obtained belong to all the main classes of chemical compounds: oxides, acids, salts and diverse complex compounds. Xenon forms chemical bonds with fluorine, chlorine, oxygen, carbon and nitrogen. It displays only positive oxidation levels: +2, +4, +6 and +8. More than 150 different xenon compounds have already been investigated. One third of them were first prepared by Soviet chemists.

In appearance these compounds produce no particular impression. Under ordinary conditions, the simple compounds are solids consisting of small, colourless, or only slightly coloured, crystals. But xenon tetroxide is a gas under ordinary conditions, and its oxytetrafluoride is a liquid. Xenon fluorides and their complex compounds are stable and are usually nonexplosive, but this is not true for the oxides and other oxygenous compounds. Xenon trioxide, for instance, is extremely dangerous.

Much fewer compounds of krypton have been found, and even fewer for radon. The reasons are different: krypton compounds have low stability, and, as mentioned above, it is difficult to deal with radon.

Are there any known compounds of helium, neon and argon? No, there are not. In any case, in the sense that we ordinarily define the concept of a chemical compound.

The accumulated data indicate the following: the reactivity of inert gases decreases with their atomic numbers. Krypton has a substantially lower reactivity than xenon. The logical conclusion is that argon should have an even lower reactivity, and that neon and helium should be quite hopeless in this respect. We recall, incidentally, that the outer electron shells of helium and neon are completely filled.

Frankly speaking: it is out of the question to prepare chemical compounds of the light inert gases by the same methods used for the heavy inert gases.

But chemistry, in its study of substances and their transformations, has long since adopted all possible "roundabout ways" of doing things.

If high additional energy is imparted to an atom or molecule, it passes over to an excited state. In these excited or, as they are called, metastable states, the chemical activity of the particle increases drastically. Scientists have established that in metastable states the atoms of inert gases can form short-lived compounds with each other (forming molecules, such as Kr_2 or Xe_2, which do not exist in nature) and with other elements, for instance, with hydrogen. It was found that even helium is capable, in this state, of producing the phantasmal chemical composition HeH^* (the asterisk indicates an excited molecule), but, it is true, only at the temperature 4 K. Excited atoms of argon combine by chemical reactions with such compounds as nitrous oxide (N_2O), ozone (O_3) and chlorine (Cl_2), forming the not very stable compounds ArO and ArCl. Surprising, but a fact, that here we observe a definite resemblance between the behaviour of argon and the alkali metals!

Are chemical compounds of xenon and krypton needed in practice? They were found to be very necessary, even if only to extend the synthesizing capacity of inorganic chemistry. The most important property of the oxygen compounds of xenon is their high oxidation potential. Besides, additional advantages are gained when pure oxides of xenon are applied as oxidizers: after accomplishing the reaction, no foreign ions remain in the solution because the gaseous xenon and the surplus oxygen are disposed of from the sphere of the reaction.

Compounds of krypton and xenon enable compounds of almost all the elements, at the highest known oxidation levels, to be obtained at ordinary temperatures. Obtained in this way, for example, were the pentafluorides of gold and palladium.

Compounds of xenon and krypton are used as original accumulators of fluorine or a noble gas.

Inert-gas chemistry and the periodic system. The news of the synthesis of the xenon fluorides caused tremendous commotion in the world of science. This event was regarded as one of the outstanding scientific discoveries of the twentieth century. Of course: “the inert gases are no longer inert”!

We have purposely enclosed this frequently used phrase in quotation marks; it is, without doubt, an exaggeration. In the first place, chemical derivatives were actually obtained for only three of the six gases. In the second place, in all up-to-date classifications of the elements according to their chemical nature, helium and its analogues belong to the inert elements, since, by themselves, they are completely deprived of any oxidizing capacities. In the third place, the number of elements with which even xenon establishes chemical bonds is extremely limited (fluorine, chlorine, oxygen, carbon and nitrogen), and there is no particular hope that this number will increase to any appreciable extent. Finally, in the fourth place, the capacity of krypton, xenon and radon to participate in chemical reactions can be comprehensively explained within the framework of modern concepts of chemical bonds, without having to think out any new theories.

In short, the synthesis of chemical compounds of a number of inert gases certainly is a great event. In assessing it, however, there is no need to run to extremes.

One such extreme is the complete abolishment of the zero group in the structure of the periodic system.

The generally accepted version today is one in which all the inert gases are arranged in the VIII*a*-subgroup. To "keep up with the fashion" we have included such a table in the present book. Many arguments can be cited in favour of this version. It is also obvious that it would look like an anachronism to leave all the inert gases in the zero group.

We could, of course, find a compromise by retaining the status of a zero group for helium and neon. It is hardly possible that future generations of chemists will succeed in involving them in ordinary chemical interactions. Besides, recall the specific feature of the atoms of these inert gases: their electron shells can be completely filled. As regards argon (though this is somewhat open to doubt), krypton, xenon and radon, their place in the eighth group does not appear to be an extreme. It really is their lawful location.

What elements are included in the *b*-subgroups? The auxiliary or *b*-subgroups contain the elements in whose atoms shells are being filled that were previously unfilled. Precisely for this reason, as you can readily understand, the first, second and third periods contain only elements that are included in the main subgroups. Elements of the auxiliary subgroups appear only beginning with the fourth period and the first such element is scandium (a 3*d*-element).

All of the *d*-elements (with rare exceptions that have almost no effect on the properties) have a constant number of *s*-electrons, equal to two. Hence, in the first place, all *d*-elements are metals. They are often called transition elements because they actually do constitute transitions, in the long periods, from *s*- to *p*-elements.

In the second place, when we go from one *d*-element to the next we do not observe such a drastic change in properties as in the *p*-elements. Instead, the changes are smooth. Sometimes so smooth that adjacent elements are very much alike.

It is here that we find violations in the symmetry of structure of the periodic system, because we must fit in these "extremely like" elements and do this in the most logical way. Thus the system acquires an annex, which corresponds to a distinctive group, the eighth. Its elements are grouped in sets of three in each long period of the table. These groups are called triads.

The elements of each triad resemble one another very closely. Even the names of some of them are due to this resemblance. In the Middle Ages, ore miners sometimes found mysterious ores, which looked like iron ore, but from which no iron could be smelted. The puzzled miners naively thought that the mountain spirits – gnomes (a kobold in the German version, a goblin or demon of the mines) and Old Nick – were playing malicious tricks on them. These are the origins of the names of two elements of the first triad: cobalt and nickel.

The elements of the two other triads are even more alike; they are even united by a common name: the platinum metals. All of them are found in nature almost exclusively in the native metallic state. It would seem that the maximum valency of the elements in the triads should equal eight. In the other groups the overwhelming majority of the elements are capable of displaying a valency equal to the number of their group. But here such "heights" are within the capacity of only ruthenium and osmium, which form the oxides RuO_4 and OsO_4. Thus the group number is of a purely formal nature. Not without reason, certain chemists have pointed this out as a weakness of the periodic system.

Completion of the preceding electron shell (the *M*-shell) by means of *d*-electrons occurs in iron, cobalt and nickel. This shell is almost completely filled. We observe exactly the same picture in the atoms of the platinum metals.

Since the preceding shell is just about to be filled to its full capacity, it is not to the advantage of atoms of the eighth group to give up many electrons from this shell. This is why the octavalent state is rare among the elements of the triads.

The platinum metals unwillingly, on the whole, permit themselves to be involved in chemical reactions, even with the most ferocious chemical aggressors.

At the present time, the triads are being included in the auxiliary VIII*b*-subgroup, even though not all chemists are in agreement on this matter.

The riddle of the rare-earth elements. So far no mention has been made of the *f*-elements that, as we know, also exist. Even a glance at the periodic system reveals an astonishing fact. There does not seem to be any place to put the 4*f*-elements. These elements, 14 in number, from cerium through lutetium, are arranged separately, under the main part of the table.

The history of the so-called rare-earth elements (included under this heading are lanthanum and the 14 elements of the lanthanide series, the 4*f*-elements) is one of the most complicated and intricate pages in the history of the periodic law.

How many rare-earth elements have to fit into one space of the periodic system?

Such a question was simply irrelevant to Mendeleev, who was sure that each space can be occupied by a single element.

Many well-known chemists, including Mendeleev himself, tried hard and long to accommodate the rare-earth elements in the periodic system. They tried, for example, to put cerium into the fourth group, praseodymium into the fifth, and to find a place for neodymium in the sixth.

But these extraordinary elements violated the very foundation of periodic system structure. Notwithstanding the efforts made to properly arrange them in the table, repetition of properties could not be achieved. There should have been like elements in the auxiliary subgroups into which they were tentatively installed. But cerium had nothing in common with zirconium, praseodymium with niobium, and neodymium had no resemblance whatsoever to molybdenum.

On the other hand, it became clearer and clearer, as their chemical properties were investigated, that these elements are as identical among themselves as twins. The rare-earth elements are so chemically similar that it is exceptionally difficult to distinguish and separate one from another. There was no doubt, however, that they were different elements. Chemists were sure of this fact.

A friend of Mendeleev's, the Czech chemist Bohuslav Brauner, suggested the simplest solution: to accommodate all of these elements into a single space in the table. But this, in essence, only increased the fundamental difficulty of the problem instead of providing a true solution.

If one space can be occupied by several different elements, then, firstly, the basic principle of the periodic

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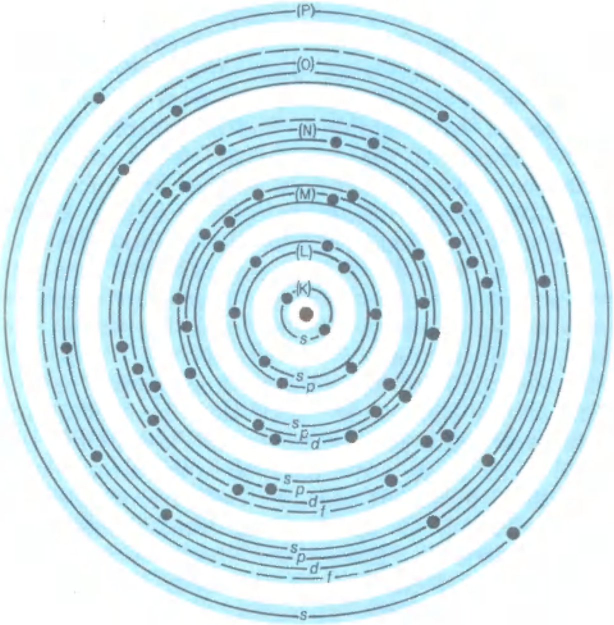
We advise you to carefully study this simplified diagram showing the structure of the complex atom of lanthanum. Note that there must be two *s*-electrons and six *p*-electrons at each of all the energy levels. Besides these electrons, there are also ten *d*-electrons each in the *M*- and *N*-shells. Note also that the subshell where the *f*-electrons should be is empty; it has no electrons whatsoever. Moreover, lanthanum has only a single 5*d*-electron and, finally, two more 6*s*-electrons. Altogether, lanthanum, as is required, has 57 electrons. It occupies the 57th space in the table.



La

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 5d\ 6s^2$

system is violated. Secondly, it then becomes impossible to foresee and predict the number of elements that can be found in nature, and how many can exist, all told. Chemists all over the world were searching for new elements zealously and with unexpected success. During a short period of about 30 years, almost a hundred (!) rare-earth elements were discovered, and the overwhelming majority of these discoveries were found to be erroneous. All attempts to find a reasonable solution of the problem of the rare earths were to no avail.

Only the quantum theory of atomic structure made it possible to finally clear up this puzzling chemical quandary. A detailed study of the spectral characteristics of the rare-earth elements showed that their atoms are of unusual structure. Their outer shells, with certain exceptions that will be mentioned below, are of entirely like structure.

The atoms of all the rare-earth elements have two *s*-electrons in their outer shell and are therefore all metals. Below this shell there is the 5*d*-subshell of the *O*-shell, which is not filled in the atoms of the rare-earth elements. It contains only one electron that can also participate in chemical transformations, but only in cerium, gadolinium and lutetium. The determination of the atomic numbers established the number of rare-earth elements that exist and an investigation of their spectra helped to clear up the structure of their atoms. It was found that they differ from one another by the number of 4*f*-electrons in the as yet unfilled *N*-shell, which is concealed deep within the atom. These electrons are shielded outside by an armour of stable $5s^2$ and $5p^6$ subshells. These electrons are almost completely blocked and cannot manifest themselves in the chemical properties of their elements.

All rare-earth elements are trivalent. Why? This question is not easy to answer. Only La, Ce, Gd and

Lu have three valence electrons on hand. All the others have only two 6*s*-electrons ready to take part in chemical bonds. Where does the third come from? As we mentioned above, the 4*f*-subshell is hidden deep within the atom. This poses a problem that has not been fully solved as yet.

Now that we know the law for the filling of the outer electron shells of the atoms, any of us, future chemists, can solve the problem on which chemists racked their brains for many decades: how many rare-earth elements exist in nature?

Obviously, an amount that exactly corresponds to the gradual filling of all the orbits with electrons. The letter *f* corresponds to the quantum number $l = 3$. We already know that there can be $2 \times 3 + 1 = 7$ such orbits. There can be no more than two electrons in each orbit. Consequently, there can be *fourteen* such elements in nature. Altogether there should be *fifteen* twin elements in nature, counting lanthanum, whose properties are close to those of the lanthanide series. And this is the number that there actually are, beginning with the 57th element, lanthanum and through the 71st, lutetium. True, nature was checked and found wanting: the 61th element was discovered only quite recently. Chemists had to obtain (synthesize) it artificially. They called this element promethium.

Can we now say that one space of the periodic system accommodates fifteen elements? This question is still being frequently discussed in our day. Mendeleev's periodic law is a universal law of nature. In the natural system of the elements each element occupies one place and, consequently, each element should occupy one space in the table. Mendeleev arranged his table in its simplest and most convenient form. But it can be depicted in different ways. We can simply remember that one space between barium and hafnium conditionally substitutes for fifteen places. Mendeleev's table can also be constructed so that all the long periods are expanded to their full length. This in no manner changes the periodic law.

A few words on the seventh period. As we have already mentioned, it is still incomplete. Like the sixth period, the seventh should also contain 32 elements. Today 21 are known, a considerable majority of them having been obtained artificially, by means of nuclear synthesis. The missing elements should be obtained, under favourable circumstances, by the same techniques (pages 144-145). The period should be concluded by an element with the atomic number 118, "eka-radon", which, if it exists, can in no way be an inert gas. Under ordinary conditions, element 118 would most likely be a liquid, and would form chemical compounds much more readily than xenon and radon. In a word, it should be of especial interest. It remains to regret that no one knows whether we shall ever have the opportunity to acquaint ourselves with this element in actual practice.

When Mendeleev worked out his periodic system, only two elements of its seventh period, uranium and thorium, were known. Their properties resembled, respectively, those of tungsten (also known as wolfram) and zirconium. Note these circumstances.

Now look at the "electron" notation of the structure of the seventh period, given on page 71. It has been written by analogy with the structure of the sixth period. If we assume that this analogy is sufficiently rigorous, we reach the following conclusion. After the 7*s*-subshell is filled in the atoms of francium ($Z = 87$) and radium ($Z = 88$), the filling of the 5*f*-subshell should begin in the atoms of actinium ($Z = 89$) or, more likely, of cerium ($Z = 90$). Like the 4*f*-subshell, the

5*f*-subshell accommodates a maximum of 14 electrons.

All this indicates that there should be a second "rare-earth family" in the seventh period. It should be a row of fourteen elements, resembling one another, and similar to the lanthanide series. The first of these elements should be thorium.

But, as a matter of fact, neither thorium, nor protactinium, nor uranium display sufficiently noteworthy similarity with one another. Though the chemical behaviour of thorium is somewhat suggestive of that of cerium, protactinium has nothing whatsoever in common with praseodymium, nor uranium with neodymium. In short, the first elements of the 5*f*-series, or actinides (as they were named by the American chemist, Glenn Theodore Seaborg, in the forties) turned out to be distinctive to a considerable degree, and their analogy with the lanthanides, slight indeed. We shall return to the actinide series on page 145 of the present book.

Consequently, the nature of the variation in the properties of the chemical elements located at the beginning of the seventh period differs from that observed for the sixth period. Even Niels Bohr, when working out the sequence for the filling of the electron shells and subshells as Z increases, reached the conclusion that 5*f*-electrons appear in the atom of uranium or of elements with higher atomic numbers. As to thorium, protactinium and uranium, many chemists dealt with them as 6*d*-elements, analogous to the 5*d*-elements of the sixth period.

The investigation of the elements of the seventh period that exist in nature was especially troublesome, but gave much satisfaction to the chemists engaged in this work. They managed to prepare as a metal such an amazing element as radium, which Vladimir Ilyich Lenin called the "great revolutionary". Radium is the element that gave its name to "radioactivity". Physicists and chemists thoroughly investigated the properties of the rare radioactive elements actinium and protactinium. Uranium displayed many new sparkling features, being intimately associated with the discovery of radioactivity and the liberation of terrestrial helium. In his declining years Mendeleev called upon future generations of chemists to subject uranium to comprehensive research, because he felt that this should lead to new discoveries. As we shall see further on, his foresight was brilliantly justified.

Is everything really so simple in the theory of the periodic system? At times with stipulations, the theory of electron shell structure can nevertheless explain many of the regular and special features of chemical behaviour of the elements. You must agree that this theory proves a very convenient working tool both for those who are just beginning to study chemistry and for those who are already employed in a research institute or in the chemical laboratory of a manufacturing plant.

Scientists call it the formal theory of the periodic system.

Formal theory? The adjective "formal" is opposed by another adjective: "actual". Consequently, is there something in the theory that does not satisfy scientists; something that does not agree with the true state of affairs? Yes, there is. The concept of an atom as a system consisting of a nucleus with electrons rotating about it in definite orbits is not in keeping with the facts. Everything is much more complicated.

The quantum-mechanical atom. You will have to take our word for much that you will read here. This is so because any clear understanding of the problems that are to be discussed requires a great deal more special knowledge than the general nonspecialist probably has.

The orderly structure and elegance of Bohr's atomic theory excited the imagination, but physicists saw in it, not only its merits, but its essential shortcomings. For example, they rightfully pointed out that Bohr's theory consists half of new (quantum) ideas and half of old ideas taken from classical mechanics. One scientist wittily joked that Bohr's theory requires that you use classical laws on Mondays, Wednesdays and Fridays, and quantum-mechanical laws on Tuesdays, Thursdays and Saturdays.

When Bohr set up his scheme for the consecutive filling of the electron shells and subshells, he was guided, firstly, by the periodic system of the elements and the accumulated knowledge about their chemical properties, and secondly, by the results obtained in investigating atomic spectra. The filling sequence was worked out in accordance with an established framework: Mendeleev's table of the elements. It was not based on any fundamental physical theory.

This too was not satisfactory to scientists.

But let us hold an unbiassed attitude. More than half a century has passed since Bohr gave his explanation for the periodic changes in the properties of the elements. Scientists still use his concepts and will continue to resort to them in the future. The reason for this is that his ideas are exceptionally visualizable. They form an approximate but excellent working model of the true state of affairs.

In the middle of the twenties, the French physicist, Louis Victor Pierre Raymond de Broglie, expounded the bold idea that all material particles (including electrons) possess, not only material, but wave properties as well. It was soon demonstrated that electrons, like light waves, can pass around obstacles.

Since the electron is a wave, its motion in the atom can be described by a wave equation. Such an equation was derived in 1926 by the Austrian physicist Erwin Schrodinger. Mathematicians call it a second-order partial differential equation, whereas for physicists it is the principal equation of quantum mechanics.

The Schrodinger wave equation is of the following form:

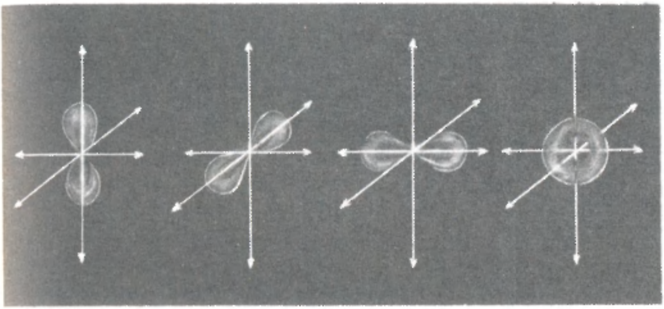
$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi=0.$$

Some of you may see in this equation the familiar notation for quantities, such as m, e, r and Z, that you have often had occasion to use in your physics lessons in school. In the equation: m is, of course, the mass and, in the given case, the mass of the electron; r is the distance of the electron from the nucleus; e is the charge of the electron; E is the total energy of the electron and is the sum of its kinetic and potential energies; and Z is the atomic number (equal to 1 for the hydrogen atom).

You are, of course, acquainted with the symbol π and, as to h, this quantity is a basic one in quantum theory and is called the quantum of action. The letters x, y and z denote the coordinates of the electron.

As you can see, there is nothing out of the ordinary so far. The only extraordinary quantity here is ψ, which is called the wave function. It is not measured in either grams or centimetres or seconds. The wave function is an abstract quantity that represents no more and no less than the probability.

It is the probability that the electron can be found at a definite point in space around the nucleus. If $\psi = 1$ the electron actually should be located at this point; but if $\psi = 0$ there is not even a ghost of a chance that



Schematic diagram of the *s*- and *p*-orbitals.

the electron is at that point.

This probability of finding an electron at a certain definite place is the central concept of quantum mechanics. The quantity ψ, or psi function (more exactly, its square ψ^2) expresses the probability that the electron is at one or another point in space.

How does a quantum-mechanical atom look?

In the first place, there are no definite electron orbits, which were so sharply defined in the Bohr model of the atom. The electron seems as if it were blurred in space in the form of a certain cloud. The density of this cloud varies, however, the thick with the thin, as they say. Greater density of the cloud corresponds to a greater probability of finding the electron at this place in space.

All of this may not yield any clear-cut mental picture, but, and you may believe us, we have tried to present the basic idea of the quantum-mechanical atom as accurately as is possible. We add that this concerns only the simplest of atoms, that of hydrogen, having a single electron. When there are two or more electrons, everything is substantially more complex because the phenomenon of electron (electron cloud) interaction has to be taken into account.

When you have read to this point, it is reasonable for you to remark that even if the atom is actually built as described by quantum mechanics, in what way can it be related to the real properties of chemical elements?

The fact is that it is related. All of the up-to-date theory of chemical bonds is based on the concept of the quantum-mechanical atom. We shall not dwell here on the how and why, and only call your attention to another matter: we can go over from the abstract quantum-mechanical model to the already familiar, so clear and visual Bohr model of the atom.

It is necessary, for this purpose, to solve the Schrödinger equation. It would certainly be no simple matter to explain how it can be solved. Consequently, we only inform you of the final result that is obtained. It is found that the wave function is associated with three different quantities that take only integral values. What is more, the sequence with which these quantities change is such that they can only be quantum numbers: the principal, orbital and magnetic numbers.

Hence, our familiar n, l and m_l are obtained on the basis of an exceptionally profound physical theory – quantum mechanics. But we know that these numbers were introduced at one time especially to explain the spectra of various atoms. Then they quite organically migrated into Bohr's atomic model. And now we find that quantum numbers are obtained as the result of the solution of the most vital equation of quantum mechanics. Such is the logic of science; even the severest sceptic can find nothing wrong within it.

But this means, in the final analysis, that the solution of the Schrödinger equation enables one to establish, on a rigorous physical basis, the sequence with which the electron shells and subshells of atoms are filled. This is the chief advantage of the quantum-mechanical atom over the Bohr atom. All the concepts that are usual for the planetary model of the atom can be revised from the point of view of quantum mechanics.

We can regard the "orbit", for instance, as a certain set of the probable positions of the electron in an atom. It corresponds to a definite wave function.

The term "orbital" or "atomic orbital" is now used in modern atomic physics and chemistry instead of "orbit". We mention, for example, the *s*-orbitals, *p*-orbitals, *d*-orbitals and *f*-orbitals. They correspond to the values $l = 1, 2, 3, \ldots$.

Thus, the Schrödinger equation is a kind of magic wand that eliminates all the shortcomings in the formal theory of the periodic system. It transforms the "formal" into the "actual".

Ideally, this is so, but in reality, it is far from being so. The reason is that the equation has an exact solution for the hydrogen atom, that simplest of atoms, and only for this atom.

It proves impossible to solve the Schrödinger equation for the helium atoms and the atoms of all subsequent elements, because this involves the forces of interaction between the electrons. To take these forces into account, to correctly assess their effect on the final result is a mathematical problem of inconceivable complexity.

This problem is beyond the capacity of human calculators. Only ultrahigh-speed electronic computers, performing hundreds of thousands of operations per second, can cope with it. And then only under the condition that numerous simplifications and approximations are resorted to in computer programming.

Artificial Elements

It would, perhaps, be better to call them synthesized elements, because they are obtained by means of nuclear reactions; they do not exist in nature. But the word “artificial”, in the sense used here, conveys two meanings. One is the antonym of natural, implying that these elements do not belong to the natural series. The other meaning is associated with the word “artifice”, with which “artificial” has a common origin and which is defined as “skill’, or “ingenuity”. It certainly required a great deal of both skill and ingenuity to produce these elements.

Chemists call synthesis the process of obtaining complex substances from simpler ones, though in many cases chemical synthesis is a more complex process. The synthesis of elements can roughly be defined as the production of an element with a higher atomic number from one with a lower atomic number. As a result of synthesis, an atomic nucleus with a certain value of Z is transformed into a nucleus with a higher Z value. The role of the second reagent is played by a bombarding particle which collides with the target nucleus and brings about its transformation.

The discovery of artificial transformation of the elements is one of the greatest achievements of twentieth-century science. It was first accomplished in 1919 by Ernest Rutherford. He irradiated gaseous nitrogen with alpha particles. The product of this nuclear reaction turned out to be oxygen. The bombarding alpha particles struck the nuclei of the nitrogen atoms and knocked protons out of them. Using the accepted form of writing chemical equations, the equation of the world’s first nuclear reaction for the artificial transformation of elements can be presented as: ${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H$.

An abbreviated form of equation is often used for nuclear reactions: ${}^{14}_{7}\mathrm{N}(\alpha, p){}^{17}_{8}\mathrm{O}$.

But no new element is formed as a result of this reaction; only an isotope, oxygen-17, of a known element.

For a long time, research on nuclear reactions by means of bombarding alpha particles was confined to two laboratories in the world: Rutherford's Cavendish Laboratory at Cambridge and the Radium Institute of Vienna.

Various chemical elements served as targets, and a great many nuclear reactions were investigated. The most important results of this research were the following: only elements with relatively low atomic numbers Z, about up to calcium with $Z = 20$, undergo transformation. The energy of the bombarding alpha particle was insufficient to penetrate the nuclei of heavier elements. This was due to the fact that the alpha particles used in these experiments were ones emitted from the atomic nuclei of natural radioactive elements, and the energy of such particles is low. Consequently, the feasibility of artificial transformation (transmutation) of the elements was limited during the twenties.

A cardinal change occurred in the situation during the thirties. It was due, mainly, to several outstanding discoveries in physics. The cyclotron, a device for accelerating charged particles (alpha particles and protons), was designed in 1931. Such acceleration imparts high energy to the particles, hundreds and thousands of times higher than that of natural alpha particles. This was followed, in 1932, by the discovery of the neutron, an elementary particle having no charge. This fact made the neutron the universal projectile for accomplishing nuclear transformations because it is not subject to repulsion by the positively charged nucleus. The phenomenon of artificial radioactivity was discovered in 1934. It consists in the forming of radioactive isotopes of various elements, which are not to be found in nature, as a result of nuclear reactions. Such isotopes have been obtained for many stable elements.

Finally, in the middle of the thirties, all the necessary prerequisites were on hand for putting on the agenda the problem of synthesizing hitherto unknown chemical elements.

Returning to page 46, we recall that the "gaps" in Mendeleev's periodic system were revealed by the research of Moseley. The missing elements had the atomic numbers 43, 61, 72, 75, 85, 87 and 91. Several of these "gaps" were soon filled.

In 1918 the element protactinium ($Z = 91$) was found; it was rightfully accommodated in the rows of radioactive transformations. The element hafnium ($Z = 72$) was found in 1923 in zirconium ores. This event turned out to be of importance in confirming Bohr's theory of the periodic system, in particular the sequence with which the electron shells and subshells are filled. This, in turn, enabled the number of lanthanides (14) to be determined at last. Finally, in 1925, rhenium ($Z = 75$) was found. It was the last of the stable chemical elements to be discovered.

Thus, by the middle of the thirties, there were still four unoccupied spaces in Mendeleev's table. They corresponded to unknown elements with the atomic numbers: 43, 61, 85 and 87. The forty-third and eighty-fifth were Mendeleev's eka-manganese and eka-iodine, respectively, whereas the eighty-seventh was eka-cesium. Way back in 1870 Mendeleev had predicted the most important properties of these elements. The sixty-first was the only one of the lanthanide series that had not been found in nature.

Scientists searched for these elements high and low, persistently and for a long time. They used many different methods and examined a great variety of natural items (to get ahead of our story, we point out that the most persevering searchers finally did manage to make out faint traces in terrestrial minerals, but this, as they say, is quite another story). From time to time, scientific journals published reports of the presupposed discoveries of these elements. Eka-manganese was found and called "nipponium" by one "discoverer" and "masurium" by another. The element with the atomic number 61 appeared on the scene as "illinium" and "florentium". Eka-iodine was also "found" several times and named "helvetium", "anglohelvetium" and "alabamium". Eka-cesium, in its turn, was named "virginium", "alcalinium" and "moldavium". History has preserved only these resounding names; all the "discoveries" turned out to be simply errors made in the experiments.

Today we know the laws that explain the absence (more exactly, the practically total absence) of all these elements in nature. We can now account for the fact that the elements with $Z = 43$ and 61, located in the middle of the periodic system, were found to be strongly radioactive, and that the elements with $Z = 85$ and 87 are not on the main lines of radioactive transformations in the natural radioactive series $4n$, $(4n + 2)$ and $(4n + 3)$.

Fifty years ago all this was still incomprehensible. In order to finally fill the annoying gaps left in Mendeleev's table, scientists had to resort to the last remaining technique: nuclear synthesis.

Technetium, promethium, astatine and francium. On June 13, 1937, two young scientists, the chemist Carlo Perrier and the Italian physicist Emilio Gino Segre wrote a short paper in Palermo on Sicily. They sent it to the London journal "Nature". The paper reported that they had succeeded in chemically separating out an extremely small amount (10^{-10} g) of an element, which, most likely, is eka-manganese, the element with the atomic number 43. The investigators proposed that it be named technetium, from a Greek word meaning "artificial". This, as a matter of fact, was the first element obtained artificially by nuclear synthesis.

In the cyclotron of the University of California at Berkeley (USA), a small plate of molybdenum was irradiated by deuterons (nuclei of the heavy isotope of hydrogen, deuterium, also used as the bombarding particles). This should have led to the following nuclear reaction: ${}_{42}\mathrm{Mo} + d \rightarrow 43 + n$, i.e. an isotope of the element with the atomic number 43 could be formed in irradiating molybdenum. As a matter of fact, the radioactivity observed among the products of radiation most likely belonged to the isotope of eka-manganese. Segrè, who was doing postgraduate work in Berkeley at that time, returned to Italy, taking the molybdenum plate with him. Together with the chemist Perrier, he performed careful radiochemical investigations of the plate. This is how technetium was discovered. In the course of time, scientists synthesized almost twenty of its isotopes. Among them is technetium-97 with a half-life of 2 600 000 years. This is certainly a long time, but substantially shorter than the age of our planet. This is why the initial quantity of the element decayed ages ago. But traces of "secondary" technetium were found. It is formed in uranium ores as the decay product of spontaneous fission of uranium (see page 116). Incidentally, the element with the atomic number 61 is formed at the same time.

Today technetium is being produced in large quantities in nuclear reactors. Among the fragments of uranium fission due to the action of slow neutrons, the technetium content is about 6%. Element 61 is obtained in the same way.

The first attempts to synthesize element 61 were made by American scientists in 1938. The physicists Marion Llewellyn Pool and Laurence Larkin Quill bombarded a neodymium target with deuterons to accomplish the reaction Nd + $d \rightarrow 61 + n$. Though the probability of initiating this reaction was quite high, Pool and Quill did not succeed in properly making out the products of nyodymium bombardment. They could only state presumably that the products might contain some isotope of the sixty-first element. No chemical research was carried out. Hence, the trustworthy date of the discovery of element 61 is 1945, when the American chemists Jacob Akiba Marinsky, Lawrence Elgin Glendenin, and Charles Dubois Coryell separated out appreciable amounts of promethium from the fragments of uranium fission in a reactor. The element was named in honour of the ancient Greek mythological Titan Prometheus.

Promethium turned out to be even shorter lived than technetium. Its most long-lived isotope has a half-life of only 30 years. Its chemical properties in no way differ from those of the rest of the lanthanide series.

Elements 85 and 87 are at the end of the periodic system, among the heavy radioactive elements. Though attempts to discover them ended in failure, there could hardly be any doubt of their radioactivity. But the radioactive families had been, by this time, well investigated, and no places had been found for the isotopes of “eka-iodine” and “eka-cesium”.

Eka-iodine became the second element, chronologically, to be discovered by means of nuclear synthesis. This was due, primarily, to the fact that only a single combination actually existed for the artificial synthesis of the eighty-fifth element: the target nucleus plus the bombarding particle. The mysterious eka-iodine was two atomic numbers away, in Mendeleev's table, from bismuth, the last stable element existing in nature. Bismuth was the only substance that could be used to make a target for synthesizing the eighty-fifth element. And the bombarding missile could only be an alpha particle.

On July 16, 1940, the American scientists Dale Raymond Corson, Kenneth Ross Mackenzie and Emilio Segrè (who had emigrated to and settled in the USA by that time) sent a long paper to the well-known physical journal *Physical Review* entitled "Artificial Radioactive Element 85". They described, in this paper, how they had succeeded in synthesizing the eighty-fifth element by means of the nuclear reaction $^{209}_{83}\mathrm{Bi}(\alpha, 2n)$. The element turned out to be short-lived, the maximum value of its half-life being 8.3 hours. For this reason they decided to call the element astatine (from the Greek word *astatos*, meaning "unstable").

By the time that Segrè and his fellow workers were ready to begin the bombardment of a bismuth target with alpha particles accelerated in a cyclotron, more than year had passed after the announcement of the discovery of eka-cesium.

The names of women scientists had appeared twice, up to this time, in the list of the discoverers of new elements. Marie Sklodowska Curie had played the key role in the discovery of polonium and radium. The discovery of rhenium is associated with the name of the German investigator Ida Eva Tacke (who later married Walter Karl Friedrich Noddack, the leader of the team).

The honour of discovering element 87 belongs to the Frenchwoman Marguerite Perey, a chemist. Of most interest is the fact that francium (as Mlle. Perey had named the element in honour of her native country) was the last element to be initially discovered in nature. Nor was any nuclear synthesis required. "Synthetic" francium was first obtained much later, in 1950, by means of a very complex nuclear reaction. Even in simplified notation this reaction, $^{238}_{92}\mathrm{U}(p, 6p21n)^{212}_{87}\mathrm{Fr}$, is quite impressive. In scientific language this reaction is said to be the spallation of uranium nuclei by protons having extremely high energy.

Mlle. Perey's paper announcing the discovery of the new element was headed "Element 87: AcK, formed from actinium". This name requires some explanation. The principal isotope of actinium, $^{227}\mathrm{Ac}$, is usually β^--radioactive. As the result of β^--decay it is transformed into the thorium isotope $^{227}_{90}\mathrm{Th}$. But, as was found, slightly more than one percent of the $^{227}\mathrm{Ac}$ nuclei are capable of another decay: with the emission of alpha particles. It is specifically in this case that an element with the atomic number 87 is formed (the atomic charge of actinium, as we know, is equal to 89).

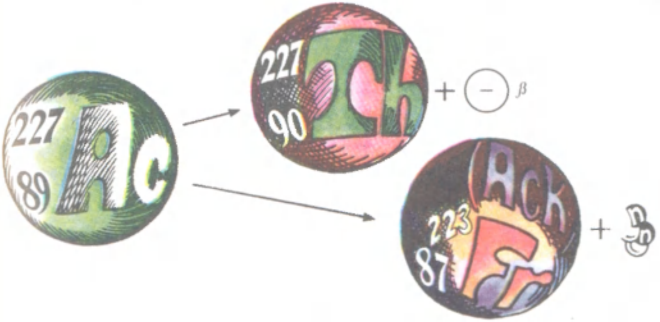


Diagram showing the formation of francium, the 87th element. Certain radioactive isotopes can decay in two ways, for instance, by means of alpha and beta decay. This phenomenon is called radioactive branching. All the natural radioactive families contain branches.

It is just this rare type of actinium nuclei transformation that Mlle. Perey had the good fortune to observe in the years when she was an assistant of the French chemist Andre Louis Debierne, who had discovered actinium.

While the longest-lived isotope of astatine has a half-life measured in hours, the record-holder for longevity among the francium isotopes is ^{223}Fr, having a half-life of 31 minutes. Consequently, the production of francium in the form of a metal, in the free state, is a practically unachievable task. Frankly speaking, this is a pity. According to predictions, francium would be liquid at ordinary temperatures, and its chemical activity would be the highest of all the metals.

The isotopes of astatine that are found in nature, like the isotope of francium, are located on the branches of the mainline radioactive transformations in the series of radio elements. Such branches are sometimes called “radioactive prongs”. The isotopes of astatine are formed with exceptionally low probability. They were therefore so difficult to find in nature in 1943.

Transuranium elements. This is the name given to artificially synthesized chemical elements located after uranium in Mendeleev’s periodic system. At the present time, 17 such elements are known. So far nobody can say how many more will be synthesized in the future. We shall return to this question later on.

In working out his periodic system of elements, Mendeleev came to the conclusion that the atomic weight of uranium had been incorrectly determined and proposed that it be doubled. Uranium thus became the last in the natural order of chemical elements, and held this end position for seventy long years.

All this time, naturally, scientists were troubled by the question: do any elements heavier than uranium

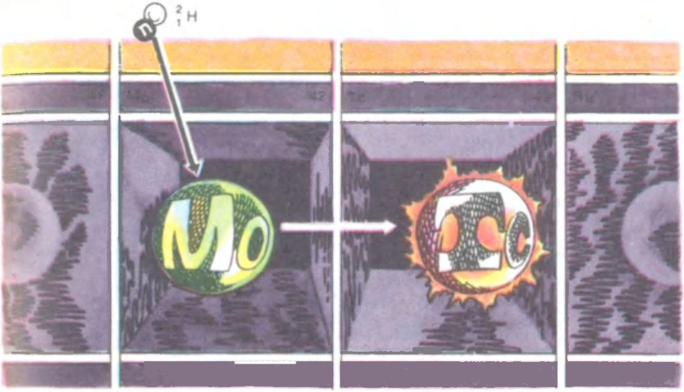


Diagram showing the synthesis of technetium, the 43rd element.

exist in nature? Did Mendeleev also try to find an answer? Yes, he did try, but his answer was an extremely careful one. He said that if any transuranium elements are ever found in terrestrial minerals, the number of such elements should be limited. But Mendeleev gave no explanations of why this is so.

A reasonable attempt to explain the absence of transuranium elements in nature was made after the discovery of radioactive phenomena. The investigators proposed that they cannot be found on the earth because their half-lives are not very long, and they decayed ages ago to lighter elements. This was supposed to have happened a very long time ago, during the earliest stages in the evolution of our planet.

But uranium, though radioactive, has such a long lifetime that it has remained to our time. Why could not nature endow at least the nearest transuranium elements with the same generous time of existence? This question remained unanswered, and no elements

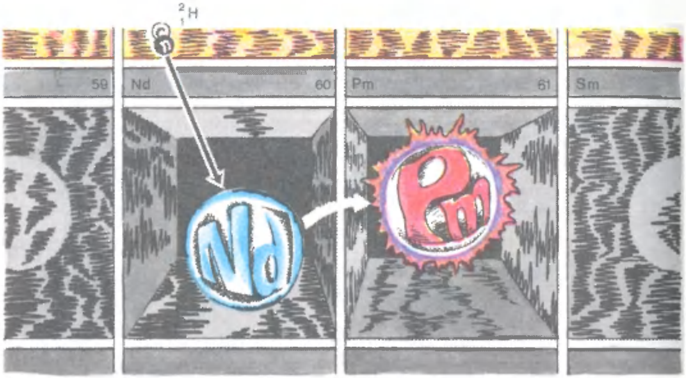


Diagram showing the synthesis of promethium, the 61st element.

heavier than uranium could be found in the earth's depths. Many reports appeared on the discovery of supposedly new elements within the system between hydrogen and uranium, but almost never did scientific journals publish anything about the discovery of transuranium elements. The only news in this field were disputes between scientists as to why the periodic system is abruptly terminated by uranium.

Only nuclear synthesis enabled many interesting matters to be established that could not even be suspected previously.

Of interest is the fact that the first research on the synthesis of new elements was aimed specifically at the artificial production of transuranium elements. Discussion concerning the first artificial transuranium element began three years before technetium made its appearance.

The stimulating factor in this new research was the discovery of the neutron. This elementary particle, deprived of charge, possessed immense penetrating

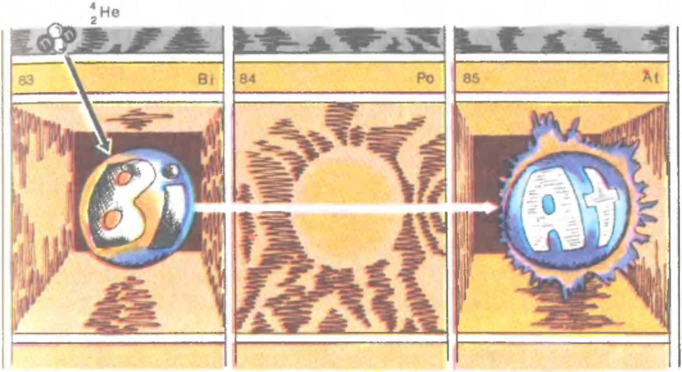


Diagram showing the synthesis of astatine, the 85th element.

capacity. It could reach the atomic nucleus without encountering any obstacles and cause the transmutation of various elements. Physicists and chemists began to bombard a great variety of substances with neutrons. A pioneer of research in this field was the eminent Italian physicist Enrico Fermi, who headed a laboratory in the University of Rome.

It was found that when uranium is bombarded by neutrons it displays some kind of activity with a short half-life. Why? The line of reasoning could be as follows: after absorbing a neutron, uranium-238 is transformed into an unknown isotope of the element uranium-239, which is β^--radioactive and should be transformed into an isotope of the element with the atomic number 93. Fermi and his co-workers reached a similar conclusion. This news was immediately seized by the newspapers and acquired nonexistent details. The reporters wrote, for instance, that Fermi had presented a test tube containing a solution of a salt of the ninety-third element to the Queen of Italy.

Actually, much effort was required to prove that the unknown activity really did pertain to the first transuranium element. Chemical operations led to the conclusion that the properties of the new element resemble those of manganese, i.e. the element belongs to the VII*b* subgroup. This was impressive because all chemists assumed, at that time (in the thirties), that if transuranium elements exist, at least the first ones would be analogues of the *d*-elements of the preceding periods. This was a mistake that undoubtedly influenced the history of the elements heavier than uranium.

In short, Fermi confidently announced in 1934 the synthesis, not only of the ninety-third element, which he named ausonium (Ao), but its right-hand neighbour in Mendeleev's table: hesperium, the element with $Z = 94$. The latter was the product of β^--decay of ausonium:

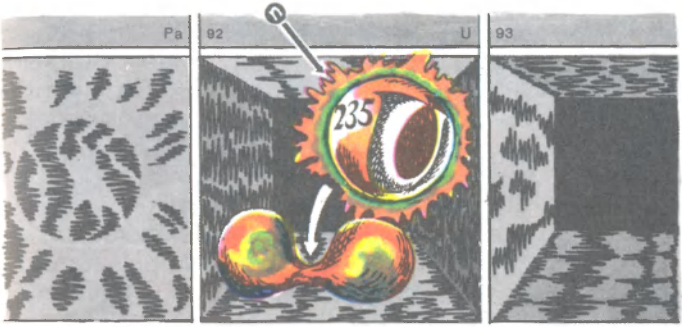
$${}^{238}_{92}\mathrm{U} + n \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Ao} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Hs}.$$

There were scientists that prolonged this series of nuclear reactions. Among them were the German scientists Otto Hahn, Lise Meitner and Fritz Strassman. By 1937 the element with the atomic number 97 was already being discussed as something that really exists:

$${}_{94}\mathrm{Hs} \xrightarrow{\beta^-} {}_{95}\text{Eka-Ir} \xrightarrow{\beta^-} {}_{96}\text{Eka-Pt} \xrightarrow{\beta^-} {}_{97}\text{Eka-Au}.$$

The immense and painstaking labour of highly skilled and eminently experienced radiochemists was required to write this short series of reactions; their names were mentioned above. But not a single of these elements was obtained in any appreciable amounts; they were not separated out in the free form. Only circumstantial evidence pointed to their syntheses.

All this gave rise to doubt that became more and



When a neutron enters a uranium-235 nucleus the latter is excited and set to oscillating strongly with a motion similar to the oscillation of a drop of water.

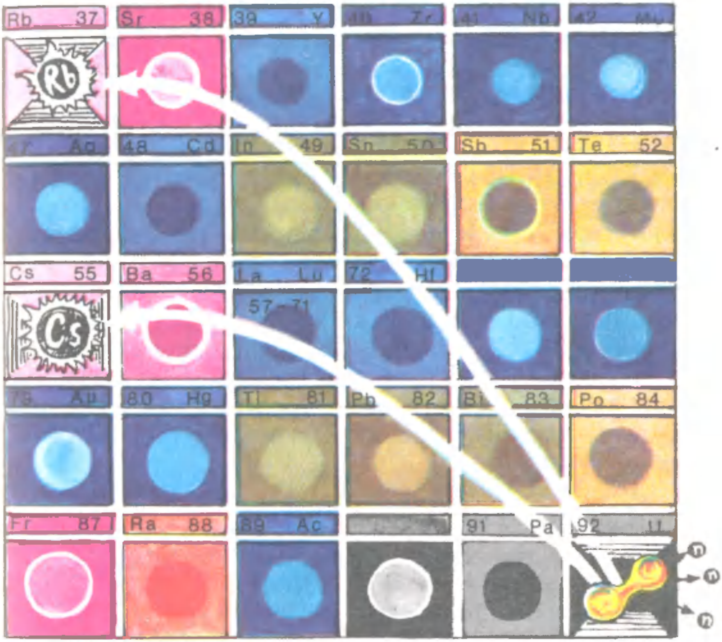
more justified. Finally, it turned out that all these ephemeral substances, considered with such enthusiasm to be transuranium elements, were in fact elements belonging to the middle of the periodic system. They were artificial radioactive isotopes of chemical elements that had been known for a long, long time.

This became clear when, on December 23, 1938, Hahn and Strassman made one of the greatest discoveries of the twentieth century: the fission of uranium bombarded by slow neutrons. These scientists indisputably established the fact that uranium bombarded by neutrons contains isotopes of barium and lanthanum with the atomic numbers 56 and 57. They could be formed only with the assumption that the neutrons seem to split the uranium nucleus into several smaller fragments.

The fission mechanism was cleared up by Meitner and the Austrian physicist Otto Robert Frisch. By this time, the liquid-drop model of the nucleus had already been proposed: the nucleus was likened to a drop of liquid. If sufficient energy is imparted to such a drop, it is set to oscillating, and may divide into smaller drops. The same could be true of an atomic nucleus brought to an excited state by a neutron and capable of fission so that it divides into smaller parts. These parts are the atomic nuclei of lighter elements. It is known today that in the fission of uranium bombarded by neutrons isotopes are formed of elements with atomic numbers in the range from 30 to 64, i.e. from zinc to gadolinium. The radioactive isotopes formed in fission are related by chains of consecutive β^--transformations that end in stable isotopes. No wonder that in such a complicated mixture anything at all could be observed and taken to be new transuranium elements.

In 1940, the Soviet physicists Georgii Nikolayevich Flerov and Konstantin Antonovich Petrzhak showed that the fission of uranium can occur spontaneously. They had thus discovered a new kind of radioactive transformation found in nature: the spontaneous fission of uranium.

Everything is relative in life, and soon it was found that it is incorrect to call the investigations of transuranium elements carried out in the thirties a complete mistake. In Fermi's experiments and in those of his German colleagues, traces of heavier-than-uranium elements had undoubtedly been produced. The point is that uranium has two principal isotopes: uranium-238 (substantially predominant) and uranium-235. It is the latter that chiefly undergoes fission when bombarded by slow neutrons, whereas the former, after absorbing a neutron, is merely transformed into the heavier isotope uranium-239. The faster the bombarding neutrons, the higher the intensity of this absorption. Hence, in the first attempts to synthesize transuranium elements, the neutron slowing-down effect made the fission process predominant in the target of natural uranium, containing ^{238}U and ^{235}U.



Excited by the impact of a neutron, the uranium-235 nucleus breaks in two. Hence, two nuclei fragments are obtained. As a rule they have different masses and charges. This phenomena, called nuclear fission, produces radioactive isotopes of elements from the middle of the periodic system. In fission, the uranium-235 nucleus emits two or three new neutrons. Each of them may cause the fission of a new uranium-235 nucleus.

But uranium-238, having absorbed a neutron, should certainly have initiated a transformation chain of transuranium elements. What was required was a reliable method of ensnaring the ninety-third element in a most complicated mixture of fission fragments. Of relatively smaller mass, these fragments should have recoiled longer distances (have a greater path length) than the quite massive atoms of the ninety-third element.

This line of reasoning was the basis for the experiments performed by the American physicist Edwin Mattison McMillan at the University of California. In the spring of 1939 he began to carefully investigate the distribution of uranium fission fragments with respect to their path lengths. He managed to separate out a small amount of fragments with negligible path lengths. It was specifically in this amount that he found traces of a radioactive substance with a half-life of 2.3 days and with high-intensity radiation. Such high activity had not been observed in other fractions of the fragments. McMillan succeeded in showing that this substance X is a decay product of the isotope uranium-239:

$$^{238}_{92}\mathrm{U} + n \rightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}X.$$

At this point the intervention of chemistry was required. That summer, a friend of McMillan's, the chemist Philip Hauge Abelson, began collaborating with him in this research. It was found that the radioactive substance with a half-life of 2.3 days can be chemically separated from uranium and thorium, and has nothing in common with rhenium. This disproved the assumption that element 93 is eka-rhenium.

In the beginning of 1940 the American journal *Physical Review* reported on the successful synthesis of neptunium (as the new element was named in honour of a planet of the solar system). This initiated the era of transuranium element synthesis, which, at the same time, has become a new era in the development of Mendeleev's theory of periodicity.

It is a matter of fact that the half-lives of even the longest-lived isotopes of transuranium elements are, as a rule, considerably shorter than the age of the earth. Hence their existence in nature at the present time is practically excluded. This fact cleared up the reason why uranium, the element with the atomic number 92, is at the end of the natural series of chemical elements.

Many more surprises were brought by research on the chemical properties of the transuranium elements, but this is to be the subject of a special discussion further on.

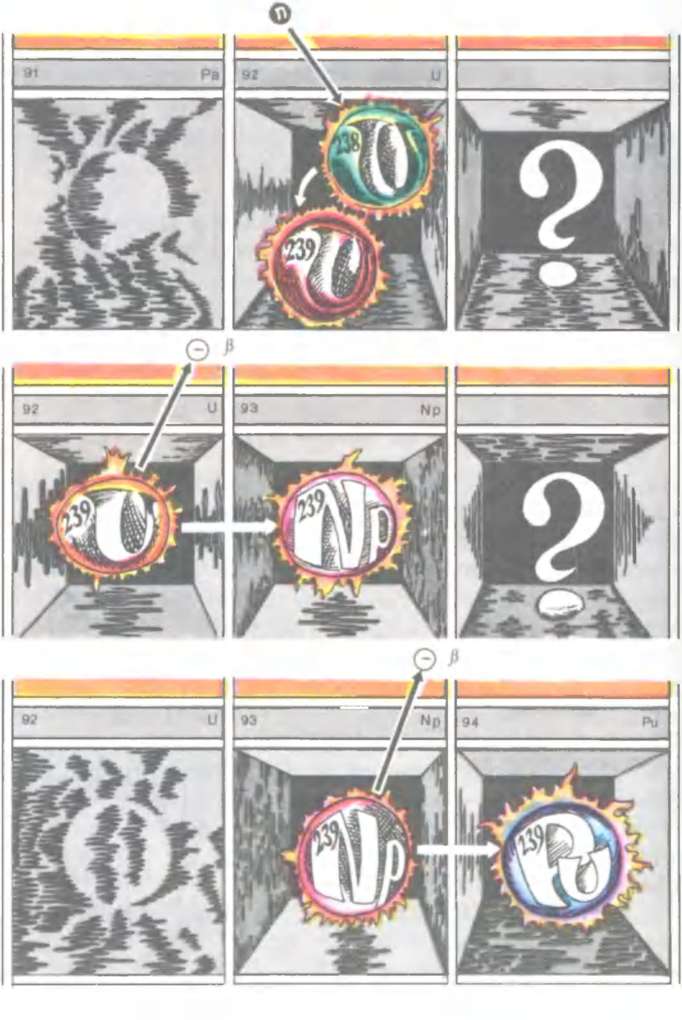
For the time being, let us return to the time, over forty years ago, marking the beginning of the synthesis of these elements.

Neptunium was followed by plutonium (also named in honour of a planet of the solar system). It was synthesized according to the nuclear reaction

$$^{238}_{92}\mathrm{U}\,(d, 2n)\,^{238}_{93}\mathrm{Nn} \xrightarrow{\beta^-} {}^{238}_{94}\mathrm{Pu}$$

during the winter of 1940-41 by the famous American chemist Glenn Theodore Seaborg and his co-workers (several more new transuranium elements were subsequently synthesized in Seaborg's laboratory). The most important isotope of plutonium turned out to be $^{239}\mathrm{Pu}$, which has a half-life of 24 360 years. In addition to the fact that it has quite a long lifetime, plutonium-239 is subject to much more intensive fission by slow neutrons than uranium-235, making it an excellent nuclear fuel. This isotope was also used in devising nuclear weapons and therefore the chemical and physical properties of plutonium have been very carefully investigated. No wonder then that element 94 is considered to be one of the most comprehensively studied among all the chemical elements.

Later, in the fifties, negligible amounts of neptunium and plutonium were found in nature. They are formed as products by the action of natural neutrons on uranium.


n
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Np
239
94
Pu
239

Three more elements heavier than uranium were synthesized in the forties. They are americium (named in honour of America), curium (named after the Curies) and berkelium (after the city of Berkeley in California, the site of the University of California). Serving as the target in the nuclear reactions for the synthesis of the elements was plutonium-239, bombarded by neutrons and alpha particles, and americium (its irradiation by alpha particles led to the synthesis of berkelium: $^{241}_{95}\mathrm{Am}\,(\alpha, 2n)\,^{243}_{97}\mathrm{Bk}$).

The fifties began with the synthesis of californium with $Z = 98$ (named after the American state). This could be accomplished when sufficient amounts of the long-lived isotope curium-242 had been accumulated and could be used to make a target. The nuclear reaction $^{242}_{96}\mathrm{Cm}\,(\alpha, n)\,^{245}_{98}\mathrm{Cf}$ gave birth to the first atoms of the ninety-eighth element.

But after successfully synthesizing californium, scientists in this field hesitated before continuing to produce element after element.

To proceed with the synthesis of the ninety-ninth and one-hundredth elements, it was necessary first to accumulate the initial raw materials: measurable quantities of berkelium and californium. Their bombardment with alpha particles presented a real basis for advancing further in the land of transuranium elements. But the half-lives of the synthesized isotopes of elements 97 and 98 were too short (hours and minutes), and this became

←

When a neutron gets into a uranium-238 nucleus it remains there. This forms a new uranium isotope: uranium-239. There is no uranium of this kind in nature. This is a short-lived atom, having beta radioactivity. Upon the loss of one beta particle, uranium-239 is transformed into the 93rd element, the transuranium element neptunium. Then, after losing another beta particle, neptunium is transformed into plutonium.

a serious obstacle in their accumulation in the required quantities.

Another method was proposed: prolonged irradiation of plutonium with an intensive source of neutrons. But results could be obtained only after many years of bombardment (previously, it had proved necessary to bombard a plutonium target in a nuclear reactor for six long years to obtain one of the berkelium isotopes in the pure form!). The synthesizing time could be reduced only by a single method: drastically raising the power of the neutron beam.

This turned out to be impossible under laboratory conditions.

At this point a thermonuclear explosion came to the aid of the investigators. On November 1, 1952, the USA exploded a thermonuclear device on the Eniwetok Atoll in the Pacific Ocean. Several hundreds of kilograms of soil were collected at the site of the explosion and specimens were carefully investigated. As a result, the investigators succeeded in finding the ninety-ninth and one-hundredth elements, which they called einsteinium (in honour of Albert Einstein) and fermium (in honour of Enrico Fermi).

How were they formed?

The neutron flux formed in the explosion had such a high density that the nuclei of uranium-238 were able to absorb large numbers of neutrons in a very short period of time:

$$^{238}_{92}\mathrm{U} + 15n \rightarrow {}^{253}_{92}\mathrm{U},$$

$$^{238}_{92}\mathrm{U} + 17n \rightarrow {}^{255}_{92}\mathrm{U}.$$

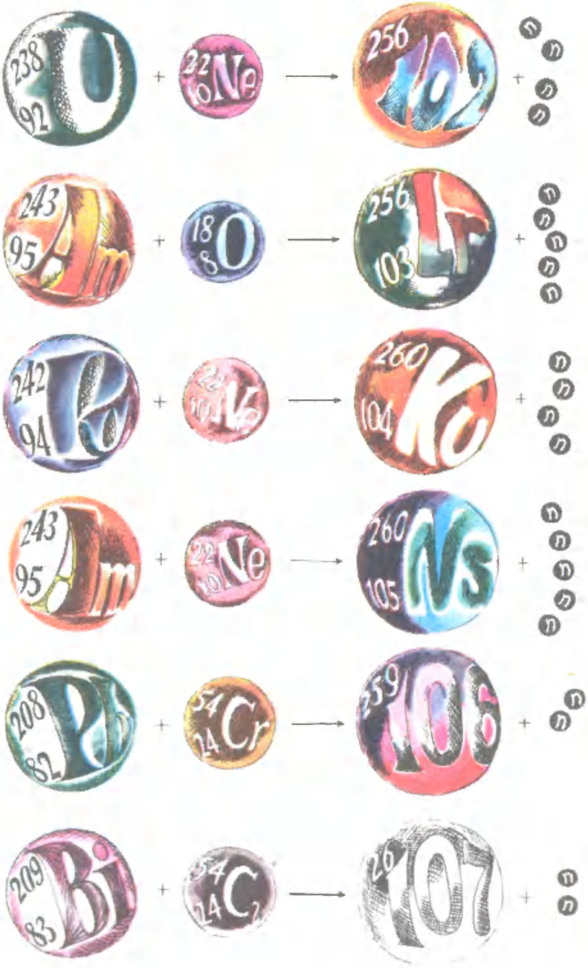
As the result of a chain of consecutive β^-–decays, these superheavy uranium isotopes were transformed into isotopes of einsteinium and fermium:

$$^{253}_{92}\mathrm{U} \xrightarrow{7\beta^-} {}^{253}_{99}\mathrm{Es} \text{ and } ^{255}_{92}\mathrm{U} \xrightarrow{8\beta^-} {}^{255}_{100}\mathrm{Fm}.$$

The element named after Mendeleev. Mendelevium is the chemical element with the atomic number 101; it was synthesized by a team of American physicists headed by G. T. Seaborg in 1955. The discoverers named the new element in recognition of the merits of the great Russian chemist who first used the periodic system to predict the properties of undiscovered elements.

In the history of transuranium element synthesis, the formation of mendelevium became a turning point; to a certain extent, its discoverers were lucky. In the first place they had succeeded in accumulating a sufficient amount of einsteinium to prepare a target (consisting of about a thousand million atoms). By bombarding it with alpha particles, they could expect that the synthesis of nuclei of the 101th element would occur according to the reaction: $^{253}_{99}\mathrm{Es}\,(\alpha, n)\,^{256}_{101}\mathrm{Md}$. In the second place, the half-life of the obtained isotope $^{256}\mathrm{Md}$ turned out to be substantially longer than the theoretical physicists had supposed. Even though only an extremely small number of mendelevium atoms were produced in the synthesis, it proved possible to investigate their chemical properties by the same methods that were used for the preceding transuranium elements. It was during the synthesis and investigation of mendelevium that a new branch of chemistry, the chemistry of single atoms, was founded.

The one hundred and first element deserves to have its synthesis described in more detail. An invisible coating – a thousand million atoms of einsteinium – was applied to the surface of an ultrathin sheet of gold foil. Compared to the price of the einsteinium, that of gold



Diagrams of the synthesis of heavy transuranium elements with $Z \geqslant 101$

was truly absurd. Impetuous alpha particles pierced the foil from the back and collided with the einsteinium atoms. Only in rare cases did these collisions initiate a nuclear reaction in which nuclei of mendelevium were synthesized. Upon recoil these nuclei left the surface of the foil and settled on another sheet of gold located adjacently. Owing to this ingenious technique, the atoms of element 101 were separated out of the complex mixture of einsteinium and its radioactive decay products. The second sheet was dissolved in acid and the solution was passed through a chromatographic column. The vital moment was to detect exactly when the portion of the solution containing the mendelevium leaves the solution. No less important was the recording of the events of spontaneous fission by means of which each nucleus decays.

In the first experiment only five such events (!) could be registered. These were five cases of the spontaneous fission of mendelevium. Besides, the chemical nature of the new element was assessed.

Why did this synthesis mark a turning point in the transuranian epic? All the previously used methods of synthesis (bombardment of a target with light nuclear missiles, such as protons, deuterons, neutrons and alpha particles) had exhausted all their potentialities. The one hundredth and first element was so short-lived that it was obviously impossible to accumulate it in amounts sufficient for preparing a target. There was no doubt that the subsequent, so far undiscovered, transuranium elements could exist for only seconds or fractions of a second. Therefore, the formerly used physicochemical techniques became unsuitable for their investigation.

This posed a problem that could be likened to an equation with many unknowns. Is there a way to synthesize transuranium elements with $Z > 101$? If so, what are the techniques that can actually be applied for studying the new elements, which will, without doubt, consist of single and, moreover, extremely short-lived atoms?

Phantom elements. This is probably the best name for them. Even though the synthesis of each such element is a genuine scientific and engineering feat and their investigation provides new information that extends our concept of the periodic system.

Figuratively speaking, the symbols of these elements, as they stand in the periodic system, are not backed by any material security. All of their synthesized isotopes live so briefly that the investigators have to display maximum ingenuity to assess the most vital properties, in the short time at their disposal, of the elements with the atomic numbers from 102 through 107. Each time that it is necessary to repeat a chemical investigation or to undertake a new one, it is necessary to provide the initial material by repeating the nuclear synthesis process.

In the table of the periodic system on page 72, the symbol of element 102, nobelium, is in parentheses: (No). This has its reason. As witnessed by the history of chemistry, the synthesis of nobelium was reported in 1957 by an international team of physicists and chemists working at the Nobel Institute in Stockholm. They applied a method that was new in principle to synthesize transuranium elements, using accelerated heavy ions (as the ions of elements with $Z > 2$ are called in nuclear physics) as the bombarding particles. Hence, targets are no longer a problem; they can be made of quite available elements. In the given case, a target of curium was bombarded by multiply charged ^{13}C ions (i.e. ones deprived of several electrons). The investigators came to the conclusion that an isotope of element 102 is formed in this nuclear reaction, and they named it nobelium.

This conclusion turned out to be somewhat hasty. Attempts made by scientists of other countries to duplicate the experiment failed to confirm the conclusion. Somebody even coined a bitter pun: only the "No" remains from nobelium. A reliable synthesis of this element was performed in 1962-67 by a team of Soviet scientists headed by Flerov in the Nuclear Reactions Laboratory of the Joint Institute for Nuclear Research at Dubna. Beginning with this time, the work of Soviet investigators began to play a leading role in the field of transuranium element synthesis.

But the symbol No still occupies its space in the periodic system. Perhaps, only because it has become customary, though the unfairness is quite evident. That is why we have put the symbol in parentheses.

Nor was the history of the one hundred and third element, lawrencium, simple and eventless. Its symbol is also given in parentheses. In 1961 a group of American scientists reported that in the bombardment of a californium target with boron ions the element with $Z = 103$ is formed, and they named it lawrencium in honour of Ernest Orlando Lawrence, the inventor of the cyclotron. This result was not found to be indisputable. It was only in 1965 that Soviet physicists synthesized an isotope of the 103rd element according to the nuclear reaction: $^{243}\mathrm{Am}(^{18}\mathrm{O},\ 5n)^{256}103$, and this data turned out to be of the highest reliability.

The year before, the Dubna investigators began their attack on the stronghold of the one hundred and fourth element. For forty hours a flux of accelerated neon nuclei bombarded a plutonium target. Only in rare cases did the fusion of neon and plutonium nuclei occur. But when they did, they formed a nuclei of the 104th element, something that nobody had ever captured so far. This was no simple matter. Physicists correctly surmised that the principal kind of radioactive transformation of this element is spontaneous fission.

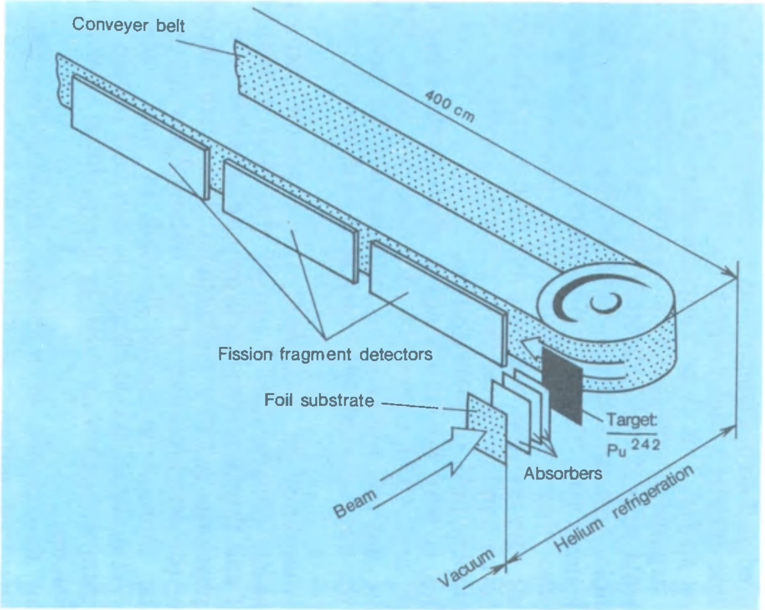
What could be done to capture the fission fragments? They used a special kind of glass on which the fission fragments made almost imperceptible traces (pits). Special belts conveyed the synthesized nuclei of the new element to the glass plates. The half-life was calculated from the number of pits and their location on the plates. It was found to be very short: 0.3 s (after several years it turned out to be even shorter). But it was also necessary to determine the chemical features of the new element. How was this to be done? The investigators, as we can see, had only a small number of atoms, existing for only fractions of a second, at their disposal.

The Soviet investigators devised a simple and novel method.

The synthesized nuclei of the one hundred and fourth element have a large momentum and they are emitted from the target. Then they are caught up by a stream of nitrogen, which slows them down. After this they are involved in a chemical reaction, being subject to the action of chlorine. This is the critical moment, when the nature of the new element is to be determined. Everything depends upon how its chloride behaves. But the properties of the chloride depend upon whether the 104th element is an analogue of hafnium or whether it continues the actinide series. The chloride is passed through a special filter. If it is $(104)Cl_4$ it passes readily through the filter; if it is $(104)Cl_3$ it sticks in the filter. Actually, the former occurred, showing that kurchatovium is a chemical analogue of hafnium and belongs to the IV*b* subgroup.

The element was named in honour of the distinguished Soviet physicist Igor Vasilyevich Kurchatov.

The seventies began with the synthesis of the element with $Z = 105$. It was obtained in Dubna by the nuclear reaction $^{243}Am(^{22}Ne, 4n)^{261}Ns$. The new element was named nilsborium after the great Danish physicist Nils



Schematic diagram of the device employed in the experiments for the synthesis of kurchatovium.

Bohr. Its chemical properties are similar to those of tantalum, i.e. an element of the V*b* subgroup. The half-life of Ns is only 2 seconds.

A chronological table lists the following: the one hundred and sixth element was synthesized in 1974, and the one hundred and seventh in 1976. They have no names so far. This is no simple matter: the discussion and arguments on priority in the synthesis of the elements with $Z = 102$ through 105 were too keen. For example, American scientists still attribute the synthesis of elements 103, 104 and 105 to their own account, and propose their name – hahnium (in honour of Otto Hahn) – for the one hundred and fifth element. Errors and even conflicting results are highly feasible in such a complex field of investigation.

This is why Soviet scientists, after synthesizing the 106th and 107th elements, declined to name them.

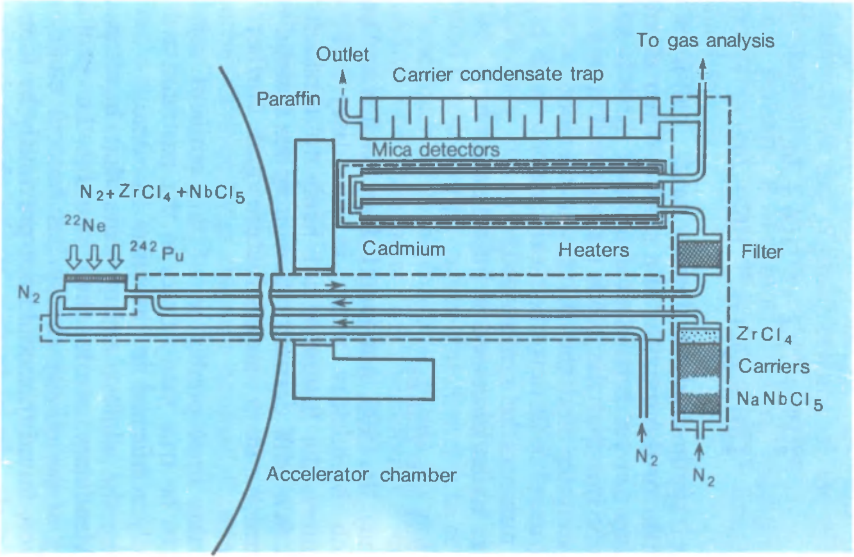
The method applied for synthesizing the last two known transuranium elements is a fundamentally new one.

In working on the other transuranium elements, physicists always used a target that was radioactive itself and therefore produced definite interference or, as the physicists call it, a background. This often hindered a correct interpretation of the obtained results.

The Dubna physicists decided to make use of a target made of stable elements: lead and bismuth. All the elements following them in the periodic system are radioactive.

But this choice of a target required the use, as bombarding particles, of the multiply charged ions of elements in the middle of Mendeleev's table.

If the aim was to synthesize the 106th and 107th elements, simple calculations indicate that it is necessary to accelerate the ions of chromium, the element with atomic number 24.



Schematic diagram of the apparatus enabling the chemical nature of individual atoms to be investigated. It was used to show that kurchatovium is an analogue of hafnium, and that nilsborium is an analogue of tantalum.

Such "luxury" is well within the capacity of up-to-date accelerating techniques.

The accelerated ions initiated the following nuclear reactions:

$$^{207}_{82}\mathrm{Pb} + ^{54}_{24}\mathrm{G} \rightarrow ^{259}106 + 2n,$$

$$^{209}_{83}\mathrm{Bi} + ^{54}_{24}\mathrm{Cr} \rightarrow ^{261}107 + 2n.$$

These synthesized isotopes have half-lives of hundredths or thousandths of a second. Their chemical nature has not yet been cleared up. But there is hardly any doubt but that the 106th element will turn out to be eka-tungsten and the 107th, eka-rhenium.

What next? Will new chemical elements with higher atomic numbers be synthesized?

This is to be discussed a little further on.

Foretelling the Future

On July 10, 1905, not long before his death, Dmitri Ivanovich Mendeleev wrote in his diary: "To all appearances, the future is not likely to threaten the periodic law with destruction; it promises instead only the erection of a superstructure and further development...".

And this final prediction of this eminent scientist proved to be true many times in the past and will be repeatedly confirmed in the years to come.

During the almost eighty years that have passed since Mendeleev wrote these words, the profound meaning of periodicity theory has become clear; new facets were found that could not previously be foreseen. Not only do the properties of the chemical elements vary periodically with an increase in their atomic numbers in Mendeleev's table, similar electron configurations of the outer shells of the atoms also vary periodically and are repeated in accordance with the increase in the nuclear charge. In this lies the explanation of the physical essence of the periodicity phenomenon.

This perhaps is the most striking example of the "superstructure" and "development" foreseen by Mendeleev.

Finally, all the chemical elements were discovered that exist in nature but were not yet known at the turn of the century. About twenty elements were synthesized that are not contained in terrestrial minerals. These elements filled the empty spaces in the periodic system and appreciably "built up its superstructure", considerably expanding its upper limits.

The application of quantum-mechanical methods enabled theoretical physicists and chemists to reveal the intimate mechanism of chemical bonds, to predict the feasibility of synthesis of previously unknown compounds, to explain the special features of chemical reactions.

All the aforesaid is convincing evidence of the development of periodicity theory. Today it can be likened to a mighty tree in whose crown there are no branches or even twigs that are doomed to wither and dry up. On the contrary, new green shoots sprout from time to time.

Our account of elementary order and the periodic law nears its end. We shall conclude, therefore, by telling about certain of its most vital problems, which are still far from their final solution. Incidentally, these are precisely the "superstructures", or, more exactly, "architectural solutions" that will enable the phenomenon of periodicity to be looked at in a new light.

The periodic law of atomic nuclei. The discovery of the neutron in 1932 led to the founding of modern experimental nuclear physics. A no less vital consequence was the development of the proton-neutron concept of atomic nuclear structure. Previously, for almost twenty years it was assumed that the nucleus consists of protons and electrons. This assumption of nuclear structure encountered more and more contradictions and had become an obstacle in the further development of science. Hence the idea that the nucleus consists of protons and neutrons was of no less importance than Rutherford's concept of the nuclear model of the atom.

This new point of view on nuclear structure is associated with the names of the Soviet scientist Dmitri Dmitrievich Ivanenko and the German physicist Werner Karl Heisenberg.

For it to become viable, the proton-neutron scheme of nuclear structure had to be invested with a definite, theoretically based model. One such model was the shell model of the nucleus. In accordance with this concept, quite definite proton and neutron shells of finite content exist in nuclei, similar to the electron shells in atoms.

As is known, the sequence in the formation of electron configurations of atoms complies with clear-cut laws and rules. Similar laws are the basis for the filling of the proton and neutron shells (called nucleon shells from the term nucleon, which is the collective name for nuclear protons and neutrons). This sequence can also be established on the basis of quantum-mechanical methods. It was found that nuclei have *s*-, *p*-, *d*-, *f*- and *g*-subshells, etc., and that each of them accommodates the same number of nucleons as the corresponding electron subshell. But the sequence in filling the nuclear subshells turned out to be different, more queer, than that of the electron subshells in atoms.

According to the shell model, of highest stability are the proton and neutron shells that contain 2, 8, 20, 50 and 82 protons or neutrons and 126 neutrons. Atomic nuclei in which these shells are filled are said to be magic nuclei. The “magic” in this case merely indicates that the corresponding nuclei possess certain special properties. For instance, isotopes with a magic number of protons or neutrons are much more abundant in nature. Elements having “magic” values of Z have many stable isotopes (tin with $Z = 50$, for example, is represented by ten natural isotopes). Finally, magic nuclei are extremely strongly bonded (having high binding energy); they are the most “inert” with respect to neutron capture (having lower cross sections with respect to neutron absorption) in nuclear reactions. All four families (series) of radioactive transformations end in stable isotopes having a magic number of protons ($^{206}_{82}\mathrm{Pb}$, $^{207}_{82}\mathrm{Pb}$, and $^{208}_{82}\mathrm{Pb}$ with $Z = 82$) or neutrons ($^{209}_{83}\mathrm{Bi}$ with $N = 126$).

After investigating various properties of atomic nuclei (abundance, mass defect and bonding energy values, and radioactive characteristics), physicists and chemists came to the conclusion that a definite periodicity is evident in the variation of these properties. It is associated with special features of nuclear structure. Here magic nuclei play a singular role.

Can we construct a periodic system of atomic nuclei? Such attempts have been frequently made. The tendency, as a rule, is to construct such a system by analogy with the periodic system of the elements. The principle of having the magic nuclei serve as the boundaries of the periods is the basis for most such systems. This is exactly the same as the inert gases with the atomic numbers 2, 10, 18, 36, 54 and 86 that serve as the boundaries of the periods in the system of elements. In many respects, however, this analogy is of an approximate nature. In the systematization of nuclei the boundaries of the periods coincide with the shell boundaries. In addition to the magic numbers of protons and neutrons, so-called submagic numbers have been found. These numbers (for instance, 14 and 28) are of vital importance in manifesting nuclear periodicity. Finally, and this is of an essential nature, there is a difference in principle between the forces acting in atoms (Coulomb forces) and those acting in nuclei (so-called nuclear forces).

In no case can it be said that a periodic system of atomic nuclei (isotopes) has already been worked out, one that is as significant as the periodic system of the elements. Incidentally, this is also true for the following reason: known so far are only 1/4 of all the atomic nuclei that are capable, in principle, of existing (i.e. those that have a definite, though extremely short, lifetime).

We know how many stable isotopes exist in nature: 280. Some of them can only conditionally be called stable. Actually, they are radioactive to a slight degree (there are about 20 such isotopes, and most of them have immense half-lives). It is undoubtedly true, however, that no new stable isotopes will ever be found in nature.

We know almost exactly how many isotopes there are in the natural radioactive series: 17 in the uranium-238 series, 14 in the uranium-235 series and 11 in the thorium-232 series. (Incidentally, it is not yet quite clear why these three chains of radioactive transformations have different "lengths".) This adds up to 45 isotopes. It may prove possible to find certain specific isotopes that are the products of "branching", or branched disintegration, in radioactive transformations (like the isotopes of astatine and francium). But they practically do not change the total number of isotopes that exist in nature.

Certain radioactive isotopes are continually being formed in natural nuclear reactions: for example, carbon-14 and tritium, the extraheavy hydrogen isotope having the mass number 3.

In the almost fifty years that have passed since the discovery of artificial radioactivity, various nuclear reactions have been used in reactors and accelerators to produce artificially about 1 600 isotopes of all the chemical elements without any exceptions. For some of the elements over 20 different varieties of artificial atoms have been prepared. So far we do not know exactly how many more isotopes of this kind we shall succeed in producing. But theoretical considerations put the number of nuclei that are capable of existing in principle at 6 000.

Much still remains to be cleared up in the world of isotopes.

Why, for example, are a fourth of all the stable elements represented in nature by only a single kind of atoms, by only a single isotope? Why is it that elements with an odd atomic number cannot have more than two isotopes? Is there any law governing the variation in the half-lives of radioactive isotopes of the same element (these half-lives may differ by many orders of magnitude)? Up-to-date versions of the periodic system of isotopes have no answers to these questions. Nor do we know whether there is any regular relationship between electron and nuclear periodicity. In other words: can the sequence of filling the nucleon shells in any way affect the filling of the electron shells?

These are all problems that await their solution in the future.

For the time being we shall return to the periodic system of the chemical elements. We shall tell about its profound mystery, one that baffles the scientists of our time.

What is the limit to the number of elements? A book, called “The Periodic System of Chemical Elements. History and Theory”, was published in Germany in 1930. It has long been out of print. This was the first monograph that discussed the structure of the atom and the theoretical basis of the periodic system in great detail. The authors, Eugene Rabinowitch and Erich Thilo, laid special emphasis on the problem of why the natural series of elements is “broken off” at uranium.

They analyzed two possible causes. The first associates the “exhaustion” of the periodic system after uranium with the instability of nuclei having charges over 92. The second reason states that the instability of transuranium elements depends upon the interaction of their electron shells with their nuclei, thereby drastically reducing the stability of the nuclei.

The second cause seemed to be the less probable one. Of interest is the fact that back in the middle of the twenties scientists performed calculations indicating that the “limiting” atom should have a charge equal to 137. For an atom with this value of Z an electron from the K-shell, nearest to the nucleus, should be instantaneously captured by the nucleus, thereby reducing its charge by one unit. True, no attention was given here to the fact that all the unknown elements, up to the 137th, could not but be strongly radioactive. Similar calculations were repeated later, but, as the mathematicians say, the initial conditions were changed. And, naturally, different results were obtained. For instance, in one such paper, the critical value of Z was assessed as 170.

We shall only bear this cause in mind. It is most likely that the location of the upper boundary of the periodic system of elements is associated with the instability of atomic nuclei with high Z values.

In short, the question of the upper limit of the system attracted no especial interest in the thirties. The very first experiments in the synthesis of transuranium elements (see pages 118-119) showed that the half-lives of these elements are quite short. This is the reason why these elements are not found in nature. But why this drastic drop in the longevity of the elements following uranium? Even today there is no unambiguous answer to this question.

The successful synthesis of transuranium elements after 1940 and the investigation of the radioactive characteristics of their isotopes led to a definite conclusion: with an increase in Z the lifetimes of even the most long-lived kinds of atoms are appreciably curtailed. The greater the value of Z, the more pronounced this reduction becomes. The main kind of radioactive transformation in the region of transuranium elements is spontaneous fission.

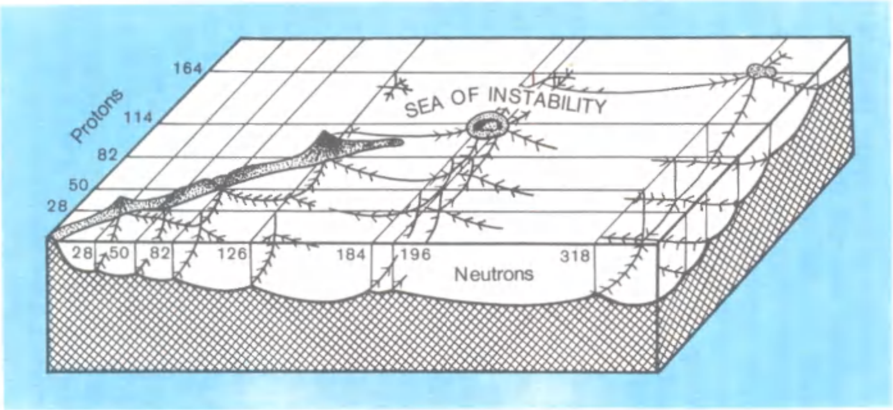
To substantiate the aforesaid, we give the half-lives of the most long-lived transuranium isotopes that decay by spontaneous fission, from neptunium to mendelevium:

$^{237}_{93}$Np	$^{244}_{94}$Pu	$^{243}_{95}$Am	$^{247}_{96}$Cm	$^{247}_{97}$Bk
2.2×10^{6} yrs	7.6×10^{7} yrs	7 370 yrs	1.64×10^{7} yrs	1 380 yrs

$^{251}_{98}$Cf	$^{254}_{99}$Es	$^{257}_{100}$Fm	$^{258}_{101}$Md
800 yrs	276 days	94 days	56 days

The half-life of the 102nd element (the most long-lived isotope being $^{259}102$) is 1.5 hours. For all the subsequent elements, the half-life drops drastically from minutes to thousandths of a second.

For this reason theoretical physicists came to the following pessimistic conclusion: the limiting value of



This allegorical representation of the “islands of stability” in the “sea of instability” was proposed by the American chemist Glenn Theodore Seaborg.

Z, at which newly synthesized nuclei will actually be subject to spontaneous fission at the very instant they are formed, lies not far away, somewhere in the region of atomic numbers from 108 to 110.

For a certain length of time, a definite clarity seemed to have been reached in the question of the upper limit of the periodic system. It was to be regretted, of course, that Nature had imposed a restriction so early in the game on the possibility of artificially synthesizing new elements.

But by the middle of the sixties, theoretical nuclear physics decided that the "last word" had been proclaimed too soon. Formulated at this time was a bold hypothesis which is called the relative stability islands hypothesis in the literature.

This hypothesis consists in the following: in the region of certain high values of Z and N (where N is the number of neutrons), the corresponding nuclei can have very large half-life values with respect to spontaneous fission. Here spontaneous fission seems to lose its capacity to "shatter" heavy nuclei.

What specific values of Z and N are implied? They are: 114, 126, 164 and even 184 for Z, and 184, 196 and 318 for N. To calculate these values, scientists made use of the shell model of the nucleus, the concept of magic numbers and the extension of these conceptions to unknown regions of the periodic system. The lifetime of nuclei that belong to these relative stability islands may exceed, according to the calculations, 10^{15} years.

Such hypothetic elements of the islands have been named superelements. Of course, spontaneous fission is not the only kind of radioactive transformation that they may be subject to. They may also undergo alpha and beta decays, and in these cases their half-lives should be substantially shorter (again according to the theoretical considerations). Therefore, the total lifetime of the superelements is reduced by many orders of magnitude. It may be measured in minutes, hours, days, years, centuries and maybe millennia. In certain cases, however, the lifetime may be considerably longer.

The proposal of the relative stability islands hypothesis immediately aroused a rising tide of optimism. It introduced an element of realism into the attempts of nuclear synthesis of the superelements. It even justified a search for them in nature. The problem of the upper limit of the periodic system acquired new significance.

During the two decades since this hypothesis was advanced, physicists and chemists have tried several times to synthesize certain "island" elements. Various, sometimes quite unexpected versions of nuclear reactions were proposed. There were times when the results of the experiments inspired hope.

But nothing more definite was accomplished.

Time and again, in these same twenty years, tentative information has been published in the literature on the discovery of unidentified activity with a very long half-life in natural specimens. There were conjectures, of course, that the bearer of the activity is one of the superelements. But this information remained only tentative, not being confirmed by subsequent investigations. These natural specimens were, in fact, quite exotic, including cosmic rays, meteorites, mineral concretions from the bottom of the Pacific Ocean and, finally, even lunar soil.

In other words, the hypothesis of relative stability islands, so vital for the further development of periodicity theory, still has no definite confirmation.

Does this mean that it is simply another fallacy; that its fate is to supplement the store of pretty scientific legends?

Hardly, as far as we are concerned, though the former enthusiasm of scientists in this field has noticeably waned.

A more just attitude, in our opinion, is to leave the question open. Attention should be paid to one extremely important circumstance: though this may sound paradoxical, the relative stability islands hypothesis enabled scientists to formulate a quite definite conception of the special features in the chemical properties of the hypothetical elements in the seventh, eighth and even ninth periods.

Before giving an account of how this was done, we shall make one important digression.

Periodicity becomes blurred. Once the well-known German inorganic chemist, Wilhelm Karl Klemm, called the periodic system of the elements somewhat differently: he said it is a system of periods. As a matter of fact, it is a system of periods of definite capacity that are repeated pairwise. An exception is the "lone" first period. It turns out that the third period is similar in structure to the second, and the fifth to the fourth. Next, we ought to say: the seventh to the sixth; but let us hesitate to utter these ordinal numbers.

In other words, each adjacent pair of periods is in itself a microsystem of periods.

Thus, the second and third periods contain *s*- and *p*-elements. In the fourth and fifth periods the *s*- and *p*-elements are separated by inserts of ten *d*-elements. The boundaries between the various shells and subshells are very clear-cut. These shells and subshells are built up in atoms beginning with precisely the nuclear charges postulated by atomic structure theory and periodicity theory. As a rule, the subshells are filled monotonically and systematically by electrons.

It can be said, therefore, that the structure of the periodic system from the first through the fifth periods is of pleasant harmony and clearly displays the periodic nature of the changes in the properties of the chemical elements depending on the Z value.

But this harmony is violated in the sixth period. True, this violation is very slight. Reread the pages in this book devoted to the rare-earth elements. Let us clear up the filling of the 4*f*-subshell with its corresponding fourteen electrons.

On the basis of the rule that *p*-electrons appear after the *s*-electrons in the second and third periods, whereas *d*-electrons appear after the *s*-electrons in the fourth and fifth periods, it is only logical to expect a 4*f*-electron to appear in the lanthanum atom ($Z = 57$). But, nothing of the sort occurs; the next ("lanthanum") electron turns out to be a 5*d*-one. Regular filling of the 4*f*-subshell begins with the following element, cerium, and is interrupted once: in the gadolinium atom ($Z = 64$), a 5*d*-electron pops up again. It follows that the boundary between the 4*f*- and 5*d*-subshells seems to be blurred. How is this circumstance manifested externally? Very simply: in the existence of fifteen rare-earth elements (from lanthanum through lutetium), with very similar properties. At the same time, the building up of the 4*f*-subshell actually takes place over a range of thirteen elements (from lanthanum through ytterbium, with gadolinium being a "dropout"). This is why lanthanum and the lanthanide series are accommodated in one space of the table. The lanthanide series is arranged in separate spaces below the main part of the periodic table. Arranged below them is another series of fourteen 5*f*-elements, called the actinide series (we have already mentioned them). In this manner, the seventh period is dealt with as one that seems to be similar to the sixth. But a comprehensive chemical investigation of the synthesized transuranium elements indicates that such a similarity of the two rows of *f*-elements is highly conditional.

The valency potentialities of the actinide series are incomparably more extensive. Predominant for the lanthanide series is the oxidation level 3+, though certain of these elements display anomalous valencies. For example, we know of tetravalent cerium, praseodymium and terbium; and bivalent samarium, europium and ytterbium. These, in essence, are the only exceptions. But the elements of the first half of the actinide series can be bi-, tri-, tetra-, penta-, hexa- and even septavalent (neptunium, plutonium and americium). The heavy actinide elements bring their surprises. Exceptionally stable in these elements is the oxidation level 2+ and, for mendelevium, even 1+. In short, each element of the actinide series is more individual in its chemical behaviour than the elements of the lanthanide series. Nevertheless, the elements of the actinide series still deserve the name of chemical counterparts (true, it is only fair to point out that when their oxidation level is 3+ the elements of the actinide series have much in common between themselves and with the corresponding elements of the lanthanide series).

But let us continue along the seventh period. The actinide series ends with the 103rd element. The subsequent elements, from kurchatovium through the one hundred and seventh element, should be transition 6*d*-elements, chemical analogues, respectively, of hafnium, tantalum, tungsten and rhenium. On the other hand, however, the analogue of hafnium was supposed to be thorium; that of tantalum, protactinium; and that of tungsten, uranium. In certain up-to-date versions of the periodic system, the symbols Th, Pa and U are put in parentheses in the seventh period under the symbols Hf, Ta and W. This poses the reasonable question: which element is to be taken as the direct analogue of hafnium, thorium or kurchatovium? Or which is the analogue of tantalum, protactinium or nilsborium? It is no simple matter to answer these questions.

Such an abundance of chemical effects displayed by a large set of elements of the seventh period makes sure that the question of their adequate arrangement in the periodic system is by no means symply a rhetorical one. The separate arrangement of the actinides under the main part of the table, similar to the row of lanthanides, is becoming simply a tribute to tradition. Other versions of distribution of the transactinium elements in Mendeleev's table were proposed, of course. They were all either far-fetched or too complicated. This is why they found no followers.

What is the cause of the extensive range of chemical behaviour of these elements? It is due, firstly, to the fact that the boundary between the 5*f*- and 6*d*-subshells is extremely vague. In the elements from thorium through americium the energies of these subshells are so close to one another that there is, in fact, no difference between the 5*f*- and 6*d*-electrons. Moreover, new effects begin to be manifested in the atoms of the heavy actinides with high Z values. Crudely, it could be said that these effects seem to promote the instability of the outer electron shells.

The phenomenon consisting in the fact that clear-cut, sharp boundaries between adjacent electron subshells in atoms are either violated or entirely absent is called "blurred" periodicity. Externally, it is manifested in the drastic unusualness of properties of the corresponding elements and in the specific manner in which these properties vary.

Why have we dealt in such detail with this phenomenon? This turns out to be a curious matter: the greater the number of chemical elements for which we analyze the phenomenon of periodicity, the more complex we find it to be. Certain complications are observed even in the sixth period, as we saw above. But in the seventh period, these "complications" become the rule rather than exceptions.

What, then, would be the case if 170 elements or more were known, instead of 107, and we had some idea about their most important properties?

What computers tell us about chemistry that is still unknown. A computer is the general name given to various calculating devices and mechanisms, including, of course, the high-speed electronic computers. Up-to-date science and engineering could not take even a step forward without the aid of computers. For example, computers enable fine details in the course of complex chemical processes to be calculated beforehand, and optimal techniques to be specified for the synthesis of a great variety of materials, unknown in nature and having preselected properties.

The application of electronic computers in problems concerning the structure of atoms enables their electronic configurations to be determined on the basis of quantum-mechanical methods. This is a labour-consuming task, even for a computer. For this reason such calculations were not very popular among physicists until a certain time ago. The distribution of the electrons among the shells and subshells was determined by other techniques, and the results obtained were in good agreement with the properties of the chemical elements.

The advent of the relative stability islands hypothesis, as we mentioned above, gave rise to attempts to synthesize certain "superelements". There was no doubt among the scientists that if the synthesis proved successful, they would have at their disposal only a few single atoms of the new elements. In order to work out a technique for rapidly determining their properties, it was necessary to presuppose the nature of these properties. The most "popular" aim was the synthesis of the 114th element. Almost nobody doubted that its properties would make it an analogue of lead. But there could be no such certainty with respect to another "island" element having the atomic number 126. The extremely peculiar behaviour of the elements at the beginning of the seventh period seemed to warn the scientists of the even greater surprises that could await them in the eighth period.

Soon reputable physical and chemical journals began to publish papers dealing with the results of computer calculations of electron configurations for atoms with especially high Z values. The most important properties of these elements were also calculated (!!!) by computers. This gave rise to a new trend in science, which one physicist jokingly called "computer chemistry".

What conjectures had scientists previously arrived at with respect to the eighth period of Mendeleev's system? First of all, that it should consist of 50 elements, beginning with "eka-francium" with $Z = 119$ and ending with "dviradon" with $Z = 168$. In the language of electron shells, the structure of the eighth period could be represented by

$8s^2$	$5g^{18}$	$6f^{14}$	$7d^{10}$	$8p^6$

A new feature, in comparison to the preceding periods, is the appearance of $5g$-elements, corresponding to the orbital quantum number $l = 4$. There would be 18 such elements, and they would complete the building-up of the *O*-shell, which began to be filled a long way back, at rubidium with $Z = 37$. It could be expected that the $5q$-elements resemble one another even more than those of the lanthanide series because they belong to the fourth shell counting from outside.

The element with $Z = 126$ exactly belongs to the 5*g*-elements. According to the previous reasoning it should logically belong to the third group of the periodic system and have an oxidation level of $3+$. In exactly the same way, superelement No. 164 would be an 8*p*-element and an analogue of lead even heavier than the one hundred and fourteenth element. All of these conclusions could be readily arrived at within the framework of commonly accepted conceptions on the structure of shells and subshells in atoms.

Calculations carried out by electronic computers indicate that the phenomenon of "blurred" periodicity is displayed to an extraordinary degree in the elements of the eighth period.

However, use your own judgement.

It is not 5*g*-, nor 6*f*-, nor even 7*d*-electrons that appear in the atoms of elements with $Z = 121$ and $Z = 122$, but 8*p*-electrons! But the filling of the *p*-subshell occurred immediately after the *s*-subshell was filled only in the second and third periods of the system. True, at $Z = 125$, a long-awaited 5*g*-electron enters a vacant 5*g*-subshell. Subsequently, over a long interval of atomic numbers, the building-up of the electron subshells is quite irregular.

This is the first surprise that the computers stagger us with. The second is even more unexpected: the completion of the eighth period, according to prediction, is at the element with $Z = 164$! It turns out to be, not an 8*p*-element, as could be expected, but an element with a full 7*d*-subshell. The outer electrons in the 8*s*- and 8*p*-subshells, the computer contends, are strongly bound and cannot participate in chemical bonds. Consequently, the one hundred and sixty-fourth element should be chemically inert.

But in this case, the third surprise pops up; it is really astonishing. The computer proposes the following structure of the ninth period:

$9s^2$	$9p^2$	$8p^4$

That is to say: (1) in elements with $Z = 165$ and $Z = 166$, the $9s$-subshell is being filled; (2) further on, in the 167th and 168th elements, the building-up of the $9p$-subshell begins; and (3) in the atoms of the elements with atomic numbers from 169 through 172, the filling of the $8p$-subshell is completed; this subshell remained incomplete through a long series of elements.

Hence, according to calculations, the ninth period, like the second and third, should contain eight elements, its p-elements being nonuniform: the p-electrons of their atoms belonging to different electron shells, with $n = 8$ and $n = 9$.

These amazing predictions will be confirmed only if and when at least several “superelements” are successfully synthesized and their most important properties are investigated in greatest possible detail.

For the time being, the remarkable picture drawn by the electronic computers is still only a captivating fantasy. But it indicates the fact that the phenomenon of the periodic variation of the properties of chemical elements, discovered by D. I. Mendeleev, actually turned out to be more complex and more fantastic than could be imagined two decades ago.

We have every reason, therefore, to expect new “superstructures” and new “developments” in the future.

The Omnipresent Law of Periodicity

The centennial of the discovery of the periodic law of the elements was celebrated in 1969. The second century of its triumphant procession has begun.

It is impossible to study chemistry except on the basis of the periodic law and the periodic system of the elements. How absurd a chemistry textbook would look without Mendeleev's table! It is insufficient, however, and quite unnecessary to simply memorize the sequence in which the elements are arranged in the table. What is really required is to understand *how* various elements are related to one another, and *why* they are thus related. Only then does the periodic system become a rich storage vault of information on the properties of elements and their compounds. It is one with which very few storehouses can be compared.

Just by glancing at the space occupied by some element in the system, an experienced chemist can tell us much about it. He can tell whether the given element is a metal or a nonmetal; whether or not it forms compounds, hydrides, with hydrogen; what oxides are typical for this element; what valencies it may display in entering a chemical compound; what compounds of this element will be stable or, on the contrary, will disintegrate; and by what techniques it is most convenient and efficient to obtain the given element in its free state. If the chemist is capable of extracting all this information from the periodic system, he has obviously mastered it properly.

But up-to-date chemical science is faced not only by the problem of obtaining new information on the properties and practical applications of already known chemical compounds. The science and engineering revolution has required the synthesis of new materials and of substances with new, unusual and preassigned properties, substances that are unknown in nature. Such materials and substances are now manufactured in huge amounts.

Many chemical processes proceed only in the presence of catalysts. Various elements and chemical compounds are used for this purpose. Gone are the days in which catalysts were found by trial and error, when a suitable accelerator of a chemical reaction could only be found after testing dozens or even hundreds of substances. Today, catalysts are selected on a strictly scientific basis and, to a considerable extent, this basis is the periodic system.

The system has also become a lodestar in the synthesis of semiconductor materials. Many examples have shown physicists and chemists that the best semiconductor properties are possessed by or should be possessed by compounds of elements occupying definite places in Mendeleev's table (mainly, in the third, fourth and fifth groups).

Alloys of metals have been known to mankind since ancient times, but, for many centuries, only a small variety were available. Their number increased drastically in the twentieth century to meet the requirements of engineering and industry. As a result, most diverse combinations of elements were produced, especially when the metallurgists began to employ rare metals. At the present time thousands of different alloys are known. In studying their structures and properties, investigators established a great many important laws. It was subsequently found that these laws are not simply random statements, but are determined to a large extent by the positions of the corresponding metals in the periodic system. Consequently, one cannot hope to obtain new alloys if the periodic system is ignored.

We are likely to note the influence of the periodicity law in any branch of modern chemistry. But it is not only chemists that pay homage to this ubiquitous law. As we have already seen, we cannot do without the periodicity in the difficult and fascinating work of synthesizing new elements. A gigantic natural process of synthesizing chemical elements and a great variety of their isotopes is continuously taking place in the stars. Scientists call this process stellar nucleosynthesis.

So far we do not know in detail by exactly what methods and as a result of what consecutive nuclear reactions the known chemical elements were formed. Many hypotheses on nucleosynthesis have been advanced, but there is still no completed theory. We contend, however, without a shadow of doubt, that even the most timid conjecture on the origin of the elements is infeasible without taking into account the consecutive arrangement of the elements in the periodic system. The laws of nuclear periodicity, and the structure and properties of atomic nuclei are the basis for the diverse nuclear reactions of nucleosynthesis.

But let us return again from the stars to our familiar earth. Also about 100 years ago scientists began to investigate the abundance of the chemical elements in the earth's crust, their distribution in various minerals and ores. This led to the founding of the science of geochemistry. Along with the chemical properties of the elements, their geochemical properties, their behaviour in nature, were also investigated. These properties were found to be extremely odd and complicated. Here again, the periodic system played the role of an amazing scientific tool; it enabled keys to be found for the solution of many geochemical puzzles.

The up-to-date geochemical classification of the chemical elements rests on Mendeleev's table, like a building rests on a strong foundation. Scientists today have a pretty clear idea of the laws that govern the distribution of the elements in the earth's crust. Before a geologist departs on an expedition in search of deposits of special ores and minerals, he will certainly consult, beforehand, with a geochemist.

It would take much space to merely enumerate the fields of mankind's knowledge and practice in which the periodic law and system of elements play a significant role. To tell the truth, we have only a faint idea of the grand scope of Mendeleev's theory of periodicity. It is destined many times again to display new and unlooked-for aspects of its profundity.

We, the authors of this book, took part in a grand occasion connected with the periodic law, whose centennial was celebrated in 1969. Scientists from many countries came to Leningrad for this purpose. In the papers they presented, eminent chemists from all over the world told about the present state and the future of the periodic law. Thus came true the prediction of Dmitri Ivanovich Mendeleev that he wrote in his diary on July 10, 1905: "To all appearances, the future is not likely to threaten the periodic law with destruction; it promises instead only the erection of a superstructure and further development...".

And you – young readers who intend to be chemists – will be convinced of this time and again in your, work!

Igor Vasilyevich Petryanov is an eminent Soviet scientist in the field of physical chemistry, and a full member of the USSR Academy of Sciences since 1966. Academician Petryanov was born in 1907 and graduated from the Moscow University in 1931. He has been engaged in scientific research for over 50 years in the Karpov Physical Chemistry Institute and is a professor of the Mendeleev Institute of Chemical Technology. He is one of the few investigators developing a new, highly important branch of science: the theory of aerosols. Academician Petryanov has been awarded the title of Hero of Socialist Labour, three Orders of Lenin, and he is a winner of Lenin and State Prizes.

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