RUSSIAN
CHEMICAL
REVIEWS
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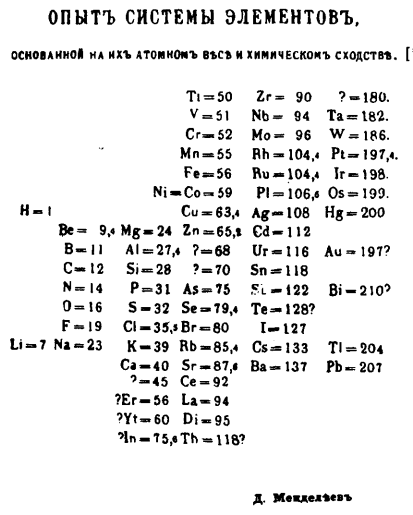
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A Century of Mendeleev's Periodic Law

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At the beginning of March 1869 D.I. Mendeleev, Professor of Chemistry at the University of St. Petersburg, distributed among many Russian and foreign scientists sheets which depicted the system of the elements which he had worked out on the basis of their atomic weights and chemical similarity (Fig. 1).



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

Figure 1. First representation of D.I. Mendeleev's Periodic System of the elements (1869).

* Trial system of the elements based on their atomic weight and chemical similarity.

A lecture on this work by Mendeleev was given at a meeting of the Russian Chemical Society held on 18th March 1869, and in May of the same year his paper "Relationship between the Properties of Elements and their Atomic Weights" was published in the next issue of the Journal of the Russian Chemical Society[1]. This contained the first formulation of the Periodic Law: "The elements, when arranged in the order of their atomic weights, exhibit a clear periodicity of properties". A few years later Mendeleev gave a still more precise formulation of the Periodic Law: "The properties of the elements, as well as the structure and the properties of their compounds, vary periodically with the atomic weights of the elements".

The discovery of the Periodic Law and the associated natural system of the chemical elements was a consequence of Mendeleev's work on "The Principles of Chemistry", his famous textbook of inorganic chemistry, which he began to write in 1868. "It contains many original ideas..., the chief of which is the periodicity of the elements, which was actually discovered in working on 'The Principles of Chemistry'", as Mendeleev subsequently pointed out[2].

It is well known that attempts to classify the elements—to arrange them into groups and tables—had been made even before Mendeleev's time. Mention may be made of Döbereiner's triads (1829)—calcium, strontium, barium; sulphur, selenium, tellurium; etc.—which developed into Pettenkofer's groups (1850)—nitrogen, phosphorus, arsenic, antimony; magnesium, calcium, strontium, barium; etc.—Chancourtois's spiral (1862), the tables of Odling (1864) and Meyer (1864), and Newlands' octaves (1866). However, these works were devoted either to particular isolated questions of the similarity of groups of elements

Ряды	Группа I — R^2O	Группа II — RO	Группа III — R^2O^3	Группа IV RH^4 RO^2	Группа V RH^3 R^2O^5	Группа VI RH^2 RO^3	Группа VII RH R^2O^7	Группа VIII — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59; Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=97	—=100	Ru=107, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Te=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=251	—	U=240	—	— — — —

Figure 2. Mendeleev's Periodic System of the elements (1872).

or to the search for relations between their atomic weights. None of these authors sought general relations between the properties of all known chemical elements; no-one before Mendeleev had formulated the Periodic Law.

It must be remarked that Mendeleev, although he stressed his view that "the value of the atomic weight determines the character of the element", considered that other characteristics of the chemical elements were also of fundamental importance. The chemical properties of the compounds formed were no less significant for determining the position of elements in the Periodic System. In some cases—cobalt and nickel, tellurium and iodine—the sequence of increasing atomic weight was disregarded in Mendeleev's table.

The outstanding scientific and philosophical value of Mendeleev's discovery consisted primarily in the establishment of an interrelationship between all the chemical elements, their physical and chemical properties. Groups and series in the Periodic System became a reliable basis for revealing families of related elements.

The first practical application of the Periodic Law was to correct the valencies and the atomic weights of certain elements, for which incorrect values had hitherto been accepted. This applied in particular to indium, cerium and other rare-earth metals, thorium, and uranium. Indium had been regarded as a bivalent element, and on the basis of its atomic weight (75.6)† was located between arsenic and selenium, although clearly not resembling them in properties. Measurement of the heat capacity of metallic indium, together with a detailed examination of the properties of its compounds, led Mendeleev to the conclusion that indium must be regarded as tervalent in its higher state of oxidation. Its atomic weight then became 113, and indium found a place in Group III of the Periodic System between cadmium (112) and tin (118), in full agreement with its chemical properties. However, this position had originally been occupied by uranium, which had been assumed to be a tervalent element having an atomic weight of 116. Mendeleev soon came to the conclusion that uranium was closer to molybdenum and tungsten than to aluminium in chemical properties, doubled the atomic weight of uranium, and placed it in Group VI of the Periodic System.

Mendeleev adduced similar considerations to justify the tervalency of the ceritic elements (lanthanum, etc.), which many chemists regarded as bivalent. He assigned the formula CeO_2 to the higher oxide of cerium, and ThO_2 (instead of ThO) to that of thorium. Hence new values were calculated for the atomic weights of these elements.

This work, of course, was by no means easy. It must be remembered that no methods were then available for measuring directly the atomic weights of elements; only Dulong and Petit's law of atomic heats gave some assistance in this direction. The great expert on the chemistry of the rare-earth metals K. Rammelsberg objected to Mendeleev's proposed changes in the atomic weights of cerium, didymium, and lanthanum, while Lothar Meyer considered that in general "it would be rash to alter the hitherto accepted atomic weights on such an unreliable basis", by which he meant the Periodic Law.

Mendeleev's view that the atomic weights of the platinum metals should be corrected so that they would increase—not diminish—in the sequence osmium–iridium–platinum (as followed from old analytical results) was soon confirmed. However, his suggestion that the atomic weight of tellurium should be lower than that of iodine was not justified, the reason for this depending, as we now know, on the nature of the isotopes of these two elements, not on the chemical properties of their atoms. In spite of the apparent inconsistency with the main rule on which the Periodic System was constructed—the arrangement of the elements in order of increasing atomic weight—Mendeleev left tellurium in Group VI, and iodine in Group VII, on the basis of their valency and chemical properties.

Thus as a result of intense creative work, overcoming immense difficulties, Mendeleev produced within a short time (less than two years) essentially the same Periodic System of the chemical elements as we continue to use nowadays (Fig. 2).

† Here and subsequently atomic weights of that time are indicated.

Nevertheless, there were clearly several unfilled positions in the Periodic System, and in the first publication on the Periodic Law Mendeleev already expressed the view that many then unknown elements existed, examples of which, for instance, should resemble aluminium and silicon, and have atomic weights of 65–75. Mendeleev was profoundly convinced that the best evidence that the main principles of the Periodic Law were correct was the fulfilment of predictions based on it. Two years after the discovery of this periodicity, therefore, he published a paper[3] in which he predicted in detail the physical and chemical properties of some hitherto undiscovered elements. "I have decided to do this so that, at least in time, when one of these bodies which I have predicted has been discovered, it will be possible finally to convince other chemists and myself of the rightness of the hypotheses underlying my proposed system". The most detailed examination was given to the expected properties of unknown analogues of boron, aluminium, and silicon, which were provisionally named by Mendeleev "ekaboron", "eka-aluminium", and "ekasilicon"‡.

The elements predicted by Mendeleev were very soon discovered. In 1875 the French chemist P. Lecoq de Boisbaudran discovered in a Pyrenean zinc blende a new element gallium, the properties of which coincided with those indicated by Mendeleev for eka-aluminium. In 1879 the Swedish chemist L. Nilson, while studying ytterbia earths, isolated from the Scandinavian minerals gadolinite and euxenite a new rare-earth element scandium, which proved to be ekaboron. In 1886 the German chemist C. Winkler, in analysing the mineral argyrodite, discovered in it a new element germanium, whose properties coincided extraordinarily closely with those predicted by Mendeleev for ekasilicon (Table 1). Winkler wrote: "It is hardly possible to find a more striking demonstration of the correctness of the concept of periodicity than the realisation of the hypothetical ekasilicon in the newly discovered element. This is not simply support for a daring theory: here we see an obvious extension of the chemical horizon, a powerful step in the field of knowledge".

Mendeleev described more briefly the expected properties of undiscovered analogues of manganese, tellurium, caesium, barium, lanthanum, and tantalum. Some of these elements—radium, actinium, and polonium—were discovered during his lifetime, and the others—technetium, rhenium, francium, and protactinium—only in the twentieth century.

At the end of the nineteenth century the Periodic System was subjected to a severe test, from which it emerged victorious. After Rayleigh and Ramsay had discovered argon in the air (1894), it appeared that this element could not find a place in the Periodic System. However, Ramsay's subsequent discovery of helium (in the gas expelled from the mineral cleveite) showed that a group of elements similar to argon existed.

In 1897 Ramsay gave a lecture on "A Still Undiscovered Gas". As he himself pointed out subsequently, in this lecture "following the example of our teacher Mendeleev, I described, as far as it was possible, the properties expected for and the presumable relations of the gaseous element which would fill the gap between helium and argon". Ramsay soon isolated this gas, of atomic weight 20, from liquid air, and called it *neon*. Heavy analogues of argon—krypton and xenon—were discovered almost simultaneously. According to the researches of that time all these elements were characterised by inertness—inability to enter into ordinary chemical reactions of oxidation and reduction—and the family of inert gases therefore found a place in the Periodic System as the newly formulated Group 0. In 1900 the radioactive element radon (radium emanation), discovered by A. Debierne, was added to this group.

Table 1. Properties of germanium predicted and found.

Property	Predicted for ekasilicon	Found for germanium
Atomic weight	Es = 72	Ge = 72.60
Valency	quadrivalent, but can exhibit also a lower valency	4 and 2
Free element		
Atomic volume	about 13	13.5
Specific gravity	about 5.5	5.36
Fusibility and volatility	"fusible metal, able to volatilise at a high temperature"	b.p.958.5°C m.p.2700°C
Highest oxide	EsO_2	GeO_2
Molecular volume	about 22	22.2
Specific gravity	4.7	4.703
Chemical properties	acidic and extremely weakly basic	amphoteric with acidic properties predominating
Highest chloride	$EsCl_4$	$GeCl_4$
Boiling point	close to 90°C	83.1°C
Specific gravity	about 1.9	1.874
Chemical properties	decomposed by water	readily hydrolysed by water
Hydrogen compounds	"a hydrogen compound can also be greatly expected" "EsH_4 should decompose readily into hydrogen and the metal"	GeH_4 and other germanium hydrides obtained GeH_4 decomposes at 350°C
Organometallic compounds	"it will, of course, form organometallic compounds"	many organometallic compounds of germanium
$(C_2H_5)_4R$, b.p.	160°C	163.5°C
$(C_2H_5)_4R$, sp. gr.	0.96	0.99

The discovery of elements predicted by Mendeleev, the exact coincidence of their properties with those calculated on the basis of the Periodic Law, and the confirmation of the corrections made by Mendeleev to atomic weights—all this reinforced the materialist view of the chemical elements, and immeasurably extended the possibilities of the understanding of Nature by man. The Periodic System became a powerful weapon for use by research workers in the further development of chemistry and physics.

Various properties of the chemical elements and their compounds began to be correlated on the basis of the Periodic Law. In 1869 Mendeleev demonstrated periodicity in the structure of compounds formed by elements, i.e. in the most important chemical property, the valency. He even established periodicity in the specific gravities and atomic volumes of elements. Other workers showed that the melting points of elements vary periodically, and this was noted also for the melting points of metal chlorides. The quantity of heat involved on formation of chlorine, bromine, and iodine compounds was found to vary periodically with increasing atomic weight of the elements interacting with the halogens.

In 1889 Mendeleev directed attention also to the periodicity of structure of the spectra of elements as a function of their atomic weights. A relation was observed between the position of elements in the Periodic System and their

‡ Here *eka* (Sanskrit) = "one" is used in the sense of the first adjacent analogue.

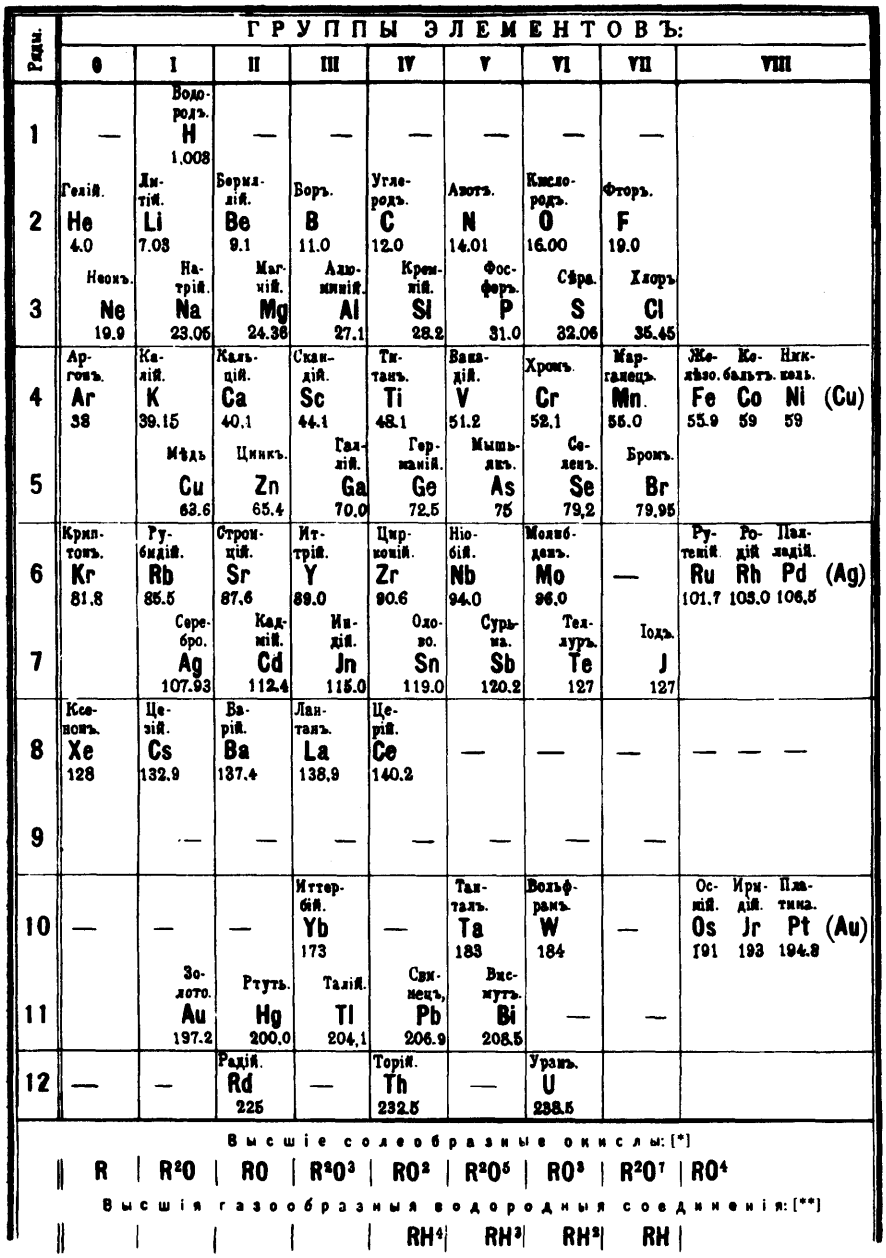


Figure 3. Mendeleev's Periodic System of the elements (1905).

* Highest saltlike oxides.

** Highest gaseous hydrogen compounds.

magnetic properties. Investigations of copper alloys by A. A. Baikov (1902) showed the applicability of periodicity principles to the composition of the intermetallic compounds formed in alloys.

For many years after the discovery of the Periodic Law Mendeleev continued to improve the appearance of his table, using both short and long forms. Fig. 3 shows the last table drawn up by Mendeleev not long before his death in 1907.

Even during Mendeleev's lifetime the Periodic Law and the system of elements based on it achieved immense success. However, several sites in the system still remained obscure. It was unknown whether elements should exist between hydrogen and helium, and the number of rare-earth elements, as also their position in the Periodic System, was indefinite. In view of all these difficulties it was impossible to compute the total number of elements between hydrogen and uranium. The actual

cause of the periodicity was obscure. One must be amazed by the genius of Mendeleev, who was able to set up the Periodic System of the elements in the almost complete absence of information on the structure of matter, and to set it up in such a way that even after a century it has not required any fundamental changes.

Since Mendeleev's death the Periodic Law has exerted an immense influence on the development of the work of physicists and chemists on the structure of matter.

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We must first note the part played by the Periodic System in unravelling the phenomenon of radioactivity and elucidating the nature of isotopes. The discovery by Becquerel in 1896 of "uranium rays" with their remarkable properties led to many investigations in this new branch of science. Another heavy element, thorium, also proved to be radioactive. In 1898 Marie and Pierre Curie discovered in uranium ores two new elements—radium and polonium—exhibiting still stronger radioactivity than uranium. They isolated a pure preparation of radium from residues from the processing of uranium ore. This element proved to be an analogue of barium, and corresponded in properties to Mendeleev's ekabarium. The properties of polonium were very close to those of ekatellurium.

In 1899 Debierne discovered yet another radioactive element, actinium, an analogue of lanthanum. The existence of this element had been predicted by Mendeleev as early as 1871.

It was established in 1900 that radium preparations evolve continuously a radioactive gas—radium emanation—which proved to be analogous to xenon in Group 0 of the Periodic System, and is now called *radon*. A remarkable property of radon is its rapid disintegration, which is half complete in 3.85 days. Ramsay and Soddy discovered in 1902 that, after radium emanation has been sealed in a discharge tube for some time, it begins to show the spectrum of helium. This was the first experimentally proved case of the transmutation of elements.

Mendeleev referred very doubtfully to the possibility of the interconversion of elements, pointing out that all reports of this kind require especially careful checking and usually are not confirmed. Nevertheless, he regarded himself as "not an opponent, but rather inclined to accept the concept of the complexity of elements". He wrote (1898) that "it would be extremely interesting to be present when data are established to prove the interconversion of elements, because I could then hope that the cause of the periodic regularity would be discovered and understood". As we shall see, the development of science made this task urgent within a few years.

In 1902, on the basis of a detailed study of the radioactivity of thorium, Rutherford and Soddy put forward the hypothesis that radioactive phenomena are due to transformations of atoms and hence of elements. Subsequent investigations completely confirmed this suggestion.

The study of radium emanation showed that the so called "active residue" remaining after its disintegration contained several elements differing from one another in radioactive properties, i.e. in the character and energy of the emission. Many radioactive elements were detected in studying the changes undergone by uranium, actinium, and thorium.

Only a proportion of the newly discovered radioactive elements could be placed in empty positions in the Periodic System. Examination of a large number of the radioactive elements which were members of the various radioactive series established that many of them, while differing in radioactive properties, could not be separated from one another or from certain ordinary elements by chemical methods. For example, one of the products of the disintegration of uranium—the radioactive element ionium—while differing in its radioactivity from thorium could not be distinguished from it chemically. One of the initial products in the disintegration of thorium—the so called radiothorium—disintegrated immeasurably more rapidly than thorium, but chemically was completely identical with it. It thus appeared that many newly discovered radioactive elements did not differ in chemical properties from uranium, thorium, radium, lead, bismuth, and other elements in the last two rows of the Periodic System. Hence one chemical element corresponded to more than one type of atoms, differing in mass and in rate of radioactive disintegration.

In 1913 Soddy suggested the name *isotopes* ("isos" = same, "topos" = place) for such varieties of elements, to indicate that they occupy the same place in the Periodic System.

The numerous radioactive elements formed in the disintegration of uranium, thorium, or actinium were now combined into series strictly related to Mendeleev's Periodic System. Each α-emission gave a product which was an isotope of an element located two places nearer to the beginning of the Periodic System. As a result of β-disintegration an element was obtained one place closer to the end of the system. This so called Fajans displacement law enabled many new radioactive elements to be discovered, and introduced order into obscure positions in radioactive series.

Electromagnetic analysis of a beam of canal rays by Thomson in 1913 yielded, with neon as example, the first information on the existence of isotopes of non-radioactive elements. Aston's development of the design of the mass spectrograph enabled isotopes of several ordinary elements to be detected.

The phenomenon of isotopy gave a additional content to the Periodic System. The ideas of A. M. Butlerov, W. Crookes, and other scientists on the possibility of varieties of atoms of the same element, differing in mass, were brilliantly confirmed. Furthermore, the subsequent observation of an appreciable difference in chemical properties between the isotopes of hydrogen opened a new chapter in science—the chemistry of isotopes, closely connected with the Periodic System.

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The discovery of the phenomena of radioactivity and the vigorous development of atomic physics at the beginning of the twentieth century led, as is known, to the nuclear theory of atomic structure (Rutherford 1911), the discovery of the law relating the wavelengths of the characteristic X-ray spectra of elements to the charges on their atomic nuclei (Moseley 1913), and the working out of the principles underlying the quantum theory of atomic structure (Bohr 1913). The Periodic Law had an extraordinary influence on the development of these scientific trends, since it gave investigators a natural system of chemical elements with all the structural regularities of atoms latent in it.

On the other hand, the contemporaneous theory of atomic structure explained the reasons for the phenomenon of periodicity itself, and improved still further the methods for predicting the properties of unknown elements. The

experimental determination of the charges on atomic nuclei, based on Moseley's law, was especially important. It provided an exact method for determining the atomic numbers of the elements in the Periodic System and establishing the total number of elements between hydrogen and uranium. The correctness of the arrangement of all the elements in Mendeleev's table was confirmed. The atomic number of iodine (53) proved to be higher than that of tellurium (52). In 1914 empty spaces remained in the Periodic System at Nos. 43, 61, 72, 75, 85, 87, and 91, of which Nos. 61, 72, 75, and 85 belonged to the third long period.

The theory of atomic structure explained the peculiar position in the Periodic System of the rare-earth metals which follow lanthanum in the third long period. It turned out that, in this part of the system, successive electrons in the atoms of elements beginning with cerium enter a lower electron shell of the fourth energy level at the 4*f*-sublevel, which may contain up to fourteen electrons and is completed at lutetium. The number of valency electrons remains unchanged, being three as in lanthanum. At the present time, therefore, it is usual to group the elements in the cerium–lutetium family under the name *lanthanides*. They fit into the same space as lanthanum, and are listed as a separate series below the table.

Table 2. Structure of electron shells in atoms of rare-earth metals.

Element	Atomic No.	Energy levels in atoms											
		n=1	*n*=2	*n*=3		*n*=4				*n*=5			*n*=6
		K	*L*	*M*		*N*				*O*			*P*
		s	*s*, *p*	*s*, *p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*
Sc	21	2	8	8	1	2							
Y	39	2	8	8	10	2	6	1		2			
La	57	2	8	8	10	2	6	10		2	6	1	2
Ce	58	2	8	8	10	2	6	10	2	2	6		2
Pr	59	2	8	8	10	2	6	10	3	2	6		2
Nd	60	2	8	8	10	2	6	10	4	2	6		2
Pm	61	2	8	8	10	2	6	10	5	2	6		2
Sm	62	2	8	8	10	2	6	10	6	2	6		2
Eu	63	2	8	8	10	2	6	10	7	2	6		2
Gd	64	2	8	8	10	2	6	10	7	2	6	1	2
Tb	65	2	8	8	10	2	6	10	9	2	6		2
Dy	66	2	8	8	10	2	6	10	10	2	6		2
Ho	67	2	8	8	10	2	6	10	11	2	6		2
Er	68	2	8	8	10	2	6	10	12	2	6		2
Tm	69	2	8	8	10	2	6	10	13	2	6		2
Yb	70	2	8	8	10	2	6	10	14	2	6		2
Lu	71	2	8	8	10	2	6	10	14	2	6	1	2

Note. *n* is the principal quantum number; *K*, *L*, *M* are energy levels in the atoms; *s*, *p*, *d*, *f* are groups of electrons.

The structure of the electron shells in atoms of the rare-earth metals, based on present-day results, is set out in Table 2. It is seen that two valency electrons of the lanthanides belong to the 6*s*-sublevel, while the third is usually detached from the 4*f*-sublevel and is located in the 5*d*-sublevel only for a few members of this series. At the start of formation of the 4*f*-shell the electrons in it are not very firmly bound. As a consequence cerium, praseodymium, and probably neodymium are capable of forming compounds in which they are quadrivalent. After this the increasing charge on the nucleus strengthens the structure of this shell. It must be added that the shell is apparently completed in two layers, each comprising seven electrons. Ability to form compounds of higher valency is therefore exhibited also by terbium, which is characterised by completion of the second layer. The elements preceding gadolinium (samarium, europium) and lutetium (ytterbium), on the other hand, may approach a more stable configuration by splitting off a smaller number of electrons, and are therefore bivalent under certain conditions.

Subsequent investigations established an important rule for the variation in size of the lanthanide atoms [4]. Electrons entering the inner 4*f*-layer do not completely screen the increasing nuclear charge. The electrons in the outer shells are therefore drawn towards the nucleus, and the overall size of the atom diminishes (lanthanide contraction). The ionic radii for the rare-earth metals in the tervalent state are given below.

Ionic radius, Å

Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.68	0.88	1.04	1.02	1.00	0.99	(0.98)	0.97	0.96	0.94	0.92	0.91	0.89	0.87	0.86	0.85	0.8

The phenomenon of the lanthanide contraction results in a weakening of the basic properties of the hydroxides in the sequence lanthanum–lutetium. Whereas lanthanum hydroxide is similar in properties to strontium hydroxide, lutetium hydroxide is a weak base, approaching in this respect the hydroxide of scandium, which is located far higher in the same group of the Periodic System. Dysprosium and holmium are similar to yttrium in this respect.

Thus the similarity in structure of the outer electron shell of the atoms and the lanthanide contraction converted scandium, yttrium, lanthanum, and the lanthanides into a closely intertwined tangle of elements, greatly resembling one another in properties and in natural occurrence. This in turn was responsible for all the difficulties involved in their separation, purification, and identification.

The theory of atomic structure made it clear that element No. 72, immediately following lutetium, should have two valency electrons in each of the sublevels 6*s* and 5*d*, and would therefore be quadrivalent, an analogue of zirconium, not a rare-earth metal. A search in zirconium preparations undertaken by G. Hevesy and D. Coster on this basis using X-rays proved successful, and in 1923 the element was discovered and named *hafnium* (Hf = 178.5). It is noteworthy that an analogue of zirconium of atomic weight 180 had been envisaged by Mendeleev in the very first form of his table (see above).

Thus the bundle of rare-earth elements in the Periodic System was disentangled. Elements which were missing from the Periodic Table at the time when Moseley's law was discovered were either isolated from natural minerals or synthesised by nuclear reactions within a fairly short period.

In 1918 L. Meitner and O. Hahn isolated the radioactive element No. 91, protactinium, from the processing wastes of a uranium ore. In 1925 W. Noddack, I. Tacke, and O. Berg detected element No. 75 in specimens of native platinum, tantalite, and molybdenite, and termed it *rhenium*. The discovery by these workers of element No. 43 was not subsequently confirmed. This latter element was found in 1937 by C. Perrier and E. Segrè in a sample of molybdenum which had undergone prolonged irradiation with a powerful beam of deuterons in a cyclotron. The nuclear reaction was represented by the scheme ${}_{42}\mathrm{Mo}(d, n)43$. After identification the element was named *technetium* to emphasise its artificial production. Considerable quantities of technetium were subsequently found in fission fragments from uranium, and it can be extracted from waste products of the atomic industry.

In 1939 Mlle Perey was studying the natural radioactive disintegration products from actinium, and found in them a radioactive isotope (half-life 21 min), similar in chemical behaviour to caesium. This proved to be element

No. 87—the ekacaesium predicted by Mendeleev—and was termed *francium*.

A radioactive isotope of ekaiodine—element No. 85 (half-life 7.5 h)—was discovered in 1940 by D. R. Corson, K. R. MacKenzie, and E. Segrè by bombarding bismuth with accelerated helium nuclei of energy 38 MeV. The process was represented by $^{209}_{83}Bi(^{4}_{2}He, 2n)^{211}85$. The name *astatine*, given to this element, is an indication of its instability.

Finally element No. 61, which had been unsuccessfully sought for a long time by many chemists in rare-earth preparations, was discovered in 1947 among the fission products of uranium. It was identified by J. A. Marinsky, L. E. Glendenin, and C. D. Coryell in the form of two radioactive isotopes having half-lives of 55 h and 2.6 years. The element acquired the name *promethium* in commemoration of the practical utilisation of atomic energy, which the authors compared with theft of fire by Prometheus.

Thus by 1947 all the places between hydrogen and uranium in the Periodic System had been filled.

Completely new problems facing the Periodic System arose in connection with the successful development of the synthesis of new heavy elements[5]. It is noteworthy that Mendeleev admitted the possibility of extending the Periodic System beyond uranium, and this suggestion of his has been justified.

The idea of synthesising transuranic elements became topical in the 1930s, when E. Fermi and his coworkers developed a method for the artifical production of radioactive isotopes by means of slow neutrons. In 1935 they detected in neutron-irradiated uranium several short-lived β-radioactive isotopes, one of which (half-life 13 min) was coprecipitated with manganese and rhenium, and was assumed to be an analogue of rhenium $^{239}_{93}$EkaRe. However, further investigations by L. Meitner, O. Hahn, and F. Strassmann showed that in these experiments many radioactive isotopes—fission products of uranium—are formed, which are coprecipitated with various elements. Among them a β-emitter was found (half-life 23 min), identical in chemical properties with uranium and assumed to be an isotope $^{239}_{92}U$. As a result of β-disintegration it should have been converted into element No. 93. However, these workers were unable to detect a new element here, owing to the weakness of the neutron source used.

Element No. 93, given the name *neptunium* (Np), was discovered by E. D. McMillan and P. H. Abelson in 1940 by irradiating thin layers of ammonium uranate with a powerful beam of neutrons obtained by bombarding a beryllium target with deuterons of energy 16 MeV in the large cyclotron at the University of California. Fragments arising from the fission of uranium were removed by the recoil phenomenon. Two types of β-activity, having half-lives of 23 min and 2.9 days, were detected in the uranium preparation. The nature of the first was known, being due to $^{239}_{92}U$. Conversion of the first into the second emitter served as proof of the formation of element No. 93. McMillan and Abelson concluded that neptunium was not an analogue of rhenium. It was found to have at least two states of oxidation, in the lower of which neptunium resembled the rare-earth metals, whereas in the higher state of oxidation it was similar to uranium.

The β-disintegration of neptunium must be expected to yield element No. 94, which was named *plutonium* (Pu). The first isotope of the latter $^{238}_{94}Pu$ (half-life 89.6 years) was synthesised at the end of 1940 by G. T. Seaborg, E. D. McMillan, J. W. Kennedy, and A. C. Wahl by bombarding uranium with deuterons in a cyclotron. The neptunium isotope $^{238}_{93}Np$ (half-life 2.1 days) was obtained as an intermediate product:

$$_{92}U^{238} + {}_{1}H^{2} = {}_{93}Np^{238} + 2n; \quad {}_{93}Np^{238} = {}_{94}Pu^{238} + \bar{\beta} \ .$$

The most important chemical properties of the new element and the principles of its separation from uranium were studied on tracer quantities of the above isotope. In its highest valency plutonium resembles uranium, but is more readily reduced. The properties of the compounds of lower valency recall thorium and the rare-earth metals. For military reasons the first information on plutonium was published only in 1946.

In 1941 a longer-lived isotope of plutonium ^{239}Pu (half-life 24 360 years), capable of fission by slow neutrons, was discovered after the prolonged bombardment of uranium with deuterons in a cyclotron. As a consequence of the above properties it subsequently acquired practical value as a form of atomic fuel.

Painstaking work on the irradiation of a few tens of kilogrammes of uranyl nitrate with neutrons in a cyclotron resulted by the end of 1942 in the isolation of 0.5 mg of plutonium in the form of pure compounds. These investigations were continued in the first laboratory uranium reactor, which became operative on 2nd December 1942 in the University of Chicago. At the same time planning went ahead for a pilot plant to isolate plutonium from uranium irradiated in the reactor, with an enrichment factor of 10^{10}, which was unprecedented in the chemical industry. The first factory-scale reactor was started up after a year. Less than seven weeks later an experimental separation plant began to operate, and plutonium was soon available to the research workers in gramme quantities. In September 1944 the first works began to operate to produce kilogrammes of plutonium. Thus less than three years elapsed between the first artificial separation of the new element and the organisation of its isolation on an industrial scale! Nowadays plutonium is manufactured in several countries, and its production is measured in many tons per annum.

The development of further investigations on the transuranium elements is due to the work of the distinguished American scientist Seaborg and his collaborators. During 1944–1955 seven further transuranium elements were discovered. Americium (Am, No. 95) was obtained by irradiating plutonium with neutrons; and curium (Cm, No. 96), berkelium (Bk, No. 97), and californium (Cf, No. 98) by the bombardment with high-energy helium ions of targets containing plutonium, americium, and curium respectively. Isotopes of einsteinium (Es, No. 99) and fermium (Fm, No. 100) were first detected when uranium was irradiated with a very intense instantaneous flux of neutrons during the thermonuclear explosion produced in 1952. Many repeated neutron captures resulted in the formation of very heavy isotopes of uranium, which then disintegrated with the emission of β-particles and the formation of several transuranium elements, including einsteinium and fermium. These elements were later synthesised by other routes. Element No. 101 was obtained by the action of high-energy (41 MeV) helium ions on einsteinium. In the first experiments seventeen atoms in all of the new element were identified from its conversion into fermium. The discoverers gave the name *mendelevium* (Md) to element No. 101 "in honour of the leading part played by the great Russian chemist Dmitrii Mendeleev, who was the first to use the Periodic System of the elements to predict the chemical properties of hitherto undiscovered elements—a principle which gives the key to the discovery of the last seven transuranic elements (actinides)...".

Table 3 indicates the nuclear reactions first used to obtain the transuranium elements, together with their discoverers.

The first information on the discovery of element No. 102 appeared in 1957. A group of research workers—P.R. Fields, J. Milsted, H. Atterling, et al.—irradiated a preparation from curium with carbon-13 ions:

$$_{96}Cm^{244}(C^{13}, 6n)\,102^{251} \text{ or } _{96}Cm^{244}(C^{13}, 4n)\,102^{253}.$$

The products of the nuclear reaction had a half-life of about 10 min. The name *nobelium* (No) was proposed for the new element. However, these results were not confirmed when checked in Seaborg's laboratory.

Table 3. History of the discovery of the transuranium elements.

Element	Atomic No.	Year	Nuclear reactions	Discoverers
Np	93	1940	$_{92}U^{238}(n, \gamma)_{92}U^{239}$; $_{92}U^{239} = {}_{93}Np^{239} + \bar{\beta}$	E.D.McMillan and P.H.Abelson
Pu	94	1940	$_{92}U^{238}(H^2, 2n)_{93}Np^{238}$; $_{93}Np^{238} = {}_{94}Pu^{238} + \bar{\beta}$	G.T.Seaborg, E.D.McMillan, J.W.Kennedy, and A.C.Wahl
Am	95	1944	$_{94}Pu^{239} + 2n = {}_{94}Pu^{241}$; $_{94}Pu^{241} = {}_{95}Am^{241} + \bar{\beta}$	G.T.Seaborg, R.H.James, L.O.Morgan, and A.Ghiorso
Cm	96	1944	$_{94}Pu^{239}(_2He^4, n)_{96}Cm^{242}$	G.T.Seaborg, R.H.James, and A.Ghiorso
Bk	97	1949	$_{95}Am^{241}(_2He^4, 2n)_{97}Bk^{243}$	S.G.Thompson, A.Ghiorso, and G.T.Seaborg
Cf	98	1950	$_{96}Cm^{242}(_2He^4, n)_{98}Cf^{245}$	S.G.Thompson, K.Street, A.Ghioreseo, and G.T.Seaborg
Es	99	1955	$_{92}U^{238} + 15n = {}_{92}U^{253}$; $_{92}U^{253} \xrightarrow[6\beta]{} {}_{98}Cf^{253} \rightarrow {}_{99}Es^{253}$	A.Ghiorso, S.G.Thompson, G.H.Higgins, and G.T.Seaborg
Fm	100	1955	$_{92}U^{238} + 17n = {}_{92}U^{255}$; $_{92}U^{255} \xrightarrow[7\beta]{} {}_{99}Es^{255} \xrightarrow{\beta} {}_{100}Fm^{255}$	ditto
Md	101	1955	$_{99}Es^{253}(_2He^4,)_{101}Md^{256}$	A.Ghiorso, B.Harvey, G.Choppin, S.G.Thompson, and G.T.Seaborg
No?	102	1957	$_{96}Cm^{244}(C^{13}, 4n)\,102^{253}$; $_{96}Cm^{246}(C^{13}, 4n)\,102^{254}$; $_{94}Pu^{241}(_6O^{16}, 4n)\,102^{253}$	various workers
Lr	103	1961	$_{98}Cf^{252}(B^{11}, 6n)\,103^{257}$; $_{98}Cf^{250}(B^{10}, 3n)\,103^{257}$	A.Ghiorso, T.Sikkeland, A.Larsh, and R.Latimer
Ku	104	1966	$_{94}Pu^{242}(_{10}Ne^{22}, 4n)\,104^{260}$	G.N.Flerov, N.A.Dugin, I.Zvara, *et al.*

In the same year G. N. Flerov, S. M. Polikanov, A. S. Karamyan, et al. in the USSR irradiated plutonium-241 with a flux of quintuply charged oxygen ions and detected α-particles of energy 8–9 MeV, which could be attributed to an isotope $^{253}102$ having a half-life between a few seconds and 1 min. No chemical identification was made.

During 1958–1959 Ghiorso, Seaborg, et al. made repeated attempts to obtain isotopes of element No. 102 by the reactions

$$_{96}Cm^{246}(C^{12}, 4n)\,102^{254} \text{ or } _{96}Cm^{244}(C^{13}, 4n)\,102^{253}$$

but detected only products having half-lives of a few seconds. The authors of the original communication on element No. 102 also changed their view, and came to think that the isotope $^{255}102$ had been obtained in their experiments. In 1963 the Soviet scientists G. N. Flerov, E. D. Donets, V. A. Shchegolev, et al. synthesised an isotope of element No. 102 having mass number 256 in a powerful accelerator of multicharged ions. Metallic uranium was bombarded with high-energy neon nuclei. The half-life of the new isotope proved to be close to 8 min. Thus the question of the synthesis of element No. 102 had been considerably clarified, but its name is still under discussion.

At the beginning of 1961 a paper appeared by A. Ghiorso, T. Sikkeland, A. Larsh, and R. Latimer on the discovery of element No. 103, named *lawrencium* (Lr). These workers bombarded a target containing 3 mg of a mixture of californium isotopes with boron (^{10}B and ^{11}B) nuclei of energy 10.3 MeV in the large cyclotron at Berkeley. An α-emitter was formed with a half-life of 8 ± 2 s, the energy of the α-particles being 8.6 MeV. Calculations led to the conclusion that an isotope of element No. 103 having mass number 257 was formed. A longer-lived isotope $^{256}_{103}Lr$ (half-life 35 s) was also obtained later.

In 1966 G. N. Flerov, N. A. Dugin, I. Zvara, et al., working at the Joint Institute for Nuclear Research (at Dubna), synthesised the first atoms of element No. 104. A plutonium-242 preparation was irradiated with neon-22 ions of energy 115 MeV on a cyclotron. The nuclear reaction $^{242}Pu(^{22}_{10}Ne, 4n)^{260}104$ took place. The isotope obtained underwent spontaneous fission with a half-life of 0.3 s. It was detected from the tracks made by the fission fragments in glass or mica. It was identified chemically from the volatility of the chlorine compounds (see below). Element No. 104 received the name *kurchatovium* (Ku).

Table 4. Initially discovered and longest-lived isotopes of transuranium elements.

Atomic No. Z	Element	Initially discovered isotope		Longest-lived isotope	
		A	$T_{1/2}$	A	$T_{1/2}$
93	Np	239	2.3 days	237	$2.2\cdot10^6$ years
94	Pu	238	86.4 years	244	$7.6\cdot10^7$ years
95	Am	241	458 years	243	$8\cdot10^3$ years
96	Cm	242	162.5 days	247	$1.6\cdot10^7$ years
97	Bk	243	4.5 h	247	$1.4\cdot10^3$ years
98	Cf	244	2.5 min	251	800 years
99	Es	246	7.3 min	254	480 days
100	Fm	254	3.2 h	257	95 days
101	Md	256	30 min	258	54 days
102	No?	256	8 min	—	—
103	Lr	257	8 s	256	35 s
104	Ku	260	0.3 s	—	—

Thus twelve transuranic elements, having atomic numbers 93–104, are now known. It is significant that their first isotopes to be isolated were usually short-lived, after which methods were found for obtaining longer-lived isotopes (Table 4). It may be supposed that this rule will apply also to the most remote transuranic elements.

The principal method for obtaining large quantities of transuranic elements is the irradiation of ordinary uranium, uranium enriched with its isotope of mass 235, or plutonium with a high-power flux of neutrons in a nuclear reactor. The method of subterranean explosions, in which extraordinarily powerful fluxes of neutrons are produced, is of value for certain far transuranic elements, e.g. fermium-257 (half-life 95 days). In this case, however, the resulting isotope must be extracted from a large quantity of rocks which have fused together during the explosion.

Nowadays the annual production of plutonium throughout the world amounts to many tons. Neptunium, a by product of the manufacture of plutonium, is obtained in tens of kilogrammes. Americium is available in kilogramme

quantities, and curium in tens and hundreds of grammes; milligrammes of berkelium and californium have been isolated, and microgrammes of einsteinium and fermium. Mendelevium (atomic number 101), element No. 102, and lawrencium (atomic number 103) are studied in tracer amounts. The question can already be posed now of expanding scientific research and developing practical applications for many transuranic elements.

The position of the transuranic elements in the Periodic System is closely connected with the structure of their atoms and the valency they exhibit. The theory of atomic structure envisages that the inner 5*f*-layer, analogous to the 4*f*-layer formed in the lanthanides, should be filled with electrons at the beginning of the fourth long period in Mendeleev's system.

Table 5. Structure of electron shells in actinide atoms.

Element	Atomic No. Z	Energy levels and groups of electrons in atoms									
		n=1	n=2	n=3	n=4	n=5		n=6			n=7
		K	L	M	N	O		P			Q
		s	s, p	s, p, d	s, p, d, f	s, p, d	f	s	p	d	s
Ac	89	2	8	18	32	18	—	2	6	1	2
Th	90	2	8	18	32	18	—	2	6	2	2
Pa	91	2	8	18	32	18	2	2	6	1	2
U	92	2	8	18	32	18	3	2	6	1	2
Np	93	2	8	18	32	18	4	2	6	1	2
Pu	94	2	8	18	32	18	6	2	6	—	2
Am	95	2	8	18	32	18	7	2	6	—	2
Cm	96	2	8	18	32	18	7	2	6	1	2
Bk	97	2	8	18	32	18	9	2	6	—	2
Cf	98	2	8	18	32	18	10	2	6	—	2
Es	99	2	8	18	32	18	11	2	6	—	2
Fm	100	2	8	18	32	18	12	2	6	—	2
Md	101	2	8	18	32	18	13	2	6	—	2
No?	102	2	8	18	32	18	14	2	6	—	2
Lr	103	2	8	18	32	18	14	2	6	1	2

In 1945 Seaborg suggested that this filling begins after actinium, resulting in a group of elements, having atomic numbers 90–103, similar to the lanthanides, which have been termed *actinides*. The actinide theory envisages an analogy between corresponding elements in the lanthanide and actinide families. However, the valency properties of the actinides have proved to be more complicated. With thorium, protactinium, and uranium the most characteristic compounds correspond to the higher valency indicated by the numbers of the groups in which Mendeleev placed them (Groups IV–VI respectively). Spectral investigations by W. F. Meggers (1947) showed that the first 5*f*-electrons probably appear only when protactinium is reached. W. H. Zachariasen's crystallographic measurements (1954) even led to the conclusion that metallic thorium, protactinium, and uraniun contain no 5*f*-electrons, and that metallic neptunium contains only one 5*f*-electron. On the other hand, the magnetic properties indicate the presence of 5*f*-electrons beginning with uranium. It is probable that the strength of bonding of 5*f*- and 6*d*-electrons is closely similar in the atoms of actinides. Furthermore, it is obviously weaker than that of 4*f*-electrons in the lanthanides.

Table 5 contains up-to-date information on the atomic structure of the actinides. For many of the elements, however, especially the higher actinides, these values are hypothetical, and have not yet been confirmed experimentally.

The original investigation of neptunium and plutonium had established that these elements exhibit variable valency—from 6 to 3—neptunium being mainly quinquevalent, and plutonium quadrivalent. It was supposed that all subsequent actinides would be tervalent. However, compounds of americium were soon obtained in which this element exhibited valencies of 4, 5, and 6, as well as compounds of quadrivalent curium and berkelium. The valencies of lanthanides and actinides are compared in Table 6.

Table 6. Valency of lanthanides and actinides.

Lanthanides			Actinides		
symbol	atomic no.	valency	valency	atomic no.	symbol
Ce	58	**3**, 4	**3**, 4	90	Th
Pr	59	**3**, 4	3, 4, **5**	91	Pa
Nd	60	3	3, 4, 5, **6**	92	U
Pm	61	3	3, 4, **5**, 6, 7	93	Np
Sm	62	2, **3**	3, **4**, 5, 6, 7	94	Pu
Eu	63	2, **3**	(2), **3**, 4, 5, 6	95	Am
Gd	64	3	**3**, 4	96	Cm
Tb	65	**3**, 4	**3**, 4	97	Bk
Dy	66	3	3, (4)	98	Cf
Ho	67	3	3	99	Es
Er	68	3	3	100	Fm
Tm	69	3	2, **3**	101	Md
Yb	70	2, **3**	2, 3	102	No
Lu	71	3	3	103	Lr

N. N. Krot and A. D. Gel'man have recently (1967) made the important discovery that neptunium and plutonium can exist in the septivalent state. If aqueous suspensions of neptunates(VI) and plutonates(VI)—K_2NpO_4 and K_2PuO_4—are oxidised with ozone in strongly alkaline medium, the deposits gradually dissolve to form dark green solutions of neptunates(VII) and plutonates(VII): e.g.

$$2K_2NpO_4 + O_3 + 2KOH = 2K_3NpO_5 + O_2 + H_2O \quad .$$

Several compounds of septivalent neptunium and plutonium have been obtained in the solid state from these solutions—$[Co(NH_3)_6]NpO_5.3H_2O$, $[PtCl(NH_3)_5]NpO_5$, $Sr_3(NpO_5)_2.nH_2O$, $Ba_3(NpO_5)_2.nH_2O$, $Ba_3(PuO_5)_2.nH_2O$—neptunium(VII) compounds being dark green, and plutonium(VII) compounds brownish black. They exhibit strong oxidising properties, this applying especially to septivalent plutonium. The oxidation of neptunium and plutonium to the septivalent state can be effected not only with ozone but also with hypochlorite, hypobromite, xenon compounds, and other active oxidants, necessarily in strongly alkaline medium.

A carrier method has recently been used to study the valency states of the shortest-lived far actinides, which have been used either in tracer quantities or as solitary atoms[6]. A bivalent state was found from entrapment with a barium sulphate precipitate, and tervalent and quadrivalent states were shown by extraction with 4-methylpentan-2-one or other solvent. The experiments showed that in aqueous solution mendelevium ($Z = 101$) occurs in the tervalent form, but can easily be reduced to the bivalent state with zinc dust, bivalent chromium, and other reductants. This distinguishes mendelevium from its formal lanthanide analogue thulium, with which the bivalent state is unknown.

In nitrate solutions element No. 102 was found to exist solely in the bivalent form, strong oxidising agents being required to convert it into the tervalent state. Here, too,

a fundamental difference from the properties of the lanthanide analogue, ytterbium, is observed.

Preliminary experiments on a small number of lawrencium atoms ($Z = 103$) indicated that this element is probably stably tervalent, although the possibility of its reduction or oxidation is not excluded. Lawrencium completes the family of actinides, and it should be similar to lutetium, which is characterised by tervalency.

The difference in properties, notably in valency, between lanthanides and actinides cannot be regarded as unexpected. It is completely explicable in terms of Mendeleev's Periodic Law. In each group of the Periodic System increase in the atomic numbers of analogous elements is accompanied by a definite change in their physical and chemical properties. This applies not only to individual elements but also to groups thereof, an example being the ionisation potentials (Fig. 4).

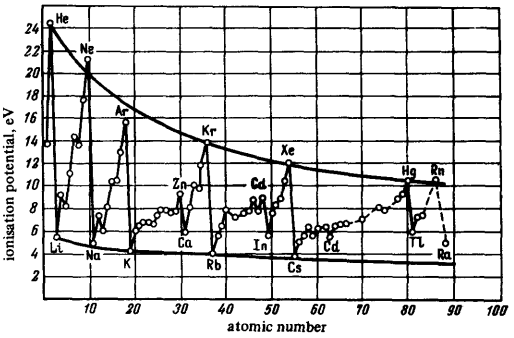


Figure 4. Ionisation potentials of the elements (for the first electron).

In each period of Mendeleev's system the highest ionisation potential corresponds to an inert gas, and the lowest to an alkali metal. With these and with other extreme elements the ionisation potentials diminish with increase in the atomic number, this undoubtedly being due to the increase in atomic radius resulting from the filling of increasingly remote electron shells of the atom. It is also significant that the difference between the ionisation potentials of the inert gas and the alkali metal shrinks considerably on passing to the end of the Periodic System. This explains the enhanced chemical activity of the heavy inert gases—xenon and radon—and also the ability of the near and intermediate actinides to exhibit a high and variable valency. It may be supposed that the far actinides will also give compounds of high valency, although under normal conditions their most characteristic valencies are 3 and 2.

The valency of element No. 104, kurchatovium, is of great interest. This element is not an actinide, but should be analogous to hafnium and quadrivalent. Zvara and coworkers[7] at the Joint Institute for Nuclear Research (in Dubna) used an elegant method to show that the valency of kurchatovium actually differs from that of the lanthanides and the far actinides (Fig. 5). The products of the nuclear reaction leading to the formation of $^{260}_{104}$Ku nuclei were carried away by a stream of nitrogen and chlorine with the addition of hafnium tetrachloride and niobium pentachloride through a special filter, which at 350°C retained the less volatile chlorides of the lanthanides and elements 101–103. After this the spontaneous fission counters detected element No. 104 as before, which indicates that it differs from the lanthanides and the actinides.

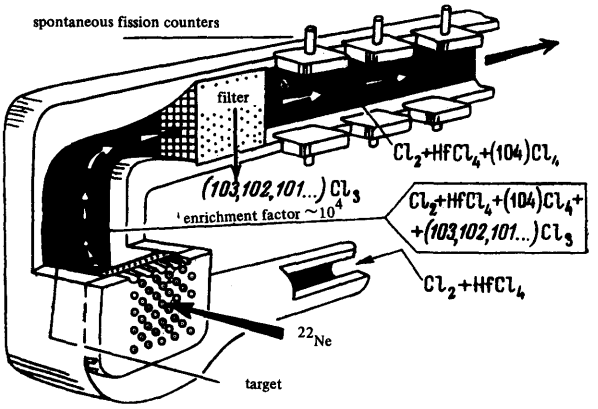


Figure 5. Diagram of apparatus for determining the valency state of element No. 104.

Formally element No. 105 should be an analogue of tantalum, element No. 106 of tungsten, and so on. However, in view of the energetic similarity of 5*f*- and 6*d*-electrons, the nearer transactinides (having $Z = 104–106$) may be expected to exhibit also an anomalous high valency, similarly to elements of the copper subgroup, where the higher valency is due to the closeness of the energy levels of the *d*- and outer *s*-electrons.

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A valuable contribution to the Periodic System has been made by a study of the chemical properties of Group 0 elements. During the 1930s B. A. Nikitin showed, using a method of cocrystallisation with sulphur dioxide hydrate $SO_2.6H_2O$, that radon and certain other inert gases form the hexahydrates $Rn.6H_2O$, $Ar.6H_2O$, $Ne.6H_2O$, etc. Later he found that radon interacts also with toluene, *p*-chlorophenol, and other organic compounds to yield the coordination compounds $Rn.2C_6H_5CH_3$, $Rn.3ClC_6H_4OH$.

The first compound of the inert gas xenon formed by means of a valency bond was obtained in 1962 by N. Bartlett, who found that platinum hexafluoride PtF_6, an extremely strong oxidant, was able to oxidise xenon to a compound having the formula $Xe^+(PtF_6)^-$. This is hydrolysed by water:

$$2XePtF_6 + 6H_2O = 2Xe + O_2 + 3PtO_2 + 12HF \ .$$

After this discovery other workers obtained the fluoride XeF_4 by the direct interaction of fluorine and xenon at 400°C followed by rapid cooling to room temperature. Xenon tetrafluoride is stable at ordinary temperatures. It is hydrolysed by water:

$$XeF_4 + 2H_2O = Xe + O_2 + 4HF \ .$$

Ultraviolet irradiation of a mixture of xenon and fluorine yields the difluoride XeF_2. With excess of fluorine at

high pressures (60–70 atm) the hexafluoride XeF_6 is also formed. On hydrolysis by water this compound forms a non-volatile solid product, which has proved to be xenon trioxide XeO_3. This solid is stable in light and air, but deliquesces in the presence of moisture. When heated, xenon trioxide explodes. It can also undergo disproportionation, with the formation of a tetroxide:

$$4XeO_3 = 3XeO_4 + Xe$$

The salts $CsHXeO_4$, $BaXeO_4$, termed *xenonates*, correspond to xenon trioxide, and *perxenonates* ($Na_4XeO_6.8H_2O$, $K_4XeO_6.9H_2O$, etc.) to xenon tetroxide.

The simple compounds of xenon known at the present time are listed below:

Valency			
2	4	6	8
XeF_2 $XeCl_2$ XeO	XeF_4 XeF_2 XeO_2	XeF_6 XeF_4 XeO_3F_2 XeO_3	(XeF_8) XeO_4

Xenon fluorides are white crystalline substances, which decompose when heated. They possess strong oxidising properties: for example, a mixture of the tetrafluoride and the hexafluoride ignites methanol and aqueous ammonia, and converts bivalent manganese into permanganic acid. Perbromates were first prepared by means of xenon fluorides.

Radon has been found to react with fluorine. Chemical compounds of radon will probably be more stable than those of the other inert gases. However, the strong radioactivity of this element makes study of its chemistry difficult. Only one compound of krypton KrF_2 has been obtained, and it is not very stable at ordinary temperatures. On theoretical grounds the formation of chemical compounds by argon, neon, and helium is improbable.

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The physical and chemical properties of elements and their compounds already began to be compared with the position of the corresponding elements in the Periodic System during the first few decades after the discovery of the Periodic Law. Increasing attention has recently been paid to the search for quantitative relations in this field. The following papers may be cited as examples.

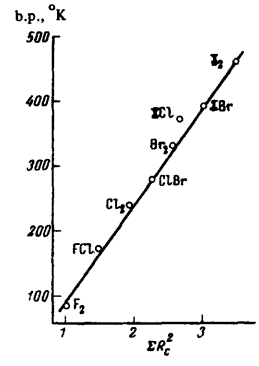


Figure 6. Dependence of boiling points of diatomic interhalogen compounds on covalent radii of halogen atoms.

G.R. Somayajulu and S.R. Palit (1957) studied the relation between the boiling point of various halogen derivatives and the dimensions of the atoms they contained. It was found that the boiling point of members of a given series of halogen derivatives, e.g. interhalogen compounds, was a linear function of the surface area of the halogen atoms calculated for the given molecule. The boiling point can be calculated by means of the formula $T_b = a\Sigma R_c^2 + b$, where T_b (°K) is the boiling point, R_c are the covalent radii of the halogen atoms in the molecule, and a and b are constants.

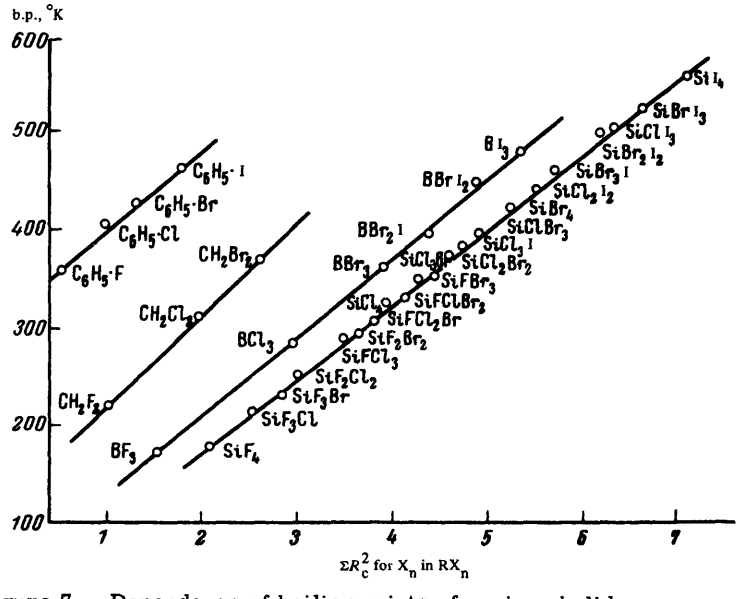


Figure 7. Dependence of boiling points of various halides on covalent radii of halogen atoms.

Fig. 6 shows the applicability of this formula to determining the boiling points of interhalogen compounds of the type X_2, and Fig. 7 those of four series of halogen derivatives of various types.

Z. Szabo and B. Lakatos (1952) put forward the view that the physical properties of uncombined elements (their melting and boiling points, heats of sublimation) depend not only on the atomic numbers but also on the fine distribution of electrons among s-, p-, and d-sublevels.

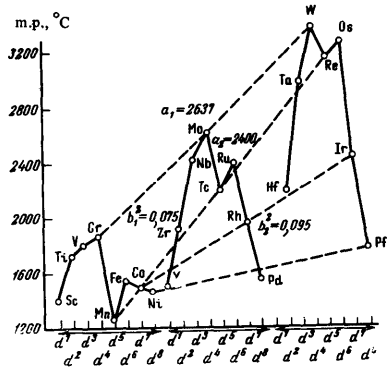


Figure 8. Melting points of the transition elements.

This leads to additional periodicity within each period of Mendeleev's system. Fig. 8 illustrates this phenomenon for the melting points of the transition metals in three long periods. Points representing the melting points of analogous elements usually lie on straight lines. To calculate the melting points of elements these workers proposed the equation

$$T = a_1 e^{-b_1^2(d-4)^2} + a' e^{-b'^2(d-5)^2}(n-n_5), \quad \text{if} \quad d \leqslant 5$$

or

$$T = a_2 e^{-b_2^2(d-6)^2} + a' e^{-b''^2(d-5)^2}(n-n_5), \quad \text{if} \quad d \geqslant 5$$

where T is the melting point, a_1, a_2, b_1, and b_2 are constants of the periodic curve, a', b', and b'' are constants in the function representing the slope of the curve, n is the principal quantum number, and d is the number of d-electrons if the whole calculation is derived from the properties of elements in the fifth period (n_5). The average difference between calculated and experimental values was 4%.

An. N. Nesmeyanov and N. E. Khandamirova (1960) found quantitative relations between the heats of sublimation of elements ΔH°_{298} and their positions in the Periodic System. Regarding the lattice energy of a solid as a function of two main variables—the interatomic distance r and the atomic weight A—these workers established that the quantity $\Delta H^\circ_{298} A/r$ is a linear function of the atomic weight within each subgroup of the Periodic System. Heats of sublimation can be calculated from the appropriate graphs. In most cases satisfactory agreement is found between calculated and experimental values. Deviation is observed in the copper and zinc subgroups, which is explained by penetration of s-electrons below the screen of d-electrons and the resultant relative decrease in size of the atoms.

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The centenary of the Periodic Law has revealed the whole multiplicity of its applications in chemistry, physics, and several related fields of knowledge. It has not only explained many known facts, but has enabled new, frequently unexpected phenomena to be predicted. However, the successes achieved do not mean that the possibilities of the Periodic Law are exhausted. As a guiding light it will always indicate to researchers the path to new discoveries, while the name of its author, the great Russian scientist Dmitrii Mendeleev, has been introduced forever into the golden tables of modern science.

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