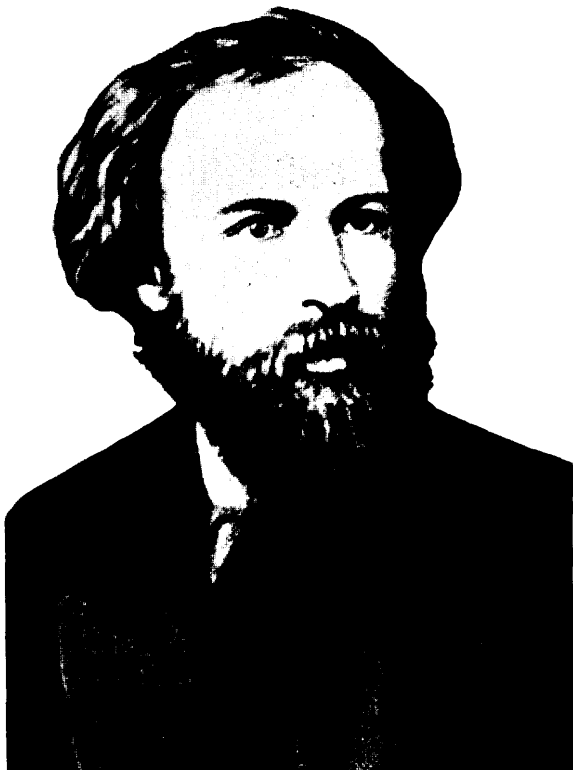# THE CENTENARY OF D.I. MENDELEEV'S PERIODIC LAW*

V.I. SPITSYN

M.V. Lomonosov
Moscow State University,
Moscow,
Union of Soviet
Socialist Republics

Dmitri Ivanovitch Mendeleev

One hundred years ago, in the early days of March 1869, Professor Dmitri Ivanovich Mendeleev of the St. Petersburg University sent to many scientists, both in Russia and abroad, a leaflet featuring his method of arranging the chemical elements using a system based on their atomic weights and chemical similarities (Fig.1).

On the 18 March 1869, Mendeleev's paper on this subject was read at the Meeting of the Russian Chemical Society, and in May of the same year the Society published in its Journal his article entitled "The correlation between properties of elements and their atomic weights" [1]. In this article Mendeleev gave his first formulation of the Periodic Law as "Elements arranged in order of their atomic weights display a marked periodicity in their properties". Later Mendeleev reformulated his Periodic Law more exactly: "Properties of elements as well as the forms and properties of their compounds are in a periodic relation to the atomic weights of the elements."

The discovery of the Periodic Law and, as a result, of a natural system for classifying chemical elements was made by Mendeleev while working on his classical textbook on inorganic chemistry entitled

---

* This talk was given at the IAEA, Vienna, in celebration of the centenary of the publication of Mendeleev's Periodic Table.

ESSAI D'UNE SYSTÉME DES ÉLÉMENTS

D'APRES LEURS POIDS ATOMIQUES ET FONCTIONS CHIMIQUES,

par D. Mendeleeff,

profess. de l'Univers. à S-Pétersbourg.

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

$$18\overset{III}{=}69$$

FIG.1. First representation of the Periodic Table of chemical elements by D.I. Mendeleev (1869).

"Principles of Chemistry", which he began in 1868. "There are many original facts there ..., and in pride of place, the periodicity of the elements, which I discovered at the time I was going through the Principles of Chemistry", noted Mendeleev later on [2].

Attempts to classify elements in groups and tables had been made before Mendeleev's efforts. One may recall the Döbereiners' triads (1829) (Ca, Sr, Ba; Li, Na, K; Cl, Br, I; S, Se, Te) that were developed to Pettenkofer's groups (1850) (N, P, As, Sb; Mg, Ca, Sr, Ba; etc.), de Chancourtois' spiral (1862), Odling's (1864) and Lothar Meyer's (1864) tables, and Newlands' octaves (1866). Yet, all this work was concerned either with some particular question of chemical resemblance between the members of the groups of elements, or with the relationships existing between their atomic weights or atomic volumes. None of these authors had attempted to elucidate the general relationship between the properties of all known chemical elements, that is no one until Mendeleev formulated his Periodic Law.

One event of historical importance that must be mentioned is the First International Chemical Congress that was held in Karlsruhe in 1860. Among the 140 delegates were Kekulé, Cannizzaro, Wöhler, Liebig, Dumas, Bunsen, Lothar Meyer, and Mendeleev. Here, Cannizzaro, filled with missionary fervour, revived Avogadro's Hypothesis, which had lain dormant for half a century, and persuaded many of the distinguished chemists that, using the hypothesis together with Gay Lussac's law of gaseous combination, Berzelius' determinations of atomic weights could be justified. It became clear that atomic weights were a basic requirement that lead to consistent sets of formulae for chemical compounds, and a measure of order was introduced into chemistry. This sense of discipline and the importance of atomic and molecular weights, already mentioned by Mendeleev in his book on organic chemistry in 1861, was the starting point for his endeavours to put some order into the jumble of chemical elements.

It is to be noted that though Mendeleev did stress that "the magnitude of the atomic weight determines the character of the element", he did not consider the atomic weights as being the only factor of importance in the characterization of chemical elements. Of no lesser importance for the determination of the position of elements in the periodic system were the chemical properties of elements as seen in the compounds formed by these elements. For this reason, Mendeleev placed certain elements in his Periodic Table not in complete accordance with the order of their atomic weights; this was the case for cobalt and nickel, tellurium and iodine.

The principle of outstanding importance for the philosophy of science in the discovery made by Mendeleev was that it disclosed the existence of specific interrelationships in the chemical and physical properties of all chemical elements. The groups and series of the periodic system could be used as a firm basis for identifying families of related elements.

The first practical application of the Periodic Law was to correct certain valencies and atomic weights that had been incorrectly assigned. This involved, in particular, indium, cerium and other rare-earth elements, thorium and uranium.

Indium had been considered to be a bivalent element and, to accord with its atomic weight[1] (75.6), was placed between arsenic and selenium - though its properties were evidently very far removed from those of the latter two elements. Measurement of the heat capacity of metallic indium and detailed considerations of its properties led Mendeleev to the conclusion that indium in its highest state of oxidation must be considered as trivalent. Hence, the revised atomic weight of this element was calculated as 113 and it was placed in Group III of the Periodic Table, between cadmium (Cd=112) and tin (Sn=118), in full agreement with its chemical properties. This position in the table had, however, been occupied by uranium, thought to be trivalent and to have the atomic weight of 116. Mendeleev studied the compounds of uranium and realized that they were more similar to those of molybdenum and tungsten (Group VI) than to those of aluminium (Group III): doubling the atomic weight of uranium made it possible to place it in Group VI of the Periodic Table.

Similar considerations were brought forward by Mendeleev in substantiating the trivalency of cerium-group rare-earth elements such as lanthanum that had been considered by many chemists as bivalent. He assigned to the highest oxide of cerium the formula CeO_2, and to that of thorium the formula ThO_2 (instead of ThO). He then estimated appropriate new values for the atomic weights of these elements.

Mendeleev's task was, of course, a very difficult one. It must be recalled that there were no direct methods for measuring atomic weights of elements at that time, and the only help was provided by the Dulong and Petit's Law of atomic heat capacity.

An eminent specialist in the field of rare-earth elements, Rammelsberg, is known to have been against changing the atomic weights of cerium, didymium and lanthanum as proposed by Mendeleev, and Lothar Meyer wrote that "it would be premature to change the currently accepted atomic weights on the basis of such a precarious starting point" – the Periodic Law.

Based on the similarities of properties of osmium, rubidium and iron, Mendeleev suggested that the then accepted atomic weights of the platinum metals would have to be revised so that they would increase as Os < Ir < Pt < Au. This was later substantiated experimentally. However, his suggestion that the atomic weight of tellurium should be lower than that of iodine was not confirmed. It is now known that this anomaly is due to the character of the natural abundances of the isotopes of these two elements rather than to the chemical properties of their atoms.

Despite the apparent contradiction to the general rule of the periodic system – placing of elements in the order of increasing atomic weights - Mendeleev left tellurium in Group VI and iodine in Group VII to correspond with their respective valencies and chemical properties.

Working very diligently Mendeleev had managed to formulate in a short time, less than two years after his original communication, the Periodic Table of chemical elements as it is, in principle, still used to-day (Fig.2).

In the course of his work, his theories suggested to him that there were vacant places in the Periodic Table, and in his first paper on the

_____

[1] This figure and the following are those used formerly for the atomic weights considered.

Ряды	Группа I — R²O	Группа II — RO	Группа III — R²O³	Группа IV RH⁴ RO²	Группа V RH³ R²O⁵	Группа VI RH² ·RO³	Группа VII RH R²O⁷	Группа VIII — RO⁴
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=88)	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=231	—	U=240	—	— — — —

FIG.2.   The Periodic Table as arranged by Mendeleev in 1872.

Periodic Law, Mendeleev had already voiced the opinion that there were still many elements to be discovered. As examples, he forecast one element that should resemble aluminium and one that should resemble silicon in chemical properties, and whose atomic weights should lie in the region 65 to 75. Mendeleev was deeply convinced that the best proof of the main assumptions of his Periodic Law would be the embodiment of his predictions. Therefore in 1871, some two years after the discovery of his Law, he published an article in which he gave a detailed description of the physical and chemical properties of some as then undiscovered elements [3]. He wrote ... "I have made up my mind to do this so that, in due time, when one of the elements that I have predicted is discovered, I shall have the opportunity to be fully convinced and to convince other chemists of the validity of the assumptions underlying the system I am advancing."

In this article Mendeleev laid special emphasis on the expected properties of three elements that he felt must be missing if his Law was to hold. These elements were analogues of boron, aluminium and silicon, and he termed them ekaboron, eka-aluminium and ekasilicon[2].

The elements predicted by Mendeleev were discovered soon afterwards. In 1875 the French chemist P.E. Lecoq de Boisbaudran, using the newly developed tool of spectroscopy, found in the Pyrenean ore sphalerite a new element whose properties coincided with those predicted by Mendeleev for eka-aluminium; Boisbaudran termed the element gallium.

Then in 1879, the Swedish chemist L.F. Nilson, studying rare-earth elements isolated from Scandinavian minerals, gadolinite and euxenite, a new rare-earth element he named scandium; his colleague Cleve pointed out that it coincided with Mendeleev's predicted properties for ekaboron.

---

[2] Eka = one (Sanskrit): it was used by Mendeleev in the sense of the first and nearest analogue.

Finally, in 1886, the German chemist C.A. Winkler, using his own system of gas analysis for determining the constituents of the mineral argyrodite, eventually isolated a new element, germanium. Its properties coincided remarkably (Table I) with the element ekasilicon predicted by Mendeleev. Winkler himself wrote..."One can hardly find a more striking proof of the Law of Periodicity than the embodiment of the hypothetical eka-silicon in the recently discovered element. This is not only a substantiation of a bold theory. This evidently points to the widening of chemical horizon, to a mighty step forward in the field of knowledge."

The expected properties of the yet undiscovered analogues of manganese, caesium, barium, lanthanum and tantalum were also pre-dicted by Mendeleev, though in less detail. Some of these elements were discovered during his lifetime (radium, actinium and polonium), others in the 20th Century (technetium, rhenium, francium and protactinium).

The periodic system emerged victorious from a serious test it had to undergo at the end of the 19th Century. When Lord Rayleigh and W. Ramsay discovered an unknown gas in air (1894), it turned out to be an element that seemed to have no place in the Periodic Table. However, the gas proved to be inert, and so it was allotted a valency of zero and named argon (Greek for inert). Then followed the discovery by Ramsay that the gas coming from the mineral cleveite was not nitrogen but helium, and this suggested that there must be a whole group of non-reactive elements like argon.

In 1897 Ramsay gave a lecture in which he discussed a still undiscovered gas: he commented ... "Following the example of our teacher Mendeleev, I have described, as far as it was possible, the expected properties and presumed relation of a gaseous element that would fill up the gap between helium and argon." The gas with atomic weight 20 was soon afterwards isolated by Ramsay from 15 litres of argon that had taken months to prepare, and he named it neon. During the fractionation he also discovered two heavy analogues of argon, krypton and xenon. The evidence obtained at that time pointed to the fact that all these gases were inert and unable to undergo common chemical redox reactions. Therefore the family of inert gases (0 valency) was added to the Periodic Table as a newly found Group 0[3]. To this group was added in 1900 the radioactive element radium emanation (radon), found by F.E. Dorn, the atomic weight of which was determined by Ramsay.

The discovery of elements predicted by Mendeleev, the good cor-respondence of estimated and measured properties, the verification of many corrections made by Mendeleev to the atomic weights of various elements, strengthened the materialistic conception of chemical elements, and vastly enlarged the possibilities of understanding nature. The periodic system became a powerful basis for the further development of chemistry and physics.

The Periodic Law enabled scientists to compare the various properties of chemical elements and their compounds. Mendeleev (1869) had de-scribed the periodicity of some forms of compounds of the elements, that is, the periodicity of that most important chemical property, valency. He had also shown a periodicity in the changes of the specific weights of

---

[3] About chemical compounds of inert gases see later.

TABLE I. GERMANIUM PROPERTIES, PREDICTED AND FOUND

Property	Predicted for ekasilicon (Es)	Found[a] for germanium (Ge)
Atomic weight	72	72.60
Valency	Tetravalent, but can exhibit lower valency states	4 and 2
Specific heat	0.073	0.076
Atomic volume	13	13.4
Specific weight	5.5	density 5.35 (5.47)
Fusibility and volatility	Meltable metal that can become volatile at high temperature	(m.p. 958.5°C) (b.p. 2700°C)
Highest oxide	EsO_2	GeO_2
Molecular volume	22	22.2
Specific weight	4.7	(4.703)
Chemical properties	Acidic, but shows some basic properties	Amphoteric, with predominance of acidic properties
Fluoride	EsF_4, not a gas	$GeF_4 \cdot 3H_2O$, solid
Highest chloride	$EsCl_4$, liquid	$GeCl_4$, liquid
m.p.	90°C	85°C (86.5°C)
Specific weight	1.9	density 1.879
Chemical properties	decomposed by water	readily hydrolysed by water
Hydrogen compounds	Hydrogeneous compounds might be also expected, especially EsH_4 EsH_4 should be readily decomposed to hydrogen and metal	GeH_4 and other germanium hydrides have been prepared GeH_4 decomposes at 350°C
Organometallic compounds	will, of course, form organo-metallic compounds	Numerous germanium organic compounds have been obtained
Typical compound	$Es(C_2H_5)_4$	$Ge(C_2H_5)_4$
b.p.	160°C	163.5°C
Specific weight	0.96	0.991

[a] Figures in parentheses are later results.

free elements in relation to the atomic weights. Other scientists showed
that melting points of free elements also exhibited periodicity.

Periodicity was observed in the melting points of the metal chlorides,
and in the heats of formation of chloro-, bromo- and iodo- compounds
with increasing atomic weight of element reacting with the halogen.

Mendeleev (1889) also pointed to a periodicity in the structure of spectra
of elements, depending on their atomic weights.

A connection between the place of elements in the Periodic Table and
their magnetic properties has been shown. A.A. Baikov (1902) showed by
his investigation of copper alloys the applicability of periodicity to the
composition of metal compounds formed in alloys.

For many years following the formulation of his Periodic Law,
Mendeleev had been busy perfecting his Table, using it both in the short
and long forms. Figure 3 shows the last version of the Periodic Table
as proposed by Mendeleev shortly before his death in 1907.

The Periodic Law and the ensuing ordering of the system of elements
became fully accepted within Mendeleev's lifetime. However, several
points in the system still remained obscure.

For example, it was not clear whether there should be elements be-
tween hydrogen and helium, the number of rare-earth elements was not
defined, neither was their position in the periodic system understood.
These unknowns made it impossible to calculate the total number of
elements between hydrogen and uranium. The very reason for the perio-
dicity itself was not clear. In retrospect, one can only wonder how
Mendeleev could have composed his periodic system of elements at a time
when there was an almost complete lack of understanding about the
structure of matter. His system even now, after a century, has not
required any basic change. This is sufficient evidence of his genius.

From the beginning of the 20th Century, the Periodic Law played a
major part in the development of chemical and physical studies on the
structure of matter.

One need only note the vital place of the Periodic Table in the elucida-
tion of the phenomena of radioactivity and discovery of isotopes.

In 1896 Becquerel discovered the so-called "uranium rays". Their
remarkable properties led to numerous investigations, and Becquerel's
realization that these rays represented matter coming from the atom,
launched a new field of science. In addition to uranium another heavy
element, thorium, was also shown to be radioactive. In 1898 Marie and
Pierre Curie described two new elements they had found in uranium
minerals – radium and polonium – both having a higher radioactivity
than uranium. They isolated their pure preparations from the wastes of
uranium ore treatments. Their radium proved to be an analogue of
barium with properties corresponding to those predicted by Mendeleev
for ekabarium. The properties of polonium were shown to be very similar
to those of ekatellurium.

In 1899 Debierne found in pitchblende yet another radioelement,
actinium, an analogue of lanthanum, predicted by Mendeleev in as early
as 1871.

In 1900 Dorn established that radium preparations continuously give
off a radioactive gas, now known as radon, that was proved to be an

Періодическая система элементовъ по группамъ и рядамъ.

Ряды	0	I	II	III	IV	V	VI	VII	VIII
					ГРУППЫ ЭЛЕМЕНТОВЪ:				
1	—	Водо-родъ **H** 1.008	—	—	—	—	—	—	—
2	**He** 4.0	**Li** 7.03	**Be** 9.1	**B** 11.0	**C** 12.0	**N** 14.01	**O** 16.00	**F** 19.0	
3	Неонъ **Ne** 19.9	**Na** 23.05	**Mg** 24.36	**Al** 27.1	**Si** 28.2	**P** 31.0	**S** 32.06	**Cl** 35.45	
4	Ар-гонъ **Ar** 38	**K** 39.15	**Ca** 40.1	**Sc** 41.1	**Ti** 48.1	**V** 51.2	**Cr** 52.1	**Mn** 55.0	**Fe Co Ni (Cu)** 55.9 59 59
5		**Cu** 63.6	**Zn** 65.4	**Ga** 70.0	**Ge** 72.5	**As** 75	**Se** 79.2	**Br** 79.95	
6	Крип-тонъ **Kr** 81.8	**Rb** 85.5	**Sr** 87.6	**Y** 89.0	**Zr** 90.6	**Nb** 94.0	**Mo** 96.0	—	**Ru Rh Pd (Ag)** 101.7 103.0 106.5
7		**Ag** 107.93	**Cd** 112.4	**Jn** 115.0	**Sn** 119.0	**Sb** 120.2	**Te** 127	**J** 127	
8	**Xe** 128	**Cs** 132.9	**Ba** 137.4	**La** 138.9	**Ce** 140.2	—	—	—	— — —
9				—	—	—	—		
10	—	—	—	**Yb** 173	—	**Ta** 183	**W** 184	—	**Os Jr Pt (Au)** 191 193 194.8
11		**Au** 197.2	**Hg** 200.0	**Tl** 204.1	**Pb** 206.9	**Bi** 208.5	—	—	
12	—	**Rd** 225	—	**Th** 232.5	—	**U** 238.5			

Высшіе солеобразные окислы

R   R²O   RO   R²O³   RO²   R²O⁵   RO⁷   R²O⁷   RO⁴

Высшіе газообразныя водородныя соединенія

RH⁴   RH³   RH²   RH

Д. Менделеевъ.
1869 – 1905.

FIG.3.   Mendeleev's representation of the Periodic Table in 1905.

analogue of xenon belonging in Group 0 of the Periodic Table. The re-markable property of this element lies in its rapid decay with a half-life of 3.85 days. Ramsay and Soddy then discovered that when radon was sealed into a discharge tube, the spectrum obtained altered with time to include a helium spectrum. This was the first experimental proof (1903) that one element was transmuted into another.

Mendeleev was rather sceptical about the possibility of transmutation of elements, pointing out that all such reports need extremely careful checking as they usually cannot be confirmed. At the same time he considered himself to be "not an adversary of the notion of complexity of elements but was, rather, in favour of it". He wrote (1898) that: "It would be very interesting to witness the establishment of proof for the transmutation of elements, because in that case I could hope that the reasons for the Periodic Law would be discovered and understood."

In 1902 Rutherford and Soddy very thoroughly studied the radioactivity of thorium and advanced a hypothesis that radioactivity resulted from the transmutation of one type of atom into another and, hence, in transmutation of elements. Further experimental evidence fully substantiated this suggestion.

The investigation of radon showed that the so-called "active precipitate" left after its decay contained a number of elements differing in their radioactive properties, i.e. in the character and energy of radiation. Many radioelements were found in these studies of the decays of uranium, actinium and thorium.

Not all new radioelements could be fitted into blank positions in the Periodic Table. The investigation of numerous radioelements, members of various radioactive families, showed that though certain of them exhibited different radioactive properties they could not be chemically distinguished from each other or from a given known element. Thus, for example, one product of uranium decay, radioelement ionium, displays radioactivity that is markedly different from that of thorium, though it cannot be separated from thorium chemically. One of the first products of thorium decay, radiothorium, disintegrates considerably faster than thorium, but they too are chemically indistinguishable. Radioelements were, in fact, found that corresponded chemically with uranium, thorium, radium, lead, bismuth and other elements of the two lower series of the Periodic Table. It appeared that a specific chemical element could be accounted for by several kinds of atoms differing in mass and the radioactive decay rate.

In 1913 Soddy proposed for these variants of a chemical entity the name isotopes (from Greek, meaning same place), thereby denoting as their characteristic the occupation of the same position in the Periodic Table.

The numerous radioelements formed on disintegration of uranium, thorium and actinium were now united in families in full agreement with Mendeleev's Periodic Law.

Every element that underwent an alpha decay gave as a product an isotope of the element that occupied the place two positions nearer to the lower end of the periodic system, and every beta decay resulted in an isotope of the element one position higher up the system. The so-called Rule of Transmutation, due to K. Fajans, led to the discovery of many new radioelements and made it possible to elucidate many unknown positions in radioactive families.

In 1912 Thomson made experiments in which he deflected streams of positively-charged ions with magnetic fields such that ions of different charge-to-mass ratios fell on different portions of a photographic plate. He discovered that neon was a mixture of two types, and realized that

non-radioactive elements could also have isotopes. The development by Aston of the mass spectrograph has led to the discovery of isotopes of a number of common elements.

The study of isotopes has brought an additional contribution to the periodic system. The ideas of A.M. Butlerov, W. Crookes and other scientists about the possible existence of variations of atoms of one and the same element with somewhat differing mass were soundly substantiated. Again, a marked difference in chemical properties has resulted in the discovery of hydrogen isotopes thus creating a new chapter of science, that of isotope chemistry, closely linked to the periodic system.

DEVELOPMENT OF ATOMIC PHYSICS

The discovery of radioactivity and the rapid development of atomic physics at the beginning of the 20th Century are known to have resulted in the nuclear theory of atomic structure (Rutherford, 1911), in the law relating the wavelengths of characteristic X-ray spectra of elements to the charges of their atom nuclei (Moseley, 1913), and in the development of fundamentals of the quantum theory of atomic structure (Bohr, 1913).

The Periodic Law strongly affected the development of these scientific theories by providing scientists with a logical system of ordering chemical elements potentially involving regularities of the atomic structures.

In return, the current theories of atomic structure helped to account for the periodicity per se and led to further improvement in methods for forecasting unknown elements.

Of particular importance was the method for experimental determination of charges of atomic nuclei, based on Moseley's rule. This method made possible a strict determination of the numbers of elements in the periodic system and made it possible to define the maximum number that lie between hydrogen and uranium. The validity of the distribution of the elements in Mendeleev's Periodic Table has thereby been proved. The atomic number of iodine (atomic No. 53) was confirmed as lower than that of tellurium (atomic No.52). In 1914 the periodic system had vacant positions for numbers 43, 61, 72, 75, 85, 87 and 91, with 61 and 72 belonging to the Group III large period.

The theory of atomic structure has provided an explanation for the peculiar status in the periodic system of the rare-earth elements that are placed after lanthanum in Group III. It was found that this part of the system involved the electrons in the atoms of the elements beginning with cerium, the electrons that are in the deep electron shell of the fourth energy level at the sublevel 4f. This shell can contain up to 14 electrons, and the series ends with lutetium. The number of valency electrons remains unchanged at three, as with lanthanum. This gave rise to the name lanthanides for the elements of the family Ce to Lu. These lanthanides are taken to occupy the same position as lanthanum, and they are usually listed separately. This classification was suggested by the Czech chemist B. Brauner in 1901.

The structure of electron shells of atoms of rare-earth elements is, according to recent data, as schematically given in Table II.

It will be seen from Table II that two valency electrons of lanthanides are referred to the sublevel 6s, the third is usually abstracted from the

TABLE II. THE STRUCTURE OF ELECTRON SHELLS OF ATOMS OF THE RARE-EARTH ELEMENTS

Element	Atomic No.	n=1 K s	n=2 L s,p	n=3 M s,p	n=3 M d	n=4 N s	n=4 N p	n=4 N d	n=4 N f	n=5 O s	n=5 O p	n=5 O d	n=6 P s
Sc	21	2	8	8	I	2							
Y	39	2	8	8	10	2	6	I		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 main quantum number; K, L, M are the energy levels in atoms; s, p, d, f are the electron groups.

sublevel 4f, whereas only some representatives of this series have an electron at the sublevel 5d. At the beginning of the formation of the 4f electron shell the electrons involved are not bound very strongly. Therefore cerium, praseodymium and, as appears to be the case, neodymium can form compounds in which they are tetravalent. Later the increasing charge on the nucleus strengthens the structure of the shell. It must be noted that it seems to fill in two layers, each consisting of seven electrons. Therefore terbium can also form compounds of higher valency because it is characterized by the filling of the second layer. Elements preceding gadolinium (samarium, europium) and lutetium (ytterbium) can, on the other hand, stabilize their structure by abstracting fewer electrons and be bivalent under certain conditions.

Further experiments have proved an important regularity concerning the change in the size of lanthanide atoms [4]. Electrons in the deep 4f

TABLE III. ION RADII OF TRIVALENT RARE-EARTH ELEMENTS

Ion radius (Å)								
Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu
0.68	0.88	1.04	1.02	1.00	0.99	(0.98)	0.97	0.96

Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
0.94	0.92	0.91	0.89	0.87	0.86	0.85	0.84

level do not completely screen the increasing charge on the nucleus.
Therefore the electrons of the outer shells are constricted around the
nucleus and the overall size of the atom actually decreases (lanthanide
contraction, see Table III).

Lanthanide contraction leads to weakening of the basic properties of the
hydroxides in the series La to Lu. If La(OH)$_3$ is similar in properties to
Sr(OH)$_2$, Lu(OH)$_3$ is a weak base that is somewhat similar in this respect
to scandium hydroxide, an element occurring far earlier in the same group
of the Periodic Table. Dysprosium and holmium correspond more nearly
in this respect to yttrium.

Thus, the structural resemblance of the outer electron shell of atoms
and the lanthanide contraction have made of scandium, yttrium, lanthanum
and the lanthanides a closely interwoven block of elements of which several
exist together in many minerals. This, of course, is what has made it so
difficult to separate, purify and then identify them.

The theory of atomic structure has shown that element No. 72, follow-
ing lutetium, must have two valency electrons at sublevels 6s and 5d each,
making it tetravalent and an analogue of zirconium rather than of the rare-
earth elements [4]. Starting from this assumption G. de Hevesy and
D. Coster in Denmark undertook to find this element in zirconium pre-
parations by means of X-ray spectroscopy. In 1923 they succeeded in
finding it and named it hafnium (Hf = 178.5). It must be noted that a
zirconium analogue with atomic weight of 180 had been envisaged by
Mendeleev in the very first variant of his Table (see Fig. 1).

Thus the enigma posed by the rare-earth elements in the periodic sys-
tem had been solved. The elements that were absent in the periodic system
when Moseley proposed his law were soon isolated from raw materials or
synthesized in nuclear reactions.

In 1918, L. Meitner and O. Hahn in Germany isolated from wastes of
uranium ore treatment a radioactive element No. 91, protactinium. In 1925
W. Noddack, I. Tacke and O. Berg discovered in native platinum, tantalite,
and molybdenite element No. 75, and named it rhenium. The discovery
claimed by the same authors of element No. 43 was not substantiated. This
element was discovered in 1937 by K. Perrier and E. Segrè in a sample of
molybdenum that had been irradiated for a long time by a powerful flux of
deuterons in a cyclotron. The nuclear reaction was $_{42}$Mo(d, n)43. When
the element had been identified, it was named technetium to stress that it
had been obtained artificially. Technetium was subsequently found in large

amounts in fission fragments of uranium and could be isolated from atomic industry wastes.

In 1939 Marguerite Perey, while investigating the products of the natural radioactive decay of actinium, found a radioactive isotope ($T_{\frac{1}{2}}$ = 21 min) similar in chemical behaviour to caesium. This proved to be element No. 87, ekacaesium, also predicted by Mendeleev. It is now known as francium.

The radioactive isotope of eka-iodine, element No. 85 ($T_{\frac{1}{2}}$ = 7.5 h), was discovered in 1940 by D.R. Corson, K.R. MacKenzie and E. Segrè by bombarding bismuth with accelerated helium nuclei having an energy of 38 MeV. The process proceeds according to the following scheme: $^{209}_{83}Bi$ ($^{4}_{2}He$, 2n) 85^{211}. The name given to the element, astatine, reflects its instability.

And, last but not least, the element No. 61, that has been unsuccessfully sought by many chemists in rare-earth preparations, was found in 1947 in uranium fission products by J. Marinsky, L. Glendenin and C. Coryell. It was obtained in the form of two radioactive isotopes with half-life decay periods of 55 h and 2.6 years. The element was named promethium in recognition of the discovery of the practical use of atomic energy, a feat that was compared by the discoverers of the element with Prometheus' in bringing fire to mortals.

Thus, by 1947 all the places of the Periodic Table between hydrogen and uranium had been filled.
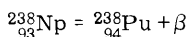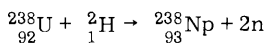

THE TRANSURANIUM ELEMENTS

Important new problems have arisen with the successful synthesis of new heavy elements [5]. Mendeleev had, in fact, allowed for the possibility that the periodic system might be extended beyond uranium, and his suggestion had been found to be justified.

The synthesis of transuranium elements gained prominence in the 1930s, when E. Fermi and his co-workers proposed their method for artificial preparation of radioisotopes, using slow (thermal) neutrons. In 1935 they found in uranium irradiated by neutrons several short-life β-radioisotopes, one of which ($T_{\frac{1}{2}}$ = 13 min) was precipitated with manganese and rhenium and considered to be an analogue of rhenium $^{239}_{93}EkaRe$. Yet, further investigations by L. Meitner, O. Hahn and G. Strassman showed these experiments to give rise to many radioisotopes, uranium fission fragments, that coprecipitated with various elements. Among them was found a β - emitter ($T_{\frac{1}{2}}$ = 28 min) whose chemical properties did not differ from those of uranium and it was considered to be the isotope $^{239}_{92}U$. β-decay should have transmuted it to element No. 98. The authors failed, however, to find the new element due to the weakness of the neutron source used.

Element No. 93, named neptunium (Np), was discovered by E. McMillan and P. Abelson in 1940 when irradiating thin layers of ammonium uranate with a powerful flux of neutrons that had been produced by bombarding the beryllium target with deuterons of 16 MeV energy in the large cyclotron of the University of California. The fragments resulting from the uranium fission were removed by recoiling. The irradiated preparation revealed two types of β-activity, with $T_{\frac{1}{2}}$ = 28 min and 2 to 3 days. The first isotope

type was recognized as being $^{239}_{92}$U. The transmutation of the first emitter into the second one was considered as proof of the formation of element No. 93. McMillan and Abelson concluded that neptunium was not an analogue of rhenium. Neptunium was found to exhibit no less than two forms of oxidation. In the lower one neptunium was similar to the rare-earth elements, in the higher one to uranium.

The β-decay of neptunium had to give rise to element No. 94, which became known as plutonium (Pu). Its first isotope, $^{238}_{94}$Pu ($T_{\frac{1}{2}}$ = 89.6 yr) was synthesized by the end of 1940 by G. Seaborg, E. McMillan, J. Kennedy and A. Wahl by deuteron bombardement of uranium in a cyclotron. The intermediate product obtained was $^{238}_{93}$Np ($T_{\frac{1}{2}}$ = 2.1d):

$$^{238}_{92}U + {}^{2}_{1}H \rightarrow {}^{238}_{93}Np + 2n$$

$$^{238}_{93}Np = {}^{238}_{94}Pu + \beta$$

The trace amounts of this isotope were used to investigate the main chemical properties of the new element and its separation from uranium. In the state of highest valency, plutonium is rather similar to uranium but is reduced more easily. The properties of its compounds of lower valency resemble those of thorium and the rare-earth elements. However, due to wartime restrictions the first data on plutonium were only published as late as in 1946.

In 1941, prolonged bombardment of uranium with deuterons had permitted the discovery of a plutonium isotope ^{239}Pu, having a longer life-time ($T_{\frac{1}{2}}$ = 24 360 yr) and capable of fission by slow neutrons. For this reason it was to become of great practical value as a fuel for atomic reactors.

Laborious work on the irradiation of tens of kilograms of uranyl nitrate with neutrons in a cyclotron had resulted by the end of 1942 in the production 0.5 mg of pure plutonium. These investigations were carried out in the first laboratory uranium reactor, started on the 2nd of December 1942 at the University of Chicago. Simultaneously, work was carried out to design a pilot plant that would isolate plutonium from uranium irradiated in the reactor with a separation coefficient of 1 part in 10^{10}, an achievement unheard of in the chemical industry. The first reactor of reasonable size was built within the next year. Forty-five days later a pilot separating unit was started, and scientists were able to work with several grams of plutonium. In September 1944 the first plant yielding kilogram quantities of plutonium was put into operation in the USA. It had taken less than three years from the first artificial preparation of the new element to see its commercial production. Nowadays, plutonium is produced in a number of countries in amounts that exceed several tons per year.

The further development of the transuranium elements is closely connected with the work of the eminent American scientist Seaborg and his co-workers. In the period 1944 to 1955 they discovered seven new trans-uranium elements. Americium (Am, No. 95) was found by irradiating plutonium with neutrons, curium (Cm, No. 96), berkelium (Bk, No. 97) and californium (Cf, No. 98) by bombarding the targets containing plutonium, americium and curium, respectively, with helium ions. Isotopes of einsteinium (Es, No. 99) and fermium (Fm, No. 100) were first discovered when irradiating uranium with a very intensive prompt neutron flux during

the thermonuclear explosion in 1952. Repeated neutron capture gave rise
to very heavy uranium isotopes that decayed emitting β-particles, and a
number of transuranium elements, including einsteinium and fermium,
were formed. Later these elements were also synthesized in a different
manner.

Element No. 101 was prepared by making helium ions of high energy
(41 MeV) act on einsteinium. The first experiments gave a total of
17 atoms of a new element that was identified by its transmutation to
fermium. The authors named element No. 101 mendelevium (Md) ... " in
recognition of the leading role of the great Russian chemist
Dmitri Mendeleev, who was the first to use the periodic system to predict
chemical properties of the yet undiscovered elements – a principle that
provided the key to the discovery of the transuranium elements
(actinides)... "

The following paragraphs describe schematically the first nuclear
reactions resulting in transuranium elements and list the authors of the
discoveries.

In 1957 came the first news about the discovery of the element No. 102.
A group of research workers, P. R. Fields, A. M. Friedman, J. Milstead,
H. Atterling, W. Forsling, L. Holm and B. Aström, used the Nobel Insti-
tute's cyclotron to irradiate a curium preparation with ions of carbon-13
according to the schemes:

$$^{244}_{96}\text{Cm}\,(^{13}\text{C},\ 6n)\,102^{253} \quad \text{or} \quad ^{244}_{96}\text{Cm}\,(^{13}\text{C},\ 4n)\,102^{253}$$
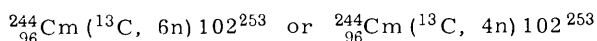
The nuclear reaction product's half-life was about 10 min. It was sug-
gested that the new element be named nobelium (No). However Seaborg
failed to confirm these results in his laboratory.

In the same year Soviet scientists G. N. Flerov, S. M. Polikanov,
A. S. Karamyan, and others were irradiating plutonium-241 with a flux of
oxygen ions (+5) and discovered an emission of α-particles of energy
8 to 9 MeV that could be assigned to isotope 102^{258} whose half-life was in
the range from several seconds to one minute. No chemical identification
was made. In 1958 – 1959 Ghiorso, Seaborg, Sikkeland and Walton made
repeated attempts to obtain isotopes of element No. 102 according to the
schemes:

$$^{246}_{96}\text{Cm}\,(^{12}\text{C},\ 4n)\,102^{254} \quad \text{and} \quad ^{244}_{96}\text{Cm}\,(^{13}\text{C},\ 4n)\,102^{253}$$
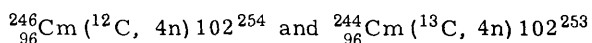
but found products with half-lives of several seconds only. The authors of
the preliminary report on element 102 had also changed their opinion and
instead claimed to have obtained isotope 102^{255}. In 1963, G. N. Flerov,
E. D. Donets, V. A. Shchegolev and others synthesized an isotope of element
No. 102 with mass number 256, using a powerful accelerator to obtain a
multiply-charged ion beam. Metallic uranium was bombarded with neon
nuclei of high energy. The half-life of the new isotope was found to be
about 8 sec. Thus the problem of synthesizing element No. 102 had be-
come much clearer, but the element, which had prematurely been given
the name nobelium, is at the present usually known just by its number.

In 1965 the group at the Joint Institute for Nuclear Research at Dubna
conducted a series of sophisticated experiments in which they studied
102^{254}. In 1967, Ghiorso, Sikkeland and Nurmia reported that this work
appeared to be correct and that their data on 102^{254} would better fit 102^{252}.

In the beginning of 1961, A. Ghiorso, T. Sikkeland, A.E. Larsh and R.M. Latimer reported on their discovery of element No.103, that was named lawrencium (Lr). In Berkeley, they bombarded in a large cyclotron a target containing 3 μg of a mixture of isotopes of californium with boron nuclei (^{10}B and ^{11}B, of 10.3 MeV energy) and observed the formation of an α-emitter whose α-particle energy was 8.6 MeV and whose half-life was 8 ± 2 sec. Calculations allowed them to suggest the formation of an isotope of element No.103 having a mass number 257 (since 1967, this assignment has been changed to mass 258 or 259). This discovery was later followed by that of a longer lived isotope $^{256}_{103}$Lr ($T_{\frac{1}{2}}$ = 35 sec) at Dubna.

In 1966, G.N. Flerov, V.A. Druin, I. Zvara and others have synthesized at the Joint Institute of Nuclear Research at Dubna the first atoms of element No.104. A plutonium-242 preparation was irradiated in the cyclotron with neon-22 ions of 115 MeV energy. This led to the nuclear reaction $^{242}_{24}$Pu ($^{22}_{10}$Ne, 4n) 104^{260}.

The resulting isotope underwent spontaneous fission with half-life of ~0.3 sec. It was observed by the tracks left on the glass or mica by fission fragments. Chemically it was identified in terms of the volatility of its chlorine compounds (see below). Element No.104 was named kurchatovium (Ku).

TABLE IV.   FIRST DISCOVERED AND LONGEST-LIVED ISOTOPES OF THE TRANSURANIUM ELEMENTS

Element	Atomic No.	First isotope to be discovered		Longest-lived isotope at present known	
		A	$T_{\frac{1}{2}}$	A	$T_{\frac{1}{2}}$
Np	93	239	2.3 d	237	2.2×10^6 yr
Pu	94	238	86.4 yr	244	7.6×10^7 yr
Am	95	241	458 yr	243	8×10^3 yr
Cm	96	242	162.5 d	247	1.6×10^7 yr
Bk	97	243	4.5 h	247	1.4×10^3 yr
Cf	98	244	2.5 min	251	~800 yr
Es	99	246	7.3 min	254	480 d
Fm	100	254	3.2 d	257	95 d
Md	101	256	30 min	258	54 d
	102	256	8 sec	-	-
Lr	103	257	8 sec	256	35 sec
Ku	104	260	0.3 sec	-	-

TABLE V. STRUCTURE AND ELECTRON SHELLS OF THE ATOMS OF THE ACTINIDES

Element	Atomic No. Z	Energy levels and electronic shells									
		n=1 K	n=2 L	n=3 M	n=4 N	n=5 O		n=6 P			n=7 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
-	102	2	8	18	32	18	14	2	6	-	2
Lr	103	2	8	18	32	18	14	2	6	1	2

So at present 12 transuranic elements having atomic numbers from 93 to 104 are known. It is worth noting that their first isotopes to be isolated were usually short lived and methods were then found to obtain longer lived isotopes (see Table IV).

It might be conceived that the same regularity would hold for the most remote transuranic elements as well.

The main procedure used to obtain a large amount of transuranium elements is to irradiate in nuclear reactors normal uranium, plutonium or enriched uranium with a powerful neutron flux. For some remote transuranic elements, such as fermium-257 ($T_{\frac{1}{2}} = 95$ days), underground explosions creating an extremely powerful neutron flux are necessary. Yet, in this case, the resulting isotope must be isolated from a great mass of molten rock obtained from the explosion.

At present, the transuranic elements are produced on vastly differing scales. The annual world production of plutonium amounts to many tons, that of neptunium, a by-product of plutonium production, to tens of kilograms. 'Americium is obtained on a kilogram scale, curium is accounted for in tens or hundreds of grams, berkelium and californium in milligrams, einsteinium and fermium in micrograms, and mendelevium, nobelium and lawrencium are available in trace amounts only.

THE FUTURE OF TRANSURANIC ELEMENTS

The time has come to pose questions about the expanding research work and to look into the practical applications of transuranic elements.

The theory of atomic structure envisages that the beginning of the fourth large period (Period 7) in Mendeleev's system is to be characterized by the filling by electrons of the deep 5f layer, similar to the way the 4f layer is filled in the lanthanide family.

In 1945 Seaborg suggested that such a filling should start after actinium, resulting in a series of elements, named the actinides, with atomic numbers from 90 to 103, that are homologues of the lanthanides. The actinide theory envisages an analogy between the respective elements of the lanthanide and actinide families. The valency properties of the actinides were, however, found to be more involved. For thorium, protactinium and uranium, the most characteristic compounds, display the highest valency, indicated by the numbers of those groups into which they were placed by Mendeleev (Groups IV, V, and VI, respectively).

Spectral investigation by V. Meggers (1947) showed that the first 5f electrons appear to start with protactinium only. Crystallographic measurements made by V. Zakhariasen (1954) even suggested that metallic thorium, protactinium and uranium have no 5f electrons, and metallic neptunium has only a single 5f electron. On the other hand, magnetic properties point to the presence of 5f electrons beginning from uranium. It appears that the strength of the 5f electron bonds and 6d electron bonds in actinide atoms is rather similar. In addition, it appears to be weaker than that of 4f electron bonding in lanthanides.

Table V contains recent data on the structure of actinide atoms. It will, however, be noted that for many elements, particularly for remote actinides, the data are only tentative and have not yet been substantiated experimentally.

The early investigation of neptunium and plutonium had already shown that these elements display a number of different valencies, from 3 to 6, that of neptunium usually being five and that of plutonium, four.

It was presumed that all subsequent actinides would be trivalent. Then followed, however, the discovery of americium compounds where this element displayed valencies of 4, 5 and 6, and of compounds of tetravalent curium and berkelium. The valency displayed by lanthanides and actinides is given in Table VI.

N. N. Krot and A. D. Gelman in my laboratory in Moscow (1947) made an important discovery. They obtained heptavalent neptunium and plutonium. Suspensions of neptunates(VI) and plutonates(VI) (K_2NpO_4, K_2PuO_4) were oxidized with ozone in a strongly alkaline medium, and the precipitates were gradually dissolved forming dark-green solutions of neptunates(VII) and plutonates(VII), as for example:

$$2K_2NpO_4 + O_3 + 2KOH = 2K_3NpO_5 + O_2 + H_2O$$
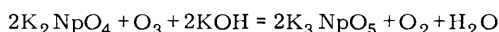
These solutions were used to obtain some solid compounds of heptavalent neptunium and plutonium: $Co(NH_3)_6NpO_5 \cdot 3H_2O$, $[Pt(NH_3)_5Cl]NpO_5$, $Sr_3(NpO_5)_2 \cdot nH_2O$, $Ba_3(NpO_5)_2 \cdot nH_2O$, $Ba_3(PuO_5)_2 \cdot nH_2O$. Neptunium(VII) compounds are dark-green, while those of plutonium(VII) are brown-black. They display strong oxidizing properties, in particular heptavalent plutonium. So neptunium could be put into the Group VII after uranium.

Neptunium and plutonium can be oxidized to the heptavalent state not only by ozone but also by hypochlorite, hypobromite, xenon compounds and other active oxidizing agents, but only in a strongly alkaline medium.

More recently, the carrier methods have been used to study the valency of the shortest-lived remote actinides used in trace amounts or as single atoms [6]. The bivalent state was determined by capture with $BaSO_4$ precipitates and the trivalent and tetravalent states by extraction with methylisobutylketone or other solvents. Experiments showed that in aqueous solutions mendelevium ($Z = 101$) is in the trivalent form but can readily be reduced to the bivalent with zinc dust, bivalent chromium, or other reducing agents. In this respect mendelevium differs from its formal lanthanide analogue, thulium, for which the bivalent state is unknown.

Element No. 102 was proved to exist in nitric acid solutions only in the bivalent form, and it could only be made trivalent with strong oxidizing agents. Here again a marked difference is observed between the properties of this element and those of its lanthanide analogue, ytterbium.

Preliminary experiments using a small number of lawrencium ($Z = 103$) atoms suggested that this element appears to be in a stable trivalent state, though the possibility of its being reduced or oxidized cannot be excluded. Lawrencium is the last member of the actinide family and should resemble lutetium, which is characteristically trivalent.

The observed differences in the properties of lanthanides and actinides, in prime of place their valencies, cannot be considered as unexpected. It is quite explicable in terms of Mendeleev's Periodic Law. In every group of the periodic system, as the atomic numbers of the element increase, the analogues of these elements display changing

TABLE VI.   VALENCY STATES SHOWN BY ELEMENT IN
THE LANTHANIDE AND ACTINIDE SERIES

Lanthanides			Actinides		
Element	Atomic No.	Valencies shown	Valencies shown	Atomic No.	Element
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	
Lu	71	3	3	103	Lr

physical and chemical properties. This holds not only for individual
elements but for their groups as well, and can be illustrated by the change
in values of ionization potentials (see Fig. 4).

It is known that in every period of Mendeleev's system the highest
value of the ionization potential corresponds to that of the inert gas, and
the lowest one to that of the alkali element. From these extremes the
ionization potentials decrease with increasing atomic numbers, this
being due to increasing atomic radii resulting from the progressive
filling of electronic shells more and more remote from the nucleus of
the atom. It is also of importance to remember that the difference be-
tween the two extreme ionization potentials (that for the inert gas and the
alkali element of a period) is much reduced as one moves to the high
atomic number end of the periodic system. This explains the increased
chemical activity of the heavy inert gases, xenon and radon, as well as
the capacity of nearest and middle actinides to exhibit a high valency and
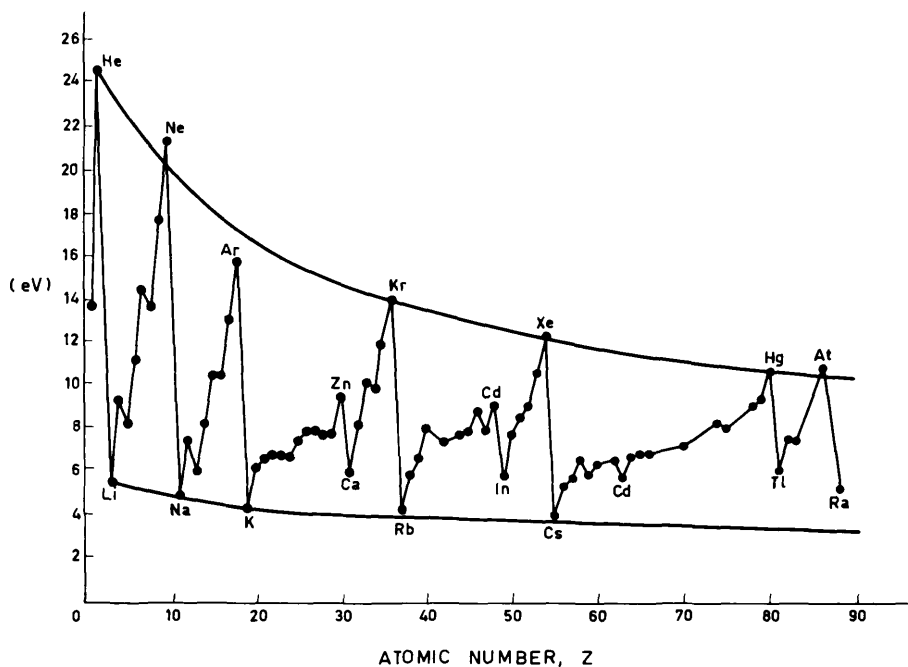various valencies.

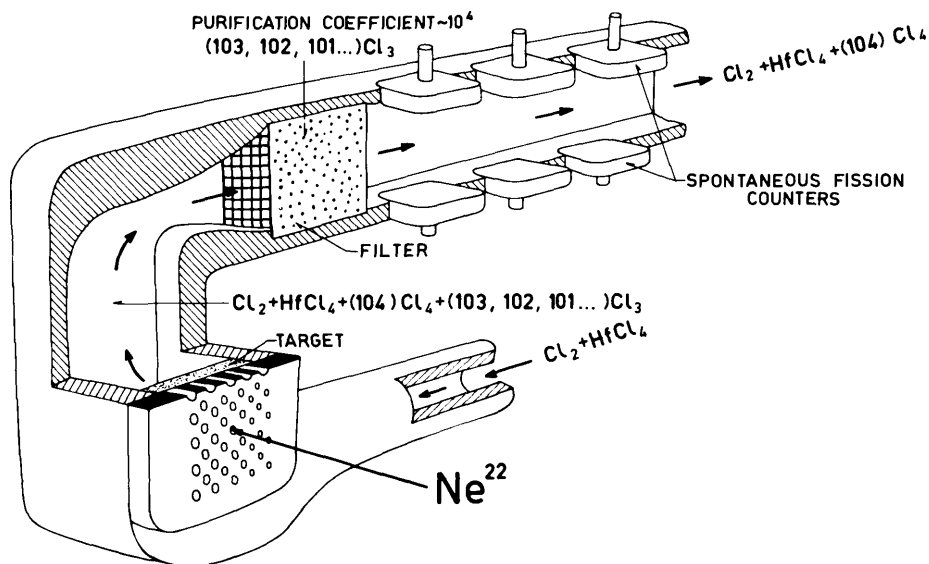FIG.4.   Ionization potentials of elements (with respect to the first electron).

FIG.5.   The flowsheet of the installation used for the chemical discovery of the atoms of element No.104.

It might be suggested that the remote actinides will also produce compounds with high valency, though under ordinary conditions their valency is usually 3 or 2.

Of great interest is the valency of the element No.104, kurchatovium. This element is not part of the actinides, and as an analogue of hafnium it should have a valency of 4. I. Zvara et al. [6] of the Joint Institute for Nuclear Research at Dubna have elegantly shown that the valency of kurchatovium is actually different from that of lanthanides and the remote actinides (Fig.5). The products of the nuclear reaction leading to the formation of nuclei of $^{260}_{104}$Ku entrained in a current of nitrogen and chlorine containing an addition of $HfCl_4$ and $NbCl_5$ were passed through a special filter that held back at 350°C the less volatile chlorine compounds of the lanthanides and of the elements Nos 101, 102, 103. After that the spontaneous fission counters again recorded the presence of element No.104, thus proving it to be different from lanthanides and actinides (Fig.5).

Formally, element No.105 should be the analogue of tantalum, element No.106 of tungsten, and so on. However, due to resemblance in energy levels of 5f and 6d electrons one might expect the nearest trans-actinides (Z = 104 to 106) to exhibit an abnormally high valency, in a way similar to the elements of the copper subgroup in which the increased valency is due to the proximity of energy levels of outer s and d electrons.


CHEMICAL PROPERTIES OF ELEMENTS IN GROUP 0

The investigation of chemical properties of the elements in Group 0 has made a valuable contribution to the periodic system. In the 1930s, B.A. Nikitin showed that radon and some other inert gases form hexahydrates ($Rn.6H_2O$, $Xe.6H_2O$, etc.,). He used the method of cocrystallization with sulphur dioxide hexahydrate ($SO_2.6H_2O$). Later he found that radon also interacts with toluene, parachlorophenol and other organic reagents to give compounds of the following composition: $Rn.2C_6H_5CH_3$, $Rn.3ClC_6H_4OH$, etc. These substances are coordination compounds.

The first compound of the inert gas xenon, formed at the expense of the valency bond, was prepared by Bartlett in 1962. He found that PtF_6, a powerful oxidizing agent, can oxidize xenon to a compound with the formula $Xe^+(PtF_6)^-$. Under the action of water it is hydrolysed:

$$2XePtF_6 + 6H_2O = 2Xe + O_2 + PtO_2 + 12HF \qquad (1)$$
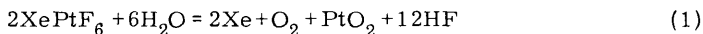
Later other authors prepared a compound of fluorine and of xenon, XeF_4, by direct interaction of fluorine and xenon at 400°C, followed by fast cooling to room temperature. Xenon tetrafluoride is stable at ordinary temperatures and is hydrolysed by water:

$$XeF_4 + 2H_2O = Xe + O_2 + 4HF \qquad (2)$$
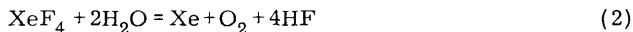
The difluoride, XeF_2, was obtained by the action of ultra-violet light on a mixture of xenon and fluorine. With an excess of fluorine

under high pressure (60 – 70 atm) XeF_6 is also formed. This compound is hydrolysed by water to give a solid non-volatile product that was shown to be xenon trioxide, XeO_3. This trioxide is stable to light and air, but 'liquefies' when moisture is introduced. It explodes on heating. XeO_3 can also undergo disproportionation to yield xenon tetroxide:

$$4XeO_3 = 3XeO_4 + Xe \tag{3}$$

The tetroxide of xenon reacting with alkalies gives perxenonates, for example:

$$XeO_4 + 4NaOH + 6H_2O = Na_4XeO_6 \cdot 8H_2O \tag{4}$$

Xenon fluorides are white crystalline substances that decompose on heating. They display strong oxidizing properties. Thus, the mixture of $XeF_4 + XeF_6$ ignites methyl alcohol and an aqueous solution of ammonia, converts bivalent manganese to permanganic acid. With xenon fluorides it proved possible to prepare for the first time salts of perbromic acid – perbromates. The data on simple compounds of xenon, at the present state of knowledge, are shown in Table VII.

TABLE VII. SIMPLE COMPOUNDS OF XENON

Valency				
2	6	4	6	8
XeF_2	$XeF_2 \cdot XeF_4$	XeF_4	XeF_6	(XeF_8)
$XeCl_2$		$XeOF_2$	$XeOF_4$	XeO_4
XeO		XeO_2	XeO_2F_2	
			XeO_3	

Radon has also been shown to interact with fluorine. It seems that chemical compounds with radon will be more stable than those with other inert gases. However, the high level of radioactivity of this element hinders the investigation of its chemical properties.

With krypton only one compound has, so far, been prepared, KrF_2. It is unstable at room temperature.

On theoretical grounds the likelihood that argon, neon or helium form chemical compounds is small.

CORRESPONDENCE BETWEEN PROPERTIES OF THE ELEMENTS IN ANY GROUP

Within the first decades after the formulation of the Periodic Law, the physical and chemical properties of elements and their compounds

began to be compared on the basis of the positions of the respective elements in the Periodic Table.

A number of regular patterns that were discovered were mentioned at the beginning of this article. In recent times, increased attention has been given to the search for quantitative regularities in this field. To illustrate this point the following work might be mentioned.

R. Somayadjulu and S. Palit of India studied (1957) the relation between the boiling temperatures of various halogen derivatives and the size of their atoms. It was found that the boiling point of representatives of a particular series of these derivatives, for instance of compounds formed by the interaction of halogens, is linearly dependent upon the surface area of halogen atoms as calculated for the given molecule. The boiling temperature can be calculated according to formula:

$$T_b = a_1 \sum R^2_c + b$$

where T_b is the boiling temperature (°K), R_c are covalent radii of halogen atoms in the molecule and a_1 and b are constants.

Figure 6 shows the use of this formula to determine the boiling points of compounds formed by the interaction of halogens of the X_2 type,
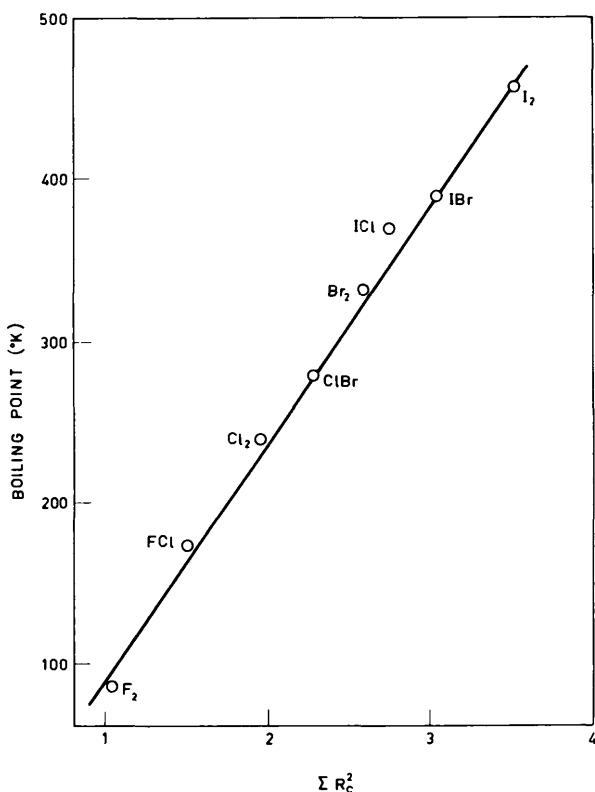

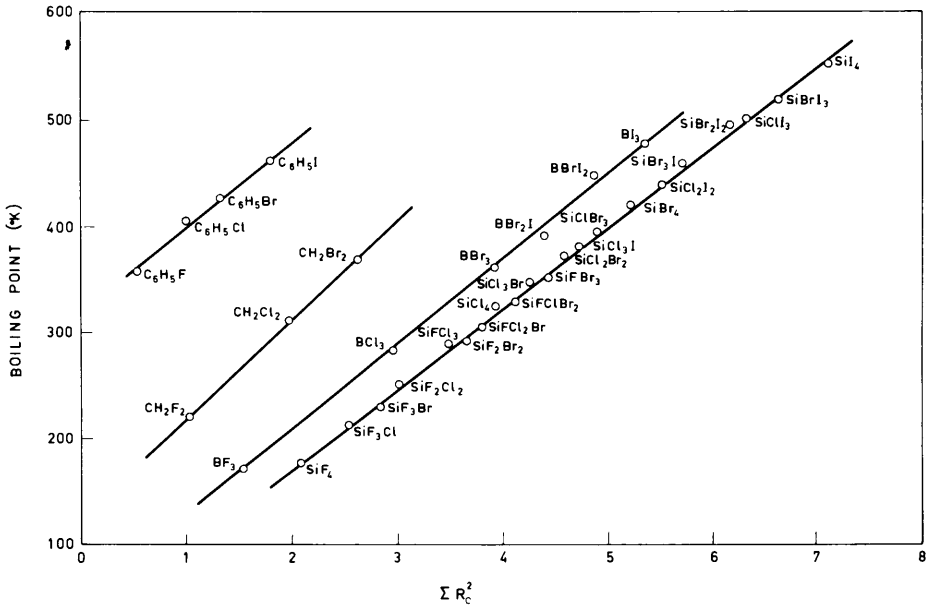FIG. 6. Boiling points of diatomic halogens as a function of the surface area of the halogen atoms.

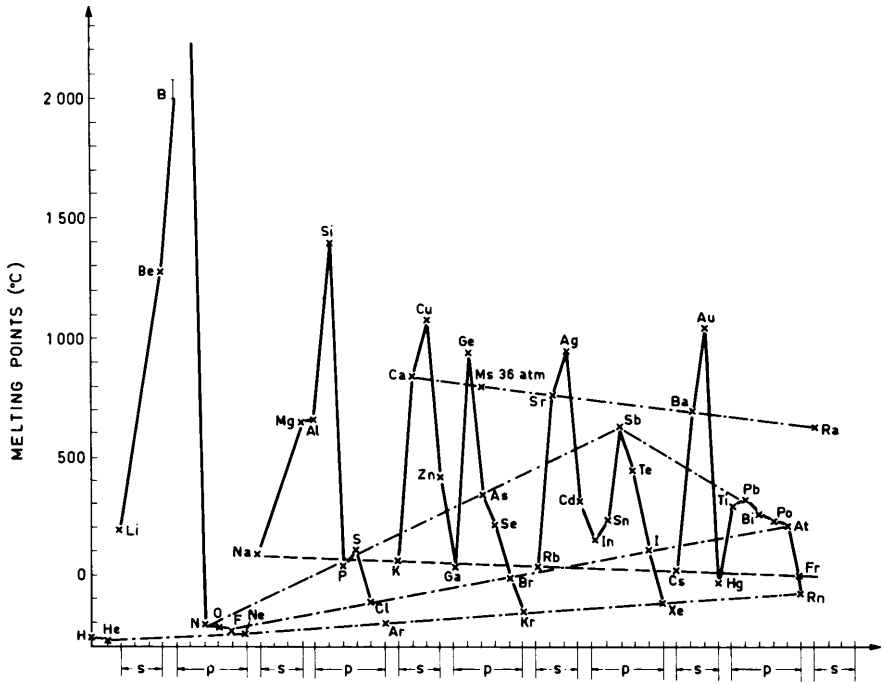FIG.7.   Boiling points of different halides as a function of the surface area of the halogen atoms.

FIG.8.   Melting point transition elements in the three large periods.

and Fig.7 shows the boiling point relations for four series of halogen derivatives of different types.

Z. Szabó and B. Lakatos of Hungary suggested (1952) that physical properties of free elements (melting point, boiling point, heat of sublimation) depend not only upon the atomic numbers but also upon the fine distribution of electrons in the s, p and d levels. This results in an additional periodicity within every period of Mendeleev's system. Such a phenomenon is shown in Fig.8 for melting points of transition elements in the three large periods (Periods 4, 5 and 6). The points connecting the melting temperature of elements and their analogues are, as a rule, on straight lines. Szabó and Lakatos have suggested special equations for calculating the melting points of elements:

$$T = a_1 \exp\{-b_1^2(d-4)^2\} + a'[\exp\{-b'^2(d-5)^2\}] (n-n_5)$$

$$\text{when } d \leqq 5$$

$$T = a_2 \exp\{-b_2^2(d-6)^2\} + a'[\exp\{-b''^2(d-5)\}] (n-n_5)$$

$$\text{when } d \geqq 5$$

where T is the melting temperature, a_1, a_2, b_1, b_2 are constants of the periodic curve, and a', b', b'' are constants of the function of the curve slope: n is the principal quantum number and d the number of d-electrons if the whole calculation is made in terms of the properties of elements of the fifth period (n_5). The calculated values differed from experimental ones on the average by 4% (Fig.8).

A.N. Nesmeyanov and N.E. Khandamirova (Moscow, 1960) found quantitative relations between the heats of sublimation of elements (ΔH_{298}^0) and their positions in the periodic system. Considering the bond energy of the lattice of a solid body as a function of two main parameters, that is, of the inter-atomic distance and of the atomic weight, A, the authors concluded that the value of $H_{298}^0 A/2$ is directly dependent upon the atomic weight within each subgroup of the periodic system. Using the appropriate charts, it becomes possible to calculate the heats of sublimation. In most cases satisfactory agreement between the calculated and experimental values was obtained. Deviations are observed in the copper and zinc subgroups. This is accounted for by s electrons penetrating under the screen of d electrons and causing a relative decrease in the size of the atoms.

*   *   *

In the 100 years that have passed since discovery of the Periodic Law, its scientific, practical and philosophical importance has not only not decreased, but has increased enormously, and there are no limits to its further development. Thorough investigation of the various properties of chemical elements on the basis of the periodic system and the discovery of quantitative relations between them, studies of the chemistry

of artificially produced nuclei, the widespread use of isotopes, all these will make it possible to produce a large number of often valuable new substances for the benefit of mankind, while at the same time enriching the scientific value of the Periodic Law itself.

REFERENCES

[1]   MENDELEEV, D.I., Zh. russk. fiz.-khim. Obshch. 1 (1869) 60.
[2]   MENDELEEV, D.I., Selected Works 2 ONTI (1934).
[3]   MENDELEEV, D.I., Zh. russk. fiz.-khim. Obshch. 3 (1871) 25.
[4]   HEVESY, G. v. (de), Die seltenen Erden vom Standpunkte des Atombaues, No. 5 of Series: Struktur der Materia in Einzeldarstellungen (BORN, M., FRANCK, J., Eds), Springer, Berlin (1927).
[5]   SEABORG, G.T., KATZ, J.J., Eds, The Chemistry of the Actinide Elements, Methuen, London (1957).
[6]   Symposium on Macroscopic Studies of the Actinides, Abstracts, Paper No.53, San Francisco, 1-5 April 1968.