

## Evolution of the modern periodic table\*

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In this review, the evolution of the Modern Periodic Table is traced beginning with the original version of Dimitri Mendeleev in 1869. Emphasis is placed on the upper end with a description of the revision to accommodate the actinide series of elements at the time of World War II and the more recent research on the observed and predicted chemical properties of the transactinide elements (beyond atomic number 103). A Modern Periodic Table includes undiscovered elements up to atomic number 118 and a Futuristic Periodic Table with additional undiscovered elements up to atomic number 168 is included.

The story begins on March 6, 1869, when Dmitri Ivanovich Mendeleev,<sup>1</sup> with the help of his associate, Nikolai Menshutkin, presented a paper to the Russian Chemical Society in St. Petersburg which postulated that the elements showed a periodicity in their chemical properties when they were arranged in the order of their atomic weights. This in itself was not novel. Several chemists in other countries had observed some kind of orderliness in the elements then known, the most prominent being the German Johan W. Döbereiner<sup>2</sup> and his triads (1829), the Frenchman A. E. Béguyer de Chancourtois<sup>3</sup> and his 'telluric screw' (1862), and the Englishman John A. R. Newlands<sup>4</sup> and his 'law of octaves' (1864).

It is not generally known that some American chemists of the 19th century also proposed various forms of periodic classifications, including Josiah P. Cooke Jr.<sup>5</sup> in 1854. The only real challenge to the generally accepted validity of Mendeleev's originality, however, has come from the work of Lothar Meyer<sup>6</sup> in Germany, who in 1870 produced independently a generalization almost identical to that of Mendeleev.

The reason for the general acceptance of Mendeleev's pre-eminence is straightforward: not only did he show that periodicity existed in the properties of the elements then known, but he had the courage and the vision to state that his method of classification constituted a fundamental law of nature, and that where there appeared to be deficiencies in his Periodic Table, they were due to gross errors in the measurement of atomic weights or simply to the fact that certain elements had not yet been discovered. Indeed, Mendeleev's claim to priority in the discovery of the period system was not completely accepted until his predictions of missing elements were proved by experimental evidence in later years.

The Periodic Table (Fig. 1) Mendeleev<sup>7</sup> published in 1871, that incorporates improvements made in the original version of 1869, predicts the existence and properties of the elements with atomic weights of 44, 68 and 72. These correspond to scandium, gallium and germanium, as we now know them. These three elements were actually found<sup>8-10</sup> in nature during the period from 1875 to 1886. Many other experimental proofs of Mendeleev's 'law' were made in the years that followed.

As time progressed, adjustments had to be made to the Periodic Table to accommodate the rapidly expanding knowledge of the properties of the elements and their atomic and nuclear structures. Also, additional elements were discovered during the late 19th century and the first part of

the 20th century which required some reconstruction of the Mendeleev periodic system. The most significant changes<sup>11,12</sup> were the addition of another vertical row, or group, of elements now known as the noble gases, and the substitution of a series of elements, the rare earth or lanthanides, in the place of a single element (placed between barium and hafnium).

By the end of the first decade of the 20th century the total number of elements had increased to 85 and soon thereafter the concept of atomic number,<sup>13,14</sup> as the fundamental basis for the ordering of the elements in the Periodic Table, was established. During the next 25 years, three more elements were discovered, leaving below uranium (element 92, the heaviest element) those having atomic number 43, 61, 85 and 87 as the missing elements. Even these properly empty places in the Periodic Table were filled under names such as masurium for element 43, illinium for element 61, alabamine for element 85 and virginium for element 87. These 'discoveries' however were erroneous. The state of the understanding of the atomic nucleus was such in the 1930s that it could be shown that the missing elements were all radioactive, with such short half-lives that their existence in appreciable concentration on earth was improbable. The Periodic Table (Fig. 2) as it looked in the 1930s when scientists first tried to produce elements beyond uranium includes elements 43, 61, 85 and 87, which were given their names<sup>15</sup> later—43 technetium (Tc), 61 promethium (Pm), 85 astatine (At) and 87 francium (Fr).

Thoughts on the position in the Periodic Table of the heaviest elements varied considerably before the final recognition that another series of elements, resulting from the addition of electrons to an inner shell (5f), should occur somewhere in the heavy-element region. This new family of elements would be similar to the 14-member rare-earth or lanthanide (chemically similar to lanthanum) series of elements which results from the addition of inner 4f electrons.

Even until World War II, however, the three heaviest known elements, thorium, protactinium and uranium, were believed to be related to hafnium, tantalum and tungsten, respectively. The next element, number 93, was thus expected to have chemical properties resembling those of rhenium. Similarly, elements 94 to 100 were expected to fit neatly into the Periodic Table (Fig. 2).

The first attempts to produce elements beyond uranium were made by Enrico Fermi and co-workers,<sup>16</sup> who bombarded uranium with neutrons in Italy in 1934. They actually found a number of interesting radioactive products, which they attributed to elements beyond uranium ('transuranium' elements). The radioactive products of the neutron bombardment of uranium were the object of chemical investigations during the following years by Otto Hahn, Lise Meitner and Fritz Strassmann<sup>17</sup> in Germany, and by numerous other

\* This article, in part, discusses elements the names of which are under active consideration by IUPAC. The nomenclature adopted in the article is not approved by IUPAC at the time of writing (June 1996). By publishing this article the Royal Society of Chemistry is not seeking to pre-empt the decisions of IUPAC, nor to influence their outcome.

REIHE	Gruppe I - R <sup>2</sup> O	Gruppe II - RO	Gruppe III - R <sup>2</sup> O <sub>3</sub>	Gruppe IV RH <sup>4</sup> RO <sup>2</sup>	Gruppe V RH <sup>3</sup> R <sup>2</sup> O <sup>5</sup>	Gruppe VI RH <sup>2</sup> RO <sup>3</sup>	Gruppe VII RH R <sup>2</sup> O <sup>7</sup>	Gruppe VIII - RO <sup>4</sup>
1	H=1							
2	Li=7	Be=94	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=273	Si=28	P=31	S=32	Cl=355	
4	K=39	Ca=40	-=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, 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=96	=100	Ru=104, 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	Tl=204	Pb=207	Bi=208	-	-	
12	-	-	-	Th=231	-	U=240	-	

Fig. 1 Mendeleev Periodic Table of 1871 predicting three elements (Sc, Ga, Ge). Reprinted with permission from the Ernest Orlando Lawrence Berkeley National Laboratory

1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	(43)	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	(85)	86
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		Rn
(87)	88	89	90	91	92	(93)	(94)	(95)	(96)	(97)	(98)	(99)	(100)				
	Ra	Ac	Th	Pa	U												
		57	58	59	60	(61)	62	63	64	65	66	67	68	69	70	71	
		La	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	

XBL 769-10601

Fig. 2 Pre-World War II Periodic Table predicting erroneous positions for transuranium elements. Reprinted with permission from the Ernest Orlando Lawrence Berkeley National Laboratory

scientists. On the basis of incomplete tracer studies, some of these activities seemed to have chemical properties such as would be expected for 'transuranium' elements with an atomic number such as 94 or 96, properties similar to those of elements such as osmium and platinum listed directly above elements 94 and 96 in the Periodic Table of the time.

However, as early as 1934, Ida Noddack<sup>18</sup> foresaw the possibility of a nuclear fission reaction, but she did not perform any experiments to confirm her interpretation and her suggestion was ignored.

Subsequent work, especially the discovery of nuclear fission by Hahn and Strassmann<sup>19</sup> with the help of Meitner, late in 1938, showed that the transuranium interpretation was not correct. This subsequent work revealed that these products of uranium bombardments with neutrons actually were radioactive isotopes of lighter elements and thus were fission-product elements such as barium, lanthanum, iodine, tellurium or molybdenum.

### Impact of Actinide Elements

During an investigation of the fission process, Edwin M. McMillan<sup>20</sup> discovered a radioisotope with a half-life of 2.3 days. Working at the University of California, Berkeley, in the spring of 1940, he was trying to measure the energies of the two

main recoiling fragments from the neutron-induced fission of uranium. He used the 60-inch cyclotron as a source of neutrons from the reaction of 16 MeV deuterons with beryllium. He placed a thin layer of uranium oxide on one piece of paper, and next to this he stacked very thin paper sheets to stop and collect the fission fragments from uranium. The paper he used was ordinary cigarette paper, the kind used by people who rolled their own cigarettes. In the course of these studies, he found that the 2.3 day activity did not recoil sufficiently to escape. This activity was further investigated by Emilio Segré<sup>21</sup> whose lack of chemical sophistication led him to identify it as a lanthanide element.

The synthesis and identification (*i.e.*, discovery) of the first element with an atomic number higher than 92, neptunium, at the University of California, Berkeley, came in 1940 as a result of the work of McMillan and Philip H. Abelson.<sup>22</sup> This was followed shortly afterwards by the discovery of the next element, plutonium, by McMillan, Joseph W. Kennedy, Arthur C. Wahl and me<sup>23,24</sup> in early 1941, also at the University of California, Berkeley. The tracer chemical experiments with neptunium (atomic number 93) and plutonium (atomic number 94) showed that their chemical properties were much like those of uranium and not at all like those of rhenium and osmium! The pre-World War II Periodic Table had misled Fermi and Hahn and their co-workers, but the ultimate result was the monumental discovery of nuclear fission.

1 H																	2 He															
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne															
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar															
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr															
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Ru	44 Rh	45 Pd	46 Ag	47 Cd	48 In	49 Sn	50 Sb	51 Te	52 I	53 Xe																
55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn															
87 Ra	88 Ac	89 Th	90 Pa	92-106 U-(106)																												
					92 U	93 Np	94 Pu	(95)	(96)	(106)																						
																		57 La	58 Ce	59 Pr	60 Nd	(61)	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

XBL 798-2509

Fig. 3 Periodic Table of 1941–1944 placing the first two transuranium elements as members of a ‘Uranide’ series. Reprinted with permission from the Ernest Orlando Lawrence Berkeley National Laboratory

For a few years following this, uranium, neptunium and plutonium were considered to be sort of ‘cousins’ in the Periodic Table, but the family relationship was not clear. It was thought that the next elements, elements 95 and 96, should be much like them in their chemical properties. Thus it was thought that these and the following elements formed a ‘uranide’ (chemically similar to uranium) group (Fig. 3).

The Periodic Table of 1941–1944 therefore implied that the chemical properties of elements 95 and 96 should be very much like those of neptunium and plutonium. These assumptions proved to be wrong and the experiments directed toward the discovery of elements 95 and 96 on this basis failed. Again, the undiscovered elements 95 and 96 apparently refused to fit the pattern indicated by this Periodic Table.

Then, in 1944, I conceived the idea that perhaps all the known elements heavier than actinium were misplaced on the Periodic Table. The theory advanced was that these elements heavier than actinium might constitute a second series similar to the series of ‘rare-earth’ or ‘lanthanide’ elements.<sup>25</sup> The lanthanides are chemically very similar to each other and usually are listed in a separate row below the main part of the Periodic Table. This would mean that all these heavier elements really belong with actinium, directly after radium in the Periodic Table, just as the known ‘lanthanides’ fit in with lanthanum between barium and hafnium.

The revised Periodic Table, then, listed the heaviest elements as a second ‘rare-earth’ series. These heaviest elements (including undiscovered elements), with the name ‘actinide’ elements, were paired off with those in the already-known lanthanide rare-earth series in a Periodic Table<sup>26</sup> published on December 10, 1945, in *Chem. Eng. News* (Fig. 4).

The new concept meant that elements 95 and 96 should have some properties in common with actinium and some in common with their rare-earth ‘sisters’, europium and gadolinium, especially with respect to the difficulty of oxidation above the III state. When experiments were designed according

to this new concept, elements 95 and 96 were soon discovered<sup>27</sup> at the wartime Metallurgical Laboratory at the University of Chicago, that is, they were synthesized and chemically identified.

Not only did this new understanding lead to the elements americium and curium (95 and 96), but to the synthesis and identification of berkelium and californium (97 and 98) in 1949 and 1950, einsteinium and fermium (99 and 100) in 1952 and 1953, mendelevium (101) in 1955 and nobelium (102) in 1958. It also signalled the end of the actinide series<sup>28</sup> at lawrencium (103), when this element was discovered in 1961.

Since all the elements beyond actinium through lawrencium, element 103, belong to the actinide group, the elements thorium, protactinium and uranium were removed from the positions they occupied in the Period Table before World War II and placed in this transition family. Elements 104, 105 and 106 took over the position previously held by thorium, protactinium and uranium.

Although it is the information on the transuranium elements that has been decisive in enabling us to come to the present view concerning the electronic structure of, or, more properly speaking, the best position in the Periodic Table for, the heaviest elements, it is interesting to conjecture, in retrospect, whether it would have been possible to arrive at a similar conclusion without this information. Actually, there has been much information about actinium, thorium, protactinium and uranium, especially about the latter, which pointed in this direction. There is the similarity among the metals of these elements with respect to electropositive character. In addition, the melting point of uranium metal seems to relate it more closely to the immediately preceding elements than to tungsten and molybdenum. Uranium differs considerably from tungsten and molybdenum in the chemistry of the lower oxidation states. Uranium(III) has great similarity to the tripositive rare-earth elements and actinium, and uranium(IV) resembles thorium(IV) and cerium(IV). Thus uranium(III) and uranium(IV) are not

1 H 1.008																	1 H 1.008	2 He 4.003													
3 Li 6.940	4 Be 9.02													5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183												
11 Na 22.997	12 Mg 24.32	13 Al 26.97											13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 Ar 39.944													
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7														
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3														
55 Cs 132.91	56 Ba 137.36	57 La 138.92	58 Ce 140.12	59 Pr 140.92	60 Nd 144.27	61 Pm	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po	85 At	86 Rn 222
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm																						

LANTHANIDE SERIES	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99
	89 Ac	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu	95	96							

XBL 769-10603

Fig. 4 Periodic Table of 1944 and 1945 showing my placement of the heaviest elements as an 'actinide' series. Reprinted with permission from the Ernest Orlando Lawrence Berkeley National Laboratory

acidic in character; they do not tend, like tungsten and molybdenum, to form such exceedingly strong complex ions in solution; they have fluorides that are insoluble and isomorphous with the fluorides of the rare-earth elements; and they have other halides with crystal structures that are in general isomorphous with the corresponding rare-earth halides. On the other hand, tungsten(III) and tungsten(IV) exist in aqueous solution predominantly as strong complex ions; e.g., tungsten(III) has a strong chloride complex ion and tungsten(IV) forms strong fluoride and cyanide complex ions.

Although molybdenum dioxide and tungsten dioxide have isomorphous crystal structures, tungsten dioxide and uranium dioxide do not, but uranium dioxide, thorium dioxide and cerium dioxide do have isomorphous structures. It is interesting that although uranium is not associated with tungsten in minerals, uranium and thorium minerals practically always have the rare-earth elements associated with them, and the rare-earth minerals practically always contain uranium or thorium.

The actinide series differs from the lanthanide series in that the early members are much more readily oxidized to oxidation states greater than III. As the atomic numbers of the members of the actinide series increase, the lower oxidation states and particularly the III state, increase in stability. The stable configuration consisting of the half-filled shell of seven 5f electrons comes at curium (element 96).

### Impact of Transactinide Elements

Rutherfordium (104), hahnium (105) and seaborgium (106) were synthesized and identified<sup>28</sup> over the next 13 years by Albert Ghiorso and co-workers at Berkeley. (It now seems clear to me that competing claims to the discovery of these elements at the Dubna Laboratory in the Soviet Union cannot be substantiated.<sup>29</sup>) Nielsbohrium (107), hassium (108) and meitnerium (109) were synthesized and identified<sup>28</sup> in the early 1980s at the Gesellschaft für Schwerionenforschung (GSI) laboratory near Darmstadt, Germany, and in the 1990s, unnamed element 110 at the GSI, Berkeley and Dubna laboratories<sup>30-32</sup> and elements 111 and 112 at the GSI laboratory.<sup>33,34</sup>

The elements beyond the actinides in the Periodic Table are termed the 'transactinides' and are shown in a Modern Periodic Table as in Fig. 5 with all of the undiscovered elements through to number 118 in their expected places.

The yields of the heaviest elements produced in bombardments of target nuclei with heavy ions become extremely small with increasing atomic number, dropping to as little as one atom per week of bombardment for elements as heavy as atomic number 112. The half-lives decrease into the millisecond and the microsecond range so that identification of the new nuclei becomes increasingly difficult. These half-lives would be impossibly short were it not for the presence of closed shells of nucleons to increase nuclear stability.

It has been possible to study the chemical properties of rutherfordium,<sup>35-42</sup> hahnium<sup>39,43-46</sup> and seaborgium<sup>47,48</sup> using the advanced techniques of one-atom-at-a-time chemistry, with the result that these properties in the main are consistent with those expected on the basis of extrapolation from those of their lighter homologues in the Periodic Table, hafnium, tantalum and tungsten. However, their chemical properties cannot be determined reliably in detail from trends exhibited by their lighter homologues, because of the important, and probably understandable, role played by relativistic effects in these heavier elements. I am looking forward to obtaining evidence for oxidation states corresponding to seaborgium, seaborgic and seaborgate ions.

It has been possible to study the chemical properties on the *macroscopic* scale for elements as heavy as einsteinium (element 99) but all elements beyond have been studied on the *tracer* scale. Much more research on the macroscopic properties of einsteinium will be possible with the availability of <sup>254</sup>Es (half-life of 276 days) in microgram amounts. It will surely be possible to study the *macroscopic* properties of fermium (element 100) and not out of the question that this will eventually be done for mendelevium (element 101). The art of one-atom-at-a-time chemistry will advance far beyond what can be imagined today to make it possible to study the chemistry of heavier and heavier elements. All of this will result in the delineation of relativistic effects on the chemical properties of these very heavy elements, which might thus be

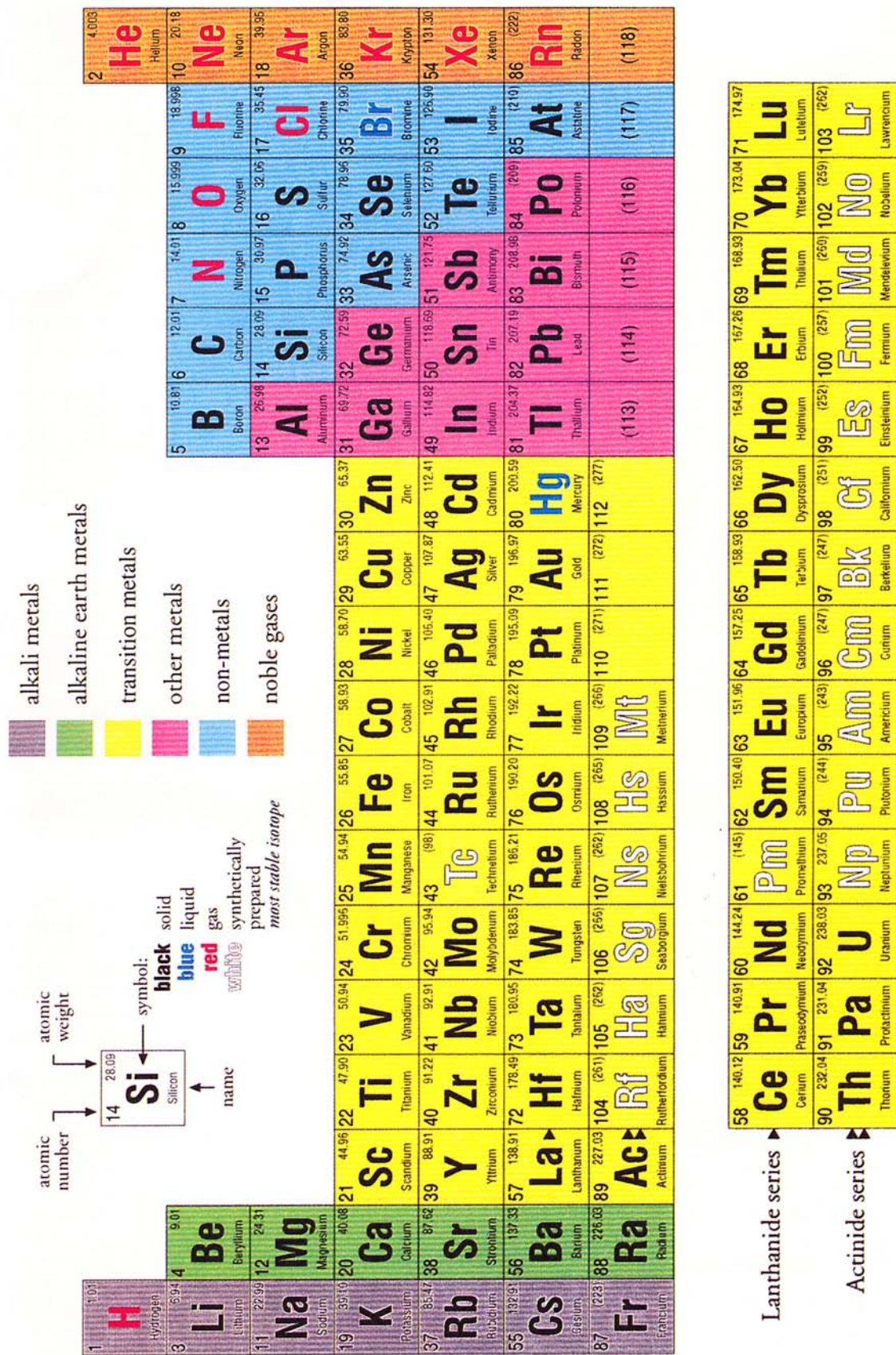


Fig. 5 Modern Periodic Table (atomic numbers of undiscovered elements in parentheses). Reprinted with permission from the Ernest Orlando Lawrence Berkeley National Laboratory

1 H																2 He	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110	111	112	(113)	(114)	(115)	(116)	(117)	(118)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

#### LANTHANIDES

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
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#### ACTINIDES

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
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#### SUPER- ACTINIDES

(122)	(123)	(124)	(125)	(126)								(153)
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Fig. 6 Futuristic Periodic Table (atomic numbers of undiscovered elements in parentheses). Reprinted with permission from the Ernest Orlando Lawrence Berkeley National Laboratory

substantially different from those expected by simple extrapolation from their lighter homologues in the Periodic Table.

Such a research program will require, for success, the availability of apparatus and equipment of increasing complexity, versatility and power. Central to this will be the need for higher neutron-flux reactors, for sustained operation as a research tool and to produce large quantities of transplutonium nuclides for use in the research and as target materials as a source of the presently known and expected nuclides. (Higher neutron fluxes will be especially valuable for the production of the heaviest nuclides,  $^{254}\text{Es}$  and  $^{257}\text{Fm}$ , springboards to the region beyond.) Better means of coping with the heat generated in the target by such intense means must be developed in order to overcome limitations due to small nuclear reaction cross-sections. Increases by orders of magnitude in heavy-ion intensity should make possible nuclear synthesis reactions with secondary (radioactive) beams of neutron-excess projectiles, which might greatly increase the yields of sought-after new nuclides. Improved methods for handling safely and efficiently increasing quantities of the highly radioactive transcurium nuclides must also be developed.

#### Role of Electronic Structure

Turning to the consideration of electronic structure, upon which chemical properties must be based, modern high-speed computers have made possible the calculation of such structures.<sup>49</sup> The calculations show that elements 104 through to 112 are formed by filling the 6d electron subshell, which makes them, as expected, homologous in chemical properties with the elements hafnium (72) through to mercury (80). Elements 113 through to 118 result from the filling of the 7p

subshell and are expected to be similar to the elements thallium (81) through to radon (86). Thus these calculations are consistent with a modern Periodic Table (Fig. 5).

The calculations (Fig. 6) indicate the 8s subshell should fill at elements 119 and 120, thus making these an alkali and alkaline-earth metal, respectively. Next these calculations point to the filling, after the addition of a 7d electron at element 121, of the inner 5g and 6f subshells, 32 places in all, which I have termed the 'superactinide' elements and which terminate at element 153. This is followed by the filling of the 7d (elements 154 through to 162) and 8p subshells (elements 163 through to 168). Element 168 should be a noble liquid because its boiling point is predicted to be above room temperature.

Although we can feel confident that this is the approximate form the Periodic Table should assume, we, unfortunately, will not be able to verify much of this experimentally because the half-lives of the nuclei are too short and there are no nuclear synthesis reactions available to reach such heavy elements. However, I believe it will be possible to add some six new known elements (perhaps slightly more) to our Periodic Table.

Actually, more careful relativistic calculations have indicated that the picture is not this simple. The calculations indicate that electrons in addition to those identified in the above discussion enter the picture as early as element 121 (or even element 104), thus further complicating the picture. These and other perturbations, caused by spin-orbit splitting, lead to predictions of chemical properties that are not consistent, element by element, with those suggested by the modern (Fig. 5) and futuristic (Fig. 6) Periodic Tables. Here again we are in danger of making wrong predictions about the chemical properties of undiscovered elements by using the Periodic Table incorrectly.<sup>49</sup>

Relativistic calculations have been made to derive the

ground-state electronic configurations and binding characteristics for the elements lawrencium (103) to seaborgium (106). Such calculations<sup>50–53</sup> have shown that lawrencium has a  $7s^2p_{\frac{1}{2}}$  electronic configuration instead of the expected  $7s^26d$  configuration, and that rutherfordium has the configuration  $7s^2p_{\frac{1}{2}}6d$  rather than  $7s^26d^2$  (while the configurations for hahnium and seaborgium are  $6d^37s^2$  and  $6d^47s^2$  respectively as expected).

The six  $7p$  electrons, because of relativistic effects, are predicted to be split into two subshells, two  $7p_{\frac{1}{2}}$  and four  $7p_{\frac{3}{2}}$  electrons, with a separation of energies such that the filled  $7p_{\frac{1}{2}}$  orbital will act as closed shell and additional  $7p_{\frac{3}{2}}$  electrons will act as electrons outside a closed shell. Thus element 115 (eka-bismuth) is predicted to have its valence electrons in the configuration  $7p_{\frac{1}{2}}^27p_{\frac{3}{2}}$  with a consequent stable I oxidation state in contrast to the stable III oxidation state of its homologue bismuth. Another predicted result of relativistic effects is that element 112 (eka-mercury) and element 114 (eka-lead) may be very noble, that is, liquids or volatile gases. These considerations raise the exciting possibility of studying 'relativity in a test-tube'. They become especially significant beyond the superactinide series, a region far beyond the region of expected nuclear stability, which is the only region where it might be possible to synthesize heavy elements.

### Predictions of Chemical Properties

A number of investigators have predicted in some detail the chemical properties of the transactinide elements. The relativistic calculations of Valeria Pershina and Burkhard Fricke<sup>54</sup> indicate that the standard reduction potentials corresponding to the transitions from the highest to the next reduced state show the following sequence in the stability of the maximum oxidation state:  $Lr^{3+} > Rf^{4+} > Ha^{5+} > Sg^{6+}$ . This means that in Group 4 the tetrachloride of rutherfordium is more stable toward thermal decomposition than the tetrachlorides of zirconium and hafnium, while in Group 6 the hexachloride of seaborgium should be less stable than tungsten hexachloride. However, the recent calculations of Gulgari Malli<sup>55</sup> indicate that volatile seaborgium hexachloride should be more stable than tungsten hexachloride and hence should be detectable in thermal chromatography experiments.

Robert A. Penneman and Joseph B. Mann<sup>56</sup> used equations developed by Jorgensen to predict the most stable states of elements 104–110 in aqueous solutions as  $Rf^{IV}$ ,  $Ha^V$ ,  $106^{IV}$ ,  $107^{III}$ ,  $108^{II}$ ,  $109^I$  and  $110^0$ . In the case of some elements, several oxidation states appear likely. One suggestion is that rutherfordium chemistry in solution may involve oxidation states of II and III, as well as IV. Jorgensen's approach is not intended to take into account the effects of oxyanion formation, such as that which stabilizes tungsten(VI) in the tungstate ion. Since rhenium and osmium are also stabilized by oxyanion formation, seaborgium (106), neilsbohrium (107) and hassium (108) may be found in higher oxidation states in solution than postulated by Penneman and Mann.

Burriss B. Cunningham<sup>57</sup> used an extrapolation by group in the Periodic Table to obtain the prominent oxidation states for elements 104–110 as:  $104^{IV}$ ,  $105^V$ ,  $106^{VI}$ ,  $107^{VII}$ ,  $108^{VIII}$ ,  $109^{VI}$  and  $110^{VI}$ . Cunningham's predictions begin to deviate from those of Penneman and Mann at 106. The higher oxidation states predicted by Cunningham are probably more appropriate for solutions where oxyanions, analogous to tungstate, may be formed.

For element 111, eka-gold, O. Lewin Keller, Charles W. Nestor, Jr., Thomas A. Carlson and Fricke<sup>58</sup> predict the most stable oxidation state as III with the I state possible in the presence of highly polarizable ligands such as  $(CN^-)$ . The II state is expected to be unstable. An unusual feature may arise in the  $(111)^-$  ion, which would be analogous to the auride ion.

Kenneth S. Pitzer<sup>59</sup> has combined relativistic quantum-

mechanical calculations with a penetrating intuition to arrive at some most useful results on the chemical and physical properties of element 112, eka-mercury. The relativistic effect on the closed  $7s^2$  shell will make element 112 more noble than mercury, so that the oxide, chloride and bromide are expected to be unstable, although  $(112)Cl_4^{2-}$  and  $(112)Br_4^{2-}$  should be found in solution and  $(112)F_2$  should be stable. Pitzer also predicts that element 112 will be a volatile liquid or even a gas, since the atoms will be bound together only by dispersion forces.

According to Keller, John L. Burnett, Carlson and Nestor,<sup>60</sup> the chemical behaviour of element 113 is expected to lie between those of  $Tl^+$  and  $Ag^+$ . The cation  $113^+$  is expected to bind anions more readily than  $Tl$ , so that  $(113)Cl$  will be soluble in an excess of HCl, whereas the solubility of  $TlCl$  is essentially unchanged. Similarly,  $(113)Cl$  is expected to be soluble in aqueous ammonia, in contrast to the behaviour of  $TlCl$ . The behaviour of the  $113^+$  ion should tend toward  $Ag^+$  in these respects. Also, although  $Tl(OH)$  is soluble and a strong base, the  $113^+$  ion should form a slightly soluble oxide that is soluble in aqueous ammonia.

Pitzer<sup>59</sup> has noted for element 114 that the effect of the  $7p_{\frac{1}{2}}$  closed shell will cause eka-lead to be a volatile liquid or even a gas like element 112. His results for element 114 are qualitatively similar to those of Keller *et al.*<sup>60</sup> According to Pitzer,  $(114)Cl_2$  and  $(114)F_2$  will be stable and probably  $(114)Br_2$  will be stable as well. For both elements 112 and 114, Pitzer recommends using their great volatility and ease of reduction as separation methods in approaches to their discovery.

The chemistry of elements 115, 116 and 117 will be most interesting, since the  $7p_{\frac{3}{2}}$  electrons will be added outside the  $7p_{\frac{1}{2}}$  closed shell. Keller, Nestor and Fricke<sup>61</sup> therefore also predict for element 115, eka-bismuth, a stable oxidation state of I, as well as III, with  $115^+$  being similar in its behaviour to  $Tl^+$ . The group oxidation state of V will probably not be found.

Although detailed predictions of the chemistry of elements 116, eka-polonium, and 117, eka-astatine, have not been made, the II and III oxidation states will probably be of considerable importance, since two and three  $7p_{\frac{3}{2}}$  electrons are present, respectively, outside the  $7p_{\frac{1}{2}}$  closed shell. The prominence of the I – state for the halogen 117 has been questioned.<sup>62</sup>

Aristid V. Grosse<sup>63</sup> has given detailed predictions of the properties of element 118, eka-radon. He expects this element to be more reactive than xenon, forming compounds with chlorine as well as oxygen and fluorine. Pitzer<sup>64</sup> has made the important observation that the fluoride of element 118 will most probably be ionic in form rather than molecular, as in the case of xenon. It is therefore predicted to be non-volatile (as has already been observed for radon fluoride, in the exceptional work by Stein<sup>65</sup>).

Penneman and Mann<sup>56</sup> find that element 119 will be the first alkali metal to have oxidation states higher than I. This result is in accord with the predictions of Grosse and Pitzer on the reactivity of element 118, since it basically means reactivity of the rare-gas 'core'. The chemistry of element 120 has not been examined in detail, but it is expected to follow alkaline-earth chemistry in a vein similar to that in which element 119 follows alkali-metal chemistry.

The chemistry of the 'superactinide' elements (atomic numbers 122–153) should be similar to that of the actinide and lanthanide elements with the important difference that a wider range of oxidation states would be observed.

### Acknowledgements

Drs. Darleane Hoffman and Albert Ghorso provided valuable insight and suggestions for this article. I would also like to thank my staff: Kristin Balder-Froid, Carol Harris Earls and Perry Hall.

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Received 23rd May 1996; Paper 6/03603A