# Introduction

#### Roald Hoffmann

Before the word for it (in any language) came to be, there was chemistry. For one defining aspect of human beings has always been the meld of mind and hands in transforming matter. Look at a wall painting in the tomb of Rekhmire at Thebes and you see men sweating at the bellows as they separate gold from dross. There, kohl, a dark cosmetic mixture, is being made. There, people are cooking.

People want to change the natural into the useful unnatural. Or, if you prefer, into the improved man- or human-made. To add value is to profit. So from the beginning transformation was essential, whether in the making of metals and alloys, in medicinal preparations, in cooking, in dyeing and colouring, in tanning leather or in cosmetics. It took some time for this most fundamental of chemical activities to be called by its contemporary name – synthesis.

Human beings are curious as well as practical. So questions are asked about matter, be it natural or transformed. They are really very simple questions: 'What have I got?', 'How did that transformation happen?', 'Why that change or structure, rather than others?'... The first of these questions was central to the work that marked the definitive emergence of chemistry as a science – Antoine Laurent Lavoisier's 1789 Elementary Treatise on Chemistry. Analysis, the weighty struggle with the question 'What is it?', remained absolutely central for a long time. So Goethe, the prime minister of a grand duchy in what is now Germany, would take two weeks off to follow a course of analysis with Johann Wolfgang Döbereiner in nearby Jena.

If analysis, at least at the elemental level, was at the heart of chemistry 200 years ago, in 1901 the questions 'How?' and 'Why?' were the ones I think most often asked and answered. At a certain level – that of the behaviour of matter on the average, at the macroscopic level – the understanding came from thermodynamics, a beautifully worked-through blend of practicality (steam engines at its origins) and sublime mathematics (the Gibbs phase rule). For the first time, industrial processes could be rationally optimized – it was around 1910 that the Haber–Bosch process for nitrogen fixation was elaborated, a synthesis of ammonia so successful that it now competes on a global scale with the natural processing of the atmosphere's nitrogen. Answering a different call for 'How?', we see the first explorations of the wondrously evolved biochemical pathways in just this period, but also the beginnings of the deplorable split between chemistry and biochemistry.

A new century opens before us. Where are we now? In what way is chemistry today different from the chemistry we admired 100 years ago? I see fantastic progress in the ways we have looked before at matter – synthesis ever more proficient and prominent; analysis answering (and asking) still more detailed questions – 'What have I got?' being replaced by 'How little have I got of what?' I see the study of the mechanisms of chemical reactions (the answer to the 'How?' question), the atomistic tracing of the transformation, pursued down to the nearly unimaginably small time interval of a femtosecond. I see theory (dealing with the 'Why' question) finally entering into real predictive competition with experiment, even as it, theory, rushes pell-mell into simulation rather than understanding. These are wonders and marvels, all in an industrial setting that is a positive contributor to the trade balance of many an industrialized country.

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However, when I look at the riches of the new chemistry, I see some leitmotifs that were just not there a century ago. Let me call them 'the molecular vision', being 'in control', and 'taking care'.

Regarding the molecular vision, leaf through this book – how many pictures of chemical reactions in a flask or coloured crystals can you see? How many representations of molecules are there? Molecular structures have been with us since the middle of the nineteenth century, but in the study of molecules both quiescent and in motion there has been a sea change in the second half of the twentieth century. Without waiting for microscopes (we're still waiting, hype to the contrary), using cool thought, hot hands and our ingenious instruments, we have probed inside recalcitrant matter. The diffraction of X-rays, modern computers and nuclear magnetic resonance (before it was denuclearized in a fit of euphemism) have taught us the arrangement of atoms in space in substantive metric detail. Today, when a chemist thinks of a reaction, he or she sees it in the light of a double flame (to adopt Octavio Paz' felicitous phrase) – the macroscopic transformation, as of old, and the microscopic, molecular change.

No, those molecules are not hard balls held together by sticks or springs. They are quantum objects that demand a dual vision. As our instruments interrogate them with light, molecules behave quantum mechanically, with the sometimes mysterious logic of such objects . . . and yet, and yet, for most practical purposes molecules may be assembled (in a hands-off manner) in very architectural, ball-and-stick ways. The twinned perspective is that these molecules are eminently manipulable geometrical objects and they are wave-packets of matter.

In thinking about molecules as they change (for that remains the essence of chemistry) we have invented incredibly fast strobe lights to freeze their motion even as they careen around at the speed of sound on a very crowded dance floor. We have also developed very specific ways to put energy into parts of a molecule, by using a new type of light – the intense, monochromatic laser beam. The chemist of 2001 makes the new surely, with a double vision, that of substance and molecule.

Regarding being in control; 100 years ago there was so much to discover – How does inheritance work?, 'What is inside diamond and graphite?' – that chemists were just entranced by the intricacy of the world as it is. True, industrial chemists were not mesemerized, simply proceeded to make in novel, unnatural ways what there was profit in making. It there were no cheap pure aluminium in the world of 1884, young Héroult and young Hall told us how to make it,

A cursory look at modern chemistry reveals it compulsively making new molecules with exquisite control. True, the makers are human and so bound to puff serendipitous creation up with *ex-post-facto* motive; and yes, obsession with control seems inordinately, sometimes humorously, male – in a science in which women are approaching parity in numbers – but these are just my carpings in contemplating a marvellous achievement: chemists, men and women, have learned to assemble incredibly complex structures with fantastic control.

The working out of that creative obsession for control is essential in a world in which as small a difference between molecules as that between a left and a right hand can spell the difference between toxicity and pharmaceutical efficacy. A catalyst that allows one company's process to be 10% more efficient can put a competitor out of business. Materials with exquisitely controlled surfaces and properties are shaping the information revolution. The genetically manipulated feedstocks (that's also chemistry) that confer resistance against a common pest have transformed agriculture.

Yes, we are taking a leaf from nature's wondrous ways of self-assembly and evolutionary strategies; and yes, by engineering properties way beyond what nature provides, we, masters of cultural evolution, make the new.

Regarding taking care; we look at nature not only as servant muse, but also with



true love. For, talented as we are, we have transformed many of the grand cycles of this planet. More than half of the sulfur atoms in your amino acids have seen the inside of a sulfuric-acid factory. Some essential renewable resources, such as the petroleum feedstocks of our chemical industry, will be depleted within the next couple of centuries. The moral tenor of this age, not just the Greens, demands that whatever we transform be done with social justice and with respect for nature.

The signal change in the chemical industry is that, when a new process is introduced, ecological and safety considerations are now paramount. This did not come about willingly, mind you – I recall the screaming of the automotive industry about how they could never, absolutely never, reduce emissions of CO, hydrocarbons and  $NO_x$  by a factor of 20. Forced to do so by public pressure and government regulation, the industry, in one of the major scientific and engineering advances of the twentieth century, devised the 'three-way' catalyst to do just what it had said could never be done.

The ecological imperative has crept down much more slowly to inventive yet unconcerned academia. However, I see its formative events there – in the interest in atmospheric chemistry and in the ingenious construction of novel organic processes to avoid the use of organic solvents. A government carrot in the form of new research funds for green chemistry would, in my unpopular opinion, be just what is needed to channel the ingenuity of my colleagues, who love to say that they just want to do what is interesting, but . . . The same nicely obsessive penchant for control as that which is used to make molecules do acrobatics can and is being turned to the attainment of a necessary balance between our given imperative to create and our love for the world. Chemists should and do care.

# The Search for New Elements

Glenn T. Seaborg and Walter D. Loveland

# 1

#### Introduction

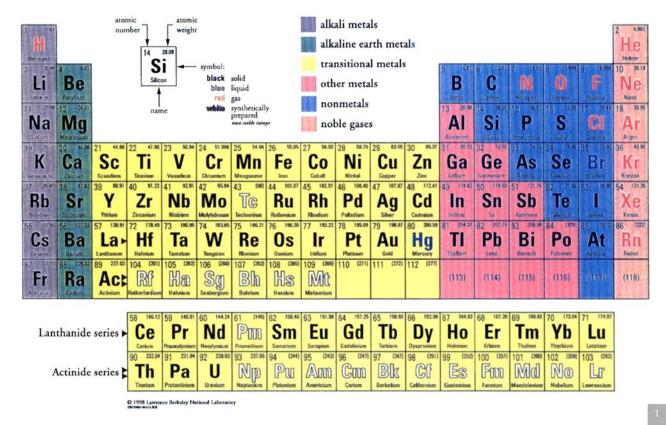
The chemical elements are the building blocks of nature. All substances are combinations of these elements. There are 112 known chemical elements, the heaviest naturally occurring element being uranium (Z=92). Twenty of the heaviest chemical elements, the transuranium elements, are man-made. The story of their synthesis, their properties, their impact on chemistry and physics and their importance to society is as fascinating as is the chance of a further expansion in their number.

In this chapter, we will discuss how to make these elements and their chemical properties and importance to chemistry. We will discuss the chances of making new elements. We will conclude by discussing the practical applications of the transuranium elements, including concerns about their presence in the environment. We show the cast of characters for our story in Table 1 that lists the names of the transuranium elements and Figure 1 that depicts their places in the modern Periodic Table.

## The History of the Chemical Elements

The story of the chemical elements begins in ancient times. At the time of Christ, people knew about nine chemical elements (C, S, Fe, Cu, Ag, Sn, Au, Hg and Pb). These elements had been isolated in pure form and put to use in various ways. From the charcoal of fires, one had carbon (C). One knew the elements that were found free in nature – gold (Au), silver (Ag) and copper (Cu). Sulfur (S) was known, as was how to extract the pure metals from ores of copper (Cu), mercury (Hg), lead (Pb) and tin (Sn).

Figure 1
The modern Periodic Table showing the transuranium elements.



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Table 1 The transuranium elements						
Atomic number	Element	Symbol				
93	Neptunium	Np				
94	Plutonium	Pu				
95	Americium	Am				
96	Curium	Cm				
97	Berkelium	Bk				
98	Californium	Cf				
99	Einsteinium	Es				
100	Fermium	Fm				
101	Mendelevium	Md				
102	Nobelium	No				
103	Lawrencium	Lr				
104	Rutherfordium	Rf				
105	<b>Hahnium</b> <sup>a</sup>	Ha				
106	Seaborgium	Sg				
107	Bohrium	Bh				
108	Hassium	Hs				
109	Meitnerium	<b>M</b> t				
110						
111						
112						

#### Note:

During the Middle Ages, alchemists discovered arsenic (As), antimony (Sb) and bismuth (Bi). The first element discovered by one person and recognized as such was phosphorus (P). The German alchemist Hennig Brand discovered phosphorus ('bearer of light') in 1669. Brand made phosphorus from dried urine and discovered that it had the remarkable property of glowing in the dark when exposed to air.

Cobalt was discovered in 1737 and nickel about 14 years later. Cobalt and nickel ores previously had been mistaken for copper ore. Since they refused to yield copper, these ores obviously were possessed by evil spirits and thus had gained the names *Kobold* (goblin) and *Kupfernickel* (Old Nick's copper). These names persisted.

The pace of the discovery of elements quickened during the latter part of the eighteenth century through the work of Henry Cavendish, Daniel Rutherford, Joseph Priestley, Karl Scheele and Antoine Lavoiser. The number of elements known to man by the middle 1770s was about twenty. During the next 25 years, eleven more elements were discovered. Between 1800 and 1869, the number of elements known to man nearly doubled.

In 1869, the great Russian chemist Dmitri Mendeleev and the German chemist Lothar Meyer independently uncovered the principle of the Periodic Table. First, they arranged the known elements (about two thirds of the naturally occurring elements) in order of increasing atomic weight. Hydrogen didn't fit in very well, so they started lining up the elements beginning with lithium and beryllium. They found that, if they finished a row and then started a second row below it, they got elements with similar chemical properties falling below one another across the table. As they extended the table, they found several groups of elements that did not fit their seven columns. These elements were incorporated into the table later.

<sup>&</sup>lt;sup>a</sup> The IUPAC has recommended the name dubnium (symbol Db) for element 105.

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Figure 2			
The Periodic	Table	of	Mendeleev.

-	GRUPPE 1.	GRUPPE II.	GRUPPE III.	GRUPPE IV.	GRUPPE V.	GRUPPE VI.	GRUPPE VII	GRUPPE VIII.
ū	-	OKOTTE II.	OKOTTE III.	RH4	RH3	RH2		GROFFE VIII.
REIHEN	R20	RO	R2O3	RO2	R205	RO3	RH R207	RO4
<u>«</u>			K-O-	KU-	Keos	KOS	M-O.	NO4
1	H=1	DISCOURSE IN		300000	CONTRACTOR OF THE PARTY OF THE			
2	Li= 7	Be = 9,4	B= 11	C=12	N=14	0=16	F=19	
3	Na = 23	Mg = 24	A1 = 27,3	Si=28	P = 31	S=32	C1 = 35,5	
4	K=39	Ca = 40	-= 44	Ti = 48	V= 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	-=68	-= 72	As = 75	Se = 78	Br = 80	The State St
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	?C8 = 140	-	-	-	
9	(-)	-	-	_	-	-	-	
10	_	-	?Er= 178	?La=180	Ta = 182	W=184	-	Os = 195, Ir = 197,
								Pt = 198, Au = 199.
11	(AU=199)	Hg = 200	TI = 204	Pb = 207	Bi = 208	-	-	
12	-	-	-	Th = 231	-	U=240	-	
						3		

Mendeleev, in particular, noticed that he had to skip several places to maintain vertical columns in which all the elements listed had similar properties (see Figure 2). Mendeleev's contribution was that he recognized the gaps in his Periodic Table and that they should be filled by elements that had not yet been discovered.

He went further than that. He had the courage to predict what three of the undiscovered elements would look like, how much they would weigh and how they would react chemically. Since he expected the three elements to have properties similar to those of boron, aluminium and silicon, respectively, he tentatively named them ekaboron, eka-aluminium, and eka-silicon (from the Sanskrit *eka*, meaning 'next'). These missing elements were discovered in Scandinavia (scandium), France (gallium) and Germany (germanium) a few years later.

By the end of the first third of the twentieth century, the total number of chemical elements had increased to 88. This included the rare-gas family that had to be fitted into the scheme of Figure 2 by adding another column and a series of elements – the rare earths or lanthanides – located in the place of a single element, lanthanum. Only four of the first 92 elements were missing, i.e. those with atomic numbers 43, 61, 85 and 87. We show in Figure 3 the Periodic Table as it was known in 1940.

The first man-made element was that with atomic number 43. Carlo Perrier and Emilio Segre identified it in 1937. A foil of molybdenum metal was irradiated with 8 MeV deuterons in the Berkeley cyclotron and sent to Perrier and Segre in Italy. They identified two radioactivities (with half-lives of 62 and 90 days) as chemically different from all the other 88 elements and thus due to element 43. These two radioactivities are known now to be <sup>95</sup>Tc<sup>m</sup> and <sup>97</sup>Tc<sup>m</sup>, where the 'm' designation represents a long-lived excited state. They later (in 1947) named the new element 'technetium' (Tc) after the Greek word TEXUETOS (artificial) because this was the first element to be produced by artificial means.

This discovery raised the possibility of filling in the other missing elements (61, 85 and 87) and possibly even extending the Periodic Table to elements beyond uranium. It also raised some general questions about the limits of the Periodic Table, methods of synthesis of elements and so on.

Element 61 was first identified by Jacob Marinsky, Lawrence Glendenin and Charles Coryell during the Manhattan Project in 1945. These investigators made a chemical identification, using ion exchange, of two isotopes of element 61, <sup>147</sup>Pm and <sup>149</sup>Pm, formed by the neutron-induced fission of uranium. The name promethium was suggested for this element by Grace Mary Coryell in honour of the figure in Greek mythology who stole fire from the gods for human use, an apt analogy for the Manhattan Project.

Element 85, astatine (At), was first identified in 1940 as the result of production of the radioactive isotope <sup>211</sup>At by the irradiation of bismuth with 32-MeV alpha-particles

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Figure 3
The Periodic Table of the 1930s; atomic numbers of undiscovered elements are in shaded squares.

*Lant	hanides	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	
87	88 Ra	89 Ac	90 Th	91 Pa	92 U	93	94	95	96	97	98	99	100	101	102	103	1
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	B1 TI	82 Pb	83 Bi	84 Po	85	F
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 	>
19 K	20 Ca	21 Sc	ZZ 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	,
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 CI	,
3 Li	4 Be											5 B	C e	7 N	9	9 F	1
н																	H

in the 60-inch cyclotron at Berkeley. In a series of experiments involving radiotracers, Dale Corson, Kenneth MacKenzie and Emilio Segre were able to show that this alphaparticle-emitting isotope (211At) was a new chemical element. The name astatine is derived from a Greek word meaning 'unstable'. Later it was found that radioactive isotopes of astatine occur as part of the natural decay series.

Element 87 (francium (Fr)) was discovered by Marguerite Perey in 1939. She showed that the alpha-decay of <sup>227</sup>Ac led to a new beta-particle-emitting substance with a half-life of 21 min (<sup>223</sup>Fr). This new substance behaved chemically like an alkali metal. Perey named the new element francium in honour of her native country.

# The Problems of Element Synthesis

The extent to which man can extend the 'natural' number of chemical elements is limited by the characteristics of the fundamental forces of nature. A commonly used model of the gross properties of nuclei predicts that a nucleus will instantaneously undergo fission when

$$E_{\rm c} = 2E_{\rm s}$$

where  $E_{\rm c}$  and  $E_{\rm s}$  are the Coulomb energy and surface energy, respectively, of the nucleus that is represented as a uniformly charged liquid drop. The quantities  $E_{\rm c}$  and  $E_{\rm s}$  are given as

$$E_{\rm c} = \frac{3}{5} \frac{(Ze)^2}{R} = k_{\rm c} \frac{Z^2}{A^{1/3}}$$

$$E_s = 4\pi R^2 \gamma = k_s A^{2/3}$$

where  $\gamma$  is the nuclear surface tension ( $\approx$ 1 MeV fm<sup>-2</sup>), Z is the atomic number and R is the nuclear radius (which is proportional to  $A^{1/3}$ , where A is the mass number). The limiting value of the atomic number,  $Z_{\text{LIMIT}}$ , is then

$$Z_{\text{LIMIT}}^2 = 2(k_s/k_c)A_{\text{LIMIT}}$$

If we remember that the neutron/proton ratio in heavy nuclei is about 1.5/1, then

$$Z_{\text{LIMIT}} = 5(k_{\text{s}}/k_{\text{c}})$$

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Thus the upper bound to the Periodic Table is proportional to the ratio of two fundamental constants related to the strengths of the nuclear (surface) and electromagnetic forces. The ratio  $k_s/k_c$  is about 20-25 and thus we expect 100-125 chemical elements. Only a moderate extension of the 'natural' Periodic Table by man would be expected to be possible.

The synthesis of a new element involves more than just colliding two nuclei whose atomic numbers are such that they sum to a value corresponding to an unknown element. Heavy nuclei are, in general, quite fissionable. If they are made with significant excitation, they will decay by fission, leaving no identifiable heavy residue of their formation. So one must balance the factors governing the 'production' of a new nucleus carefully with those factors governing its 'survival'. The 'production factors' determine the yield of the primary reaction products whereas the 'survival factors' determine which primary product nuclei de-excite by particle emission, which allows them to survive, and which nuclei de-excite by fission, which destroys them. Amongst the 'production factors' are items such as the 'starting material', the target nuclei, which must be available in sufficient quantity and suitable form. We must have enough transmuting projectile nuclei also. The transmutation reaction must occur with adequate probability to ensure a good yield of the product nucleus in a form suitable for further study. Equally important is that the product nuclei be produced with distributions of excitation energy and angular momentum such that the product nuclei will de-excite by particle or photon emission rather than the disastrous fission process. The competition between particle emission and fission as de-excitation paths depends on the excitation energy, angular momentum and intrinsic stability of the product nucleus, which is related to the atomic and mass numbers of the product (see Box 1). For a description of the detection of product nuclei, see Box 2.

Nuclear synthesis is similar in some ways to inorganic and organic chemical syntheses in that the synthetic chemist or physicist has to understand the reactions involved and the structures and stabilities of the intermediate species. Although, in principle, the outcome of any synthesis reaction is calculable, in practice such calculations are, for the most part, very difficult. Instead, the cleverness of the scientists involved, their manipulative skills and the instrumentation available for their use determine the success of many synthetic efforts.

The synthesis reactions used to 'discover' the man-made elements are given in Table 2. All these reactions are complete fusion reactions in which the reacting nuclei fuse, equilibrate and de-excite in a manner that is independent of their mode of formation. The nucleus is said to have 'amnesia' about its mode of formation. Other production reactions involving partial capture of the projectile nucleus are also possible.

The reactions in Table 2 can be divided into four classes: the neutron-induced reactions (Z=61, 93, 95, 99 and 100); the light-charged-particle-induced reactions (Z=43, 85, 94, 96–98 and 101); the 'hot fusion' reactions (Z = 102-106) and the 'cold fusion' reactions (Z = 107 - 112). In the neutron-induced reactions to make the transuranium nuclei, the capture of a neutron does not create a new element, but the subsequent β decays do. Reactions of light charged particles with exotic actinide target nuclei allow one to increase the atomic number of the product by one or two units from that of the target nucleus. To make the heaviest elements, one needs to add several protons to the target nucleus by a reaction with a heavy ion. Such 'hot fusion' reactions with actinide target nuclei lead to highly excited intermediate species that decay mostly by fission but occasionally by emitting neutrons, thus producing new nuclei. However, as the atomic number of the product nuclei increases, so does the probability of fission leading to very poor probabilities of survival for the putative new species. The Russian nuclear physicist Yuri Oganessian pointed out that a way around this problem was to fuse heavier projectile nuclei with nuclei in the



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# **Box 1** Element-synthesis calculations

The reactions used to synthesize heavy nuclei are, quite often, Władysław Świątecki and William Myers. Taking as a rough very improbable reactions, representing minor branches relative to the main reaction. Their probabilities of occurrence with respect to the main synthesis reaction are frequently less than 10<sup>-6</sup>. Hence it is intrinsically difficult to describe these reactions accurately from a theoretical point of view. Instead, workers in this field have frequently resorted to involved the reaction semi-empirical prescriptions to guide their efforts.

The German physicist Peter Armbruster constructed a systematic diagram of the probability of fusion of two heavy nuclei at energies near the reaction barrier. This is shown in numbers of projectile and target nuclei and reads off the overall cross section for producing 265Hs to be expected value for the cross section for producing a completely fused species. The excitation energy of the completely fused species can then be read from Figure 5, which is based (The measured cross section was  $2 \times 10^{-35}$  cm<sup>2</sup>.) upon the nuclear masses of Peter Möller, J. Rayford Nix,

rule of thumb that, for each 10 MeV of excitation energy, the probability of survival of the fused system drops by a factor of 102, one can then compute the cross section for producing a given species.

For example, the successful synthesis of <sup>265</sup>Hs (<sup>265</sup>108)

$$^{58}\text{Fe} + ^{208}\text{Pb} \rightarrow ^{265}\text{Hs} + \text{n}$$

From Figure 4, one predicts the fusion cross section to be 10<sup>-32</sup> cm<sup>2</sup>, while Figure 5 would suggest an excitation energy Figure 4. To use this graph, one picks values of the atomic of about 20 MeV. Thus one would roughly estimate the

$$10^{-32} \times (10^{-2})^2 \simeq 10^{-36} \text{ cm}^2$$

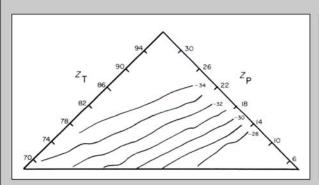


Figure 4 A plot of the contours of  $\log_{10}\sigma_{\mathrm{fus}}$  (where  $\sigma_{\mathrm{fus}}$  is the s-wave fusion cross section at the interaction barrier).

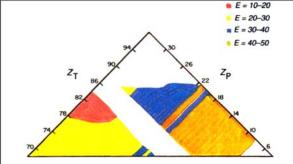


Figure 5 Plot of the excitation energy of the completely fused species formed from a given target-projectile combination. Reactions are assumed to take place at the interaction barrier.

lead-bismuth region. Because of the special stability of the lead-bismuth nuclei, the resulting fused species would be formed 'cold' and could, with some reasonable probability, decay by emitting only a single neutron.

## The History of the Discovery of Transuranium Elements

The first scientific attempts to prepare the elements beyond uranium were made by Enrico Fermi, Emilio Segre and co-workers in Rome in 1934, shortly after the existence of the neutron had been discovered. This group of investigators irradiated uranium with slow neutrons and found several radioactive products, which were thought to be due to new elements. However, chemical studies by Otto Hahn and Fritz Strassman in Berlin showed that these species were isotopes of the known elements formed by the fission of uranium into two approximately equal parts. This discovery of nuclear

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#### Box 2 How to detect heavy-element atoms

The detection of atoms of a new element has always focused on measuring the atomic number of the new species and showing that it is different from all known values of Z. Unambiguous methods for establishing the atomic number include chemical separations, measurement of the X-ray spectrum accompanying a nuclear decay process and establishment of a genetic relationship between the unknown new nucleus and some known nuclide. As the quest for new elements focuses on still heavier species, the probability of producing the new elements has decreased and one has had to devote more attention to the problem of detecting a few atoms of a new species amidst a background of many orders of magnitude more atoms of other elements. Thus, modern attempts to make new heavy-element atoms usually involve some kind of 'separator.'

An example of a modern separator is the velocity filter SHIP (Figure 6) at the GSI in Darmstadt, Germany. In this separator, nuclear reaction products (from the target wheel) undergo different electrostatic deflections (in a crossed magnetic field) depending on whether they are fission fragments, scattered beam particles or the desired heavy-element residues. The efficiency of the separator is about 50% for heavy-element residues, while transfer products and scattered beam nuclei are rejected by factors of 10<sup>14</sup> and 10<sup>11</sup>, respectively. The heavy recoil atoms are implanted in the silicon detectors. Their implantation energies and positions are correlated to any subsequent decays of the nuclei to establish genetic relationships to known nuclei.

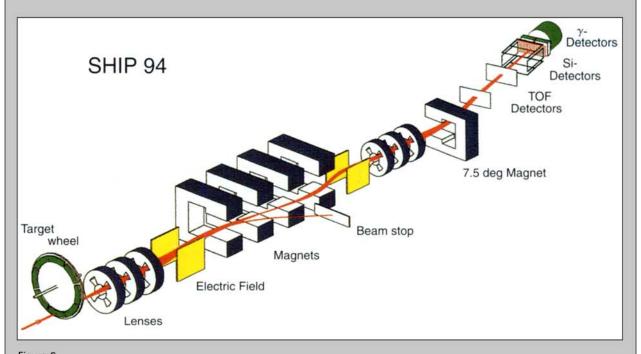


Figure 6 The velocity filter SHIP.

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Table 2	A summary of synthe	ses of man-made elements	
Atomic number	Name and symbol	Synthesis reaction	Half-life
43	Technetium (Tc)	$^{94}\text{Mo} + ^{2}\text{H} \rightarrow ^{95}\text{Tc}^{\text{m}} + \text{n}$	61 days
61	Promethium (Pm)	$^{96}\text{Mo} + ^{2}\text{H} \rightarrow ^{97}\text{Tc}^{\text{m}} + \text{n}$ $^{235}\text{U} + \text{n} \rightarrow ^{147}\text{Pm}, ^{149}\text{Pm}$	90.5 days 2.6 years 53.1 h
85	Astatine (At)	$^{209}\text{Bi} + ^{4}\text{He} \rightarrow ^{211}\text{At} + 2\text{n}$	7.2 h
87	Francium (Fr)	$^{227}$ Ac $\rightarrow$ $^{223}$ Fr $+\alpha$	21.8 min
93	Neptunium (Np)	$^{238}U + n \rightarrow ^{239}U +$ $^{239}U \stackrel{\beta}{\rightarrow} ^{239}Np$	2.35 days
94	Plutonium (Pu)	$^{238}\text{U} + ^{2}\text{H} \rightarrow ^{238}\text{Np} + 2\text{n}$ $^{238}\text{Np} \xrightarrow{\beta} ^{238}\text{Pu}$	86.4 years
95	Americium (Am)	$^{239}$ Pu + n $\rightarrow$ $^{240}$ Pu + $^{240}$ Pu + n $\rightarrow$ $^{241}$ Pu + $^{241}$ Pu $^{\beta-}$ $^{241}$ Am	433 years
96	Curium (Cm)	$^{239}$ Pu + $^{4}$ He $\rightarrow$ $^{242}$ Cm + n	162.5 days
97	Berkelium (Bk)	$^{241}\text{Am} + ^{4}\text{He} \rightarrow ^{243}\text{Bk} + 2\text{n}$	4.5 h
98	Californium (Cf)	$^{242}$ Cm + $^{4}$ He $\rightarrow$ $^{245}$ Cf + n	44 min
99	Einsteinium (Es)	'Mike' thermonuclear explosion (leading to <sup>253</sup> Es)	20 days
100	Fermium (Fm)	'Mike' thermonuclear explosion (leading to <sup>255</sup> Fm)	20 h
101	Mendelevium (Md)	$^{253}\text{Es} + ^{4}\text{He} \rightarrow ^{256}\text{Md} + \text{n}$	76 min
102	Nobelium (No)	$ \begin{array}{l} ^{244}\text{Cm} + {}^{12}\text{C} \rightarrow {}^{252}\text{No} + 4n \\ ^{250}\text{Cf} \\ ^{251}\text{Cf} \\ ^{4}\text{H} \rightarrow {}^{258}\text{Lr} + \begin{cases} 3n \\ 4n \end{cases} $	2.3 s
103	Lawrencium (Lr)	$ \begin{array}{c} 252\text{Cf} \\ 250\text{Cf} \\ 251\text{Cf} \\ 252\text{Cf} \end{array} + {}^{10}\text{B} \rightarrow {}^{258}\text{Lr} + \begin{cases} 2n \\ 3n \\ 4n \end{cases} $	4.3 s
104	Rutherfordium (Rf)	$^{249}\text{Cf} + ^{12}\text{C} \rightarrow ^{257}\text{Rf} + 4\text{n}$ $^{249}\text{Cf} + ^{13}\text{C} \rightarrow ^{259}\text{Rf} + 3\text{n}$	3.4 s 3.8 s
105	Hahnium (Ha)	$^{249}\text{Cf} + ^{15}\text{N} \rightarrow ^{260}\text{Ha} + 4\text{n}$	1.5 s
106	Seaborgium (Sg)	$^{249}\text{Cf} + ^{18}\text{O} \rightarrow ^{263}\text{106} + 4\text{n}$	0.9 s
107	Bohrium (Bh)	$^{209}\text{Bi} + ^{54}\text{Cr} \rightarrow ^{262}107 + \text{n}$	102 ms
108	Hassium (Hs)	$^{208}\text{Pb} + ^{58}\text{Fe} \rightarrow ^{265}108 + \text{n}$	1.8 ms
109	Meitnerium (Mt)	$^{209}\text{Bi} + ^{58}\text{Fe} \rightarrow ^{266}109 + \text{n}$	3.4 ms
	,	$^{209}\text{Bi} + ^{59}\text{Co} \rightarrow ^{267}110 + \text{n}$	4 μs
***		$^{208}\text{Pb} + ^{62}\text{Ni} \rightarrow ^{269}\text{110} + \text{n}$	170 μs
110		$^{208}\text{Pb} + ^{64}\text{Ni} \rightarrow ^{271}110 + \text{n}$	56 ms
		$^{244}$ Pu + $^{34}$ S $\rightarrow$ $^{273}$ 110 + 5n	118 ms
111		$^{209}\text{Bi} + ^{64}\text{Ni} \rightarrow ^{272}111 + \text{n}$	1.5 ms
112		$^{208}\text{Pb} + ^{70}\text{Zn} \rightarrow ^{277}112 + \text{n}$	240 μs

fission in December of 1938 was thus a by-product of man's quest for the transuranium elements.

With poetic justice, the actual discovery of the first transuranium element came as part of an experiment performed to study the nuclear fission process. Edwin McMillan, working at the University of California at Berkeley in the spring of 1939, was trying to measure the energies of the two recoiling fragments from the neutron-induced fission of uranium. He placed a thin layer of uranium oxide on one piece of paper. Next to this

he stacked very thin sheets of cigarette paper to stop and collect the fission fragments of uranium. During his studies he found that there was another radioactive product of the reaction – one that did not recoil enough to escape the uranium layer as did the fission products. He suspected that this product was formed by the capture of a neutron by the more abundant isotope of uranium,  $^{238}_{92}$ U. McMillan and Philip Abelson (Figure 7), who joined him in this research, showed in 1940, by chemical means, that this product is an isotope of element 93,  $^{239}_{93}$ Np, formed in the following sequence:

$${}^{238}_{92}\text{U} + \text{n} \rightarrow {}^{239}\text{U} + \gamma$$

$${}^{239}\text{U} \xrightarrow{f_{1/2} = 23.5 \text{ min}} {}^{239}_{93}\text{Np } (t_{1/2} = 2.36 \text{ days})$$

Neptunium, the element beyond uranium, was named after the planet Neptune because this planet is beyond the planet Uranus, after which uranium had been named.

Plutonium was the second transuranium element to be discovered. By bombarding uranium with charged particles, in particular, deuterons ( $^2$ H), using the 60-inch cyclotron at the University of California at Berkeley, Glenn T. Seaborg, McMillan, Joseph W. Kennedy and Arthur C. Wahl (Figure 8) succeeded in preparing a new isotope of neptunium,  $^{238}$ Np, which decayed by  $\beta^-$  emission to  $^{238}$ Pu, that is,

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

$${}^{239}_{93}\text{Np} \frac{\beta^{-}}{t_{1/2} = 2.12 \text{ days}} \rightarrow {}^{238}_{94}\text{Pu} \ (t_{1/2} = 87.7 \text{ years})$$

Early in 1941, <sup>239</sup>Pu, the most important isotope of plutonium, was discovered by Kennedy, Segre, Wahl and Seaborg. <sup>239</sup>Pu was produced by the decay of <sup>239</sup>Np, which had been produced by the irradiation of <sup>238</sup>U by neutrons, using the reaction

$$^{239}_{92}U + {}^{1}_{0}n \rightarrow ^{239}_{92}U + \gamma$$

$$^{239}_{92}\frac{\beta^{-}}{t_{1/2} = 23.5 \text{ min}} \rightarrow ^{239}_{93}\text{Np} \frac{\beta^{-}}{t_{1/2} = 2.35 \text{ days}} \rightarrow ^{239}_{94}\text{Pu (}t_{1/2} = 24 \text{ 110 years)}$$

This isotope, <sup>239</sup>Pu, was shown to have a cross section for thermal neutron-induced fission that exceeded that of <sup>235</sup>U, a property that made it important for nuclear weapons, considering that no isotope separation was necessary for its preparation, unlike for <sup>235</sup>U. Plutonium was named after the planet Pluto, following the pattern used in naming neptunium.

The next transuranium elements to be discovered, americium and curium (Am and Cm; Z=95 and 96, respectively) represent an important milestone in chemistry, namely the recognition of a new group of elements in the Periodic Table, the actinides. According to the Periodic Table of Figure 3, one expected americium and curium to be eka-iridium and eka-platinum, i.e. to have chemical properties similar to those of iridium and platinum. In 1944, Seaborg conceived the idea that all the known elements heavier than actinium (Z=89) had been misplaced in the Periodic Table. He postulated that the elements heavier than actinium form a second series similar to the lanthanide elements (Figure 1), called the actinide series. This series would end in element 103 (Lr) and, analogously to the lanthanides, these elements would have a common oxidation state of  $\pm 3$ .

Once this redox property had been understood, the use of a proper chemical procedure led quickly to the identification of an isotope of a new element. Thus, a new alpha-particle-emitting nuclide, now known to be  $^{242}_{94}$ Cm (half-life 162.9 days), was produced by Seaborg, Albert Ghiorso and Ralph James in the summer of 1944 by the bombardment of  $^{239}_{94}$ Pu with 32–MeV helium ions:

# 1 The Search for New Elements







Figure 7
The discoverers of neptunium, Edwin
M. McMillan (top) and Philip H.
Abelson (bottom).

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Glenn T. Seaborg and Walter D. Loveland





Figure 8
The co-discoverers of plutonium,
Joseph W. Kennedy (25 December
1940), Arthur C. Wahl and Glenn T.
Seaborg. Seaborg and Wahl are
shown (in February 1966) with the
sample of <sup>239</sup>Pu in which fission was
demonstrated in 1941 (the cigar box
was that of G. N. Lewis).

$${}^{239}_{94}Pu + {}^{4}_{2}He \rightarrow {}^{242}_{96}Cm + {}^{1}_{0}n$$

The bombardment took place in the Berkeley 60-inch cyclotron, after which the material was shipped to the Metallurgical Laboratory at Chicago for chemical separation and identification. A crucial step in the identification of the alpha-particle-emitting nuclide as an isotope of element 96,  $^{242}_{96}$ Cm, was the identification of the known  $^{238}_{96}$ Pu as the alpha-decay daughter of the new nuclide.

The identification of an isotope of element 95, by Seaborg, Ghiorso, James and Leon Morgan in late 1944 and early 1945, followed the identification of this isotope of element 96 (<sup>242</sup>Cm) as a result of the bombardment of <sup>239</sup>Pu with neutrons in a nuclear reactor. The production reactions, involving multiple neutron capture by plutonium, are

$$^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \rightarrow ^{240}_{94}\text{Pu} + \gamma$$

$$^{240}_{94}\text{Pu} + {}^{1}_{0}\text{n} \rightarrow ^{241}_{94}\text{Pu} + \gamma$$

$$^{241}_{94}\text{Pu} \xrightarrow{}^{241}_{1/2} = 14.4 \text{ years} \rightarrow ^{241}_{95}\text{Am} \ (t_{1/2} = 432.7 \text{ years})$$

$$^{241}_{95}\text{Am} + {}^{1}_{0}\text{n} \rightarrow ^{242}_{95}\text{Am} + \gamma$$

$$^{242}_{95}\text{Am} \xrightarrow{}^{242}_{95}\text{Cm}$$

The years after World War II led to the discovery of elements 97–103 and the completion of the actinide series. Although the story of the discovery of each of these elements is fascinating, we shall, in the interests of brevity, refer the reader elsewhere (see the references) for detailed accounts of most of these discoveries. As an example of the techniques involved, we shall discuss the discovery of element 101 (mendelevium).

The discovery of mendelevium was one of the most dramatic in the sequence of syntheses of transuranium elements. It was the first case in which a new element was produced and identified one atom at a time. By 1955, scientists at Berkeley had prepared an equilibrium amount of about 10<sup>9</sup> atoms of <sup>253</sup><sub>99</sub>Es by neutron irradiation of plutonium in the Materials Testing Reactor in Idaho. From a 'back of the envelope' calculation done by Ghiorso during an airplane flight, they thought that it might be possible to prepare element 101 using the reaction

$$^{253}_{99}$$
Es  $+ {}^{4}_{2}$ He $\rightarrow {}^{256}_{101}$ Md  $+ {}^{1}_{0}$ n

The amount of element 101 expected to be produced in an experiment can be calculated using the formula

$$N_{101} = \frac{N_{\rm Es}\sigma\varphi(1-e^{-\lambda t})}{\lambda}$$

where  $N_{101}$  and  $N_{Es}$  are the numbers of atoms of element 101 produced and of  $^{253}_{99}Es$  target atoms, respectively,  $\sigma$  is the reaction cross section (estimated to be of the order of  $10^{-27}$  cm<sup>2</sup>),  $\varphi$  is the flux of helium ions ( $\approx 10^{14}$  particles s<sup>-1</sup>),  $\lambda$  is the decay constant of  $^{256}_{101}Md$  (estimated to be  $\approx 10^{-4}$  s<sup>-1</sup>) and t is the duration of each bombardment ( $\approx 10^4$  s):

$$N_{101} \approx \frac{10^9 \times 10^{-27} \times 10^{14} (1 - e^{-10^{-4} \times 10^{+4}})}{10^{-4}} \approx 1 \text{ atom}$$

Thus the production of only one atom of element 101 per experiment could be expected!