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The Synthetic Elements

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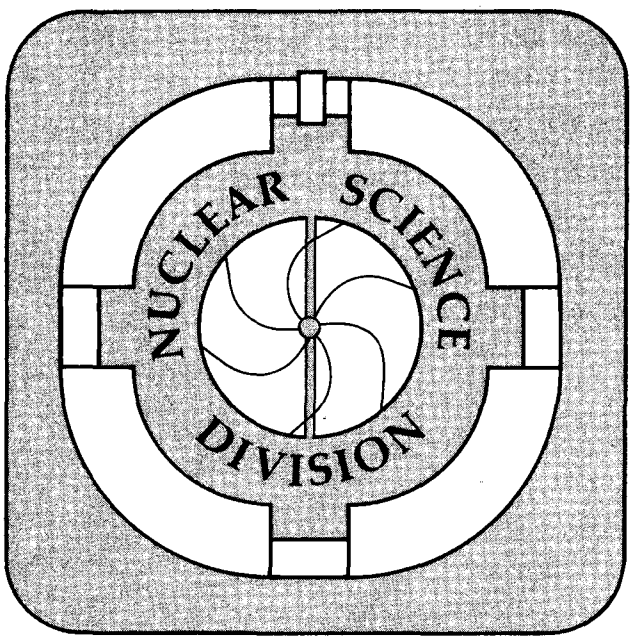

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The Synthetic Elements

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August 5–9, 1990, Atlanta, GA
"Topics in Nuclear and Radiochemistry for College Curricula and
High School Science Programs"

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THE SYNTHETIC ELEMENTS

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ABSTRACT

Prior to 1940, the heaviest element known was uranium, discovered in 1789. Since that time the elements 93 through 109 have been synthesized and identified and the elements 43, 61, 85, and 87 which were missing from the periodic tables of the 1930's have been discovered. The techniques and problems involved in these discoveries and the placement of the transuranium elements in the periodic table will be discussed. The production and positive identification of elements heavier than Md (Z=101), which have very short half-lives and can only be produced an atom-at-a-time, are very difficult and there have been controversies concerning their discovery. Some of the new methods which have been developed and used in these studies will be described. The prospects for production of still heavier elements will be considered.

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THE SYNTHETIC ELEMENTS

I. INTRODUCTION

Our modern concept of a chemical element which relates it to proton number (or Z) is of necessity of rather recent origin because it is related directly to atomic theory which was only developed in this century. However, even the ancient Greeks were interested in the elements of which matter was composed and Aristotle had even defined four elements from which everything else could be derived! The development in 1869 of the periodic tables of Mendeleev and Meyer in which the elements were arranged according to their atomic weights was invaluable in indicating errors in existing assignments and in predicting the existence and properties of undiscovered elements, but there were certain problems because, for example, argon with Z=18 has a practical weight heavier than that of potassium with Z=19. However, Moseley's brilliant work (1910-14) showed the linear relationship between the square root of the frequency of a given characteristic X-ray line of an element and its atomic number. This allowed placement of elements according to proton number or Z and showed clearly any missing elements. In addition, measurement of their characteristic X-ray spectra provided an unequivocal method of identification for new elements.

A periodic table from about 1935 is shown in Fig. 1. The heaviest element known at that time was uranium which had been discovered in 1789, some 145 years earlier. You will further note that elements 43, 61, 85, and 87 are missing. By comparison with the current periodic table shown in Fig. 2, you can see that since then, those 4 missing elements plus 11 actinide elements and 6 transactinide elements have been discovered. Except for element 87, francium, which was first discovered in 1939 by Marguerite Perey at the Curie Laboratory in Paris by chemical isolation from natural uranium ores, all of these are classified as "synthetic" elements because they were first identified via transmutation reactions carried out in the laboratory. However, minute quantities of all of these elements up through plutonium (Z=94) have subsequently been discovered in nature where they are present because of various nuclear processes which continuously occur. In addition, the long-lived isotope plutonium-244 has been found in nature [Hoffman et al., Nature 234, 132 (1971)] and may either be a remnant of the last nucleosynthesis prior to formation of our solar system or from accretion via a cosmic ray source.

II. Discovery of Elements 43, 87, 85, and 61

A. Technetium (Z=43).

Element 43, technetium, was the first previously unknown element to be created by "artificial" means and unequivocally

identified. In fact, the name is derived from the Greek word meaning artificial. In 1937, Perrier and Segre [C. Perrier and E. Segre, J. Chem. Phys. 5, 1937], produced, radiochemically separated, and furnished positive evidence for several radioactive isotopes of element 43 in the products of deuteron (hydrogen-2) bombardment of molybdenum in the cyclotron. Technetium is also a high yield product of the fission of uranium and, therefore, can now be obtained in rather large quantities (kilograms) as a by-product of nuclear fission. It has no known stable isotopes but its longest known isotope, technetium-99, has a half-life of more than 200,000 years.

Earlier, it had been extensively sought in nature and in 1925 Ida Noddack-Tacke, her husband, Walter Noddack, and O. Berg claimed to have detected its X-ray spectrum in the same series of experiments [Naturwiss. 13, 567 (1925)] in which they discovered its homolog, rhenium. They called it masurium, but their findings were not confirmed by other researchers. In fact, we now know that extremely minute quantities of element 43 do actually exist in high-grade natural uranium ores as a result of the spontaneous fission and neutron-induced fission of uranium. Consequently, there has been some recent revival of support for the Noddack's claim to discovery [P. H. M. Van Assche, Nucl. Phys. A480, 205 (1988)], but their sensitivity for measurement of the claimed X-ray spectrum was certainly not sufficient nor was the claim sufficiently well-documented to consitute discovery of element 43. This has been throroughly discussed by Herrmann [G. Herrmann, Nucl Phys. A505, 352 (1990)].

B. Francium (87).

The next of the missing elements to be discovered was francium (87) in 1939. It also has no known stable isotopes and the longest of the known isotopes and the one which M. Perey discovered [M. Perey, J. physique et radium 10, 435 (1939)] is Fr-223 with a half-life of only 22 minutes. As mentioned earlier it is present in nature because it is a decay product ("daughter") of uranium-235 which is present in natural uranium in an abundance of about 0.7%. Perey discovered francium, the heaviest alkali metal, after first isolating its longer-lived parent, actinium-227 (22 years), from uranium ores. Actinium-227 decays only about 1% of the time to francium which, therefore, exists in only rather small quantities in nature. Other shorter-lived isotopes have been produced "artificially". The new element was named francium in honor of France.

C. Astatine (85).

Astatine, the heaviest of the halogens, was first identified in 1940 by Corson, Mackenzie and Segre [Phys. Rev. 58, 662 (1940)] at the University of California who produced the isotope with mass 211 and a half-life of 7.5 hours by bombardment of bismuth (83) with helium (2) ions. Its name is taken from the Greek word "astatos" which means unstable. Although astatine-

218 and 219 are also present in natural uranium ores as decay products of rare branches, their half-lives of only 2 seconds and 0.9 minutes, respectively, make their isolation very difficult and they were not initially discovered in this way. Again, we see that the distinction between "synthetic" and "natural" elements is in itself somewhat artificial!

D. Promethium (61).

The last of the missing lighter elements, promethium (61), is the only rare earth element that has no stable isotopes. It does not occur naturally except for the small amounts resulting from fission of uranium. The first conclusive chemical proof of its existence was given by Marinsky et al. [J. A. Marinsky, L. E. Glendenin, and C. D. Coryell, J. Am. Chem. Soc. 69, 2781 (1947)]. In 1945, during research on the wartime Plutonium Project at Oak Ridge, Tennessee, they chemically isolated isotopes of mass 147 (2.7 years) and mass 149 (47 hours) from the fission products of uranium. Their proposal that element 61 be named promethium after Prometheus who in Greek mythology is said to have stolen fire from the gods for the benefit of mankind was accepted by IUPAC. In 1943 other researchers had reported production of element 61 in proton bombardment of neodymium (Z=60) and proposed the name "cyclonium", but did not furnish sufficient proof of atomic number. Still earlier researchers claimed to have found it in naturally occuring rare earth ores and proposed the names illinium and florentium, but these claims were not subsequently confirmed.

III. DISCOVERY OF THE TRANSURANIUM ELEMENTS

This year marks the 50th anniversary of the discovery in 1940 of neptunium and in 1940 and 1941 of plutonium, the first transuranium elements. These were also among the first so-called "synthetic" elements to be produced and identified. Since 1940, the nine remaining actinides (the last being element 103, lawrencium) and six transactinide elements, rutherfordium (104) through element 109 (as yet unamed) have been synthesized and identified. None of these elements has a stable isotope although neptunium-237 (2.1×10^7 years), plutonium-244 (8.2×10^7 years), and curium-248 (1.6×10^7 years) are very long-lived.

A. Neptunium (93) through Mendelevium (101).

Between 1940 and 1955, during what might be called the "golden age of discovery", 9 new elements, neptunium through mendelevium, were produced and identified. These were all produced either by neutron or alpha bombardment and were identified with very little controversy, perhaps because their half-lives were long enough to permit chemical separation and identification. Table I gives the year of discovery, production

reaction, isotope produced, half-life, decay mode, and method of identification for these elements.

Element 93 was discovered by McMillan and Abelson at the University of California, Berkeley in the Spring of 1940. Eelement 94 was produced soon after and chemical proof that a new element had been made was obtained in February, 1941. This work, dated March 7, 1941, was published much later due to self-imposed secrecy because of the potential military applications, by Seaborg, McMillan, Wahl, and Kennedy [Phys. Rev. 69, 367 (1946)]. The names neptunium and plutonium were selected for elements 93 and 94 after the planets Neptune and Pluto which are beyond the planet Uranus for which uranium was named.

Americium (95) and curium (96) were discovered by Ghiorso, James, Morgan, and Seaborg at the Metallurgical Laboratory in Chicago during World War II and announced by Prof. Seaborg on the November 11, 1945 radio program, "The Quiz Kids"! An article by Prof. Seaborg [J. Chem. Ed. 62, 463 (1985)] gives a fascinating historical account of these discoveries and the actinide series, proposed by him in 1945, as a new heavy rare earth series with actinium as the prototype. The names americium after America and curium after Pierre and Marie Curie were proposed for elements 95 and 96 by analogy to their rare earth homologs, which had been named europium after Europe, and gadolinium after J. Gadolin, the Finnish rare earth chemist.

Berkelium (97) and californium (98) were discovered shortly after World War II by Professor Seaborg's group which had returned to the University of California, Berkeley from the Chicago Metallurgical Laboratory. A chart of the known isotopes of the transamericium isotopes is shown in Fig. 3.

The next two elements, einsteinium (99) and fermium (100) were unexpectedly produced in the test of the first thermonuclear device, Mike, which took place in the Eniwetok Atoll in the South Pacific on November 1, 1952. The isotopes Es-253 (20 days) and Fm-255 (20 hours) were chemically separated from the debris collected from that explosion and identified by scientists working at the Los Alamos Scientific Laboratory, the Radiation Laboratory and Department of Chemistry of the University of California, Berkeley, and the Argonne National Laboratory near Chicago. Plutonium-244, the longest-lived isotope of plutonium, was also discovered in that debris. The identification of fermium-255 indicated that 17 successive neutron captures had taken place in uranium-238 to make uranium-255 which then decayed by successive emission of beta-particles to fermium!

Mendelevium (101) was produced at Berkeley by irradiation of the highly radioactive target einsteinium-253 with alpha particles in the cyclotron to produce the 76-minute isotope of mass 256. It was the first element to be produced and identified on an atom-at-a-time basis. However, it was still chemically identified using the reliable technique of elution from a cation exchange resin column with the complexing agent, ammonium

alpha-hydroxyisobutyrate, which separates individual actinides and lanthanides on the basis of their ionic radii. In later experiments larger targets were used and thousands of atoms of mendelevium were produced which confirmed the original conclusions made on the basis of only 17 atoms.

B. Nobelium (102) through Element 109.

Studies of elements heavier than 101 again required identification of new elements based on production and measurement of one-atom-at-a-time, but with even smaller production rates and shorter half-lives. Heavier ions, such as isotopes of boron, carbon, nitrogen, and oxygen were required as projectiles. Thus the development of the cyclotron and heavy ion accelerators and the availability of exotic actinide targets such as Es-253, Cf-249, Cm-246, and Cm-248 in the U. S. accelerated the pace of these discoveries. A summary of the discovery of these elements is given in Table II.

The necessity for identifying these elements based on a very few atoms, often with very short half-lives, and without chemical identification has caused a re-examination of what the criteria for discovery of a new element should be. You are probably aware of the controversies associated with the discovery of many of these elements. One of the most difficult problems arises when the first discovered isotope of a new element decays only by spontaneous fission. Then the Z and A of the fissioning nucleus are effectively destroyed and there is no simple way of relating products to parent as in the case of beta or alpha decay to a known daughter or granddaughter. For example, in the latter case, one simply adds back in the Z and A of the alpha particle, i.e., Z=2, A=4 to the Z and A of the detected known daughter isotope.

Criteria for discovery of a new element were proposed in an article in Science in 1976 written by an international group of scientists. They also suggested that names for new elements not be proposed until the discovery has been confirmed by an independent group. A summary of the criteria from this paper is given in Fig. 4. Even some of the classical chemical methods have run in to difficulty when they have been applied. For example, in the case of element 102, although chemistry was performed by an international group working at the Nobel Institute in Stockholm, the chemistry was not definitive enough to exclude non-actinide elements and the observed 10-minute activity may actually have been due to Pb-213, which eluted prior to the actinides. The first actual identification of 102 was of the isotope 254 (1 minute) produced by bombardment of curium 246 with carbon-12 ions and identified by the alpha daughter correlation technique in which a known daughter, Fm-250 (1 minute) was identified. This was the first element to be initially identified in a heavy ion bombardment. The name nobelium was allowed to stand even though the original claim to discovery was erroneous.

A basic difference in approach between American and Russian scientists has been the primary cause of many of the controversies that have arisen concerning priority of discovery, particularly in the case of elements 104 and 105. The American group at Berkeley has typically used the alpha-genetic relationship method utilizing rather complex instrumentation. The Russian group at Dubna has chosen to rely on detection of spontaneous fission, half-life measurements, cross bombardments, and systematics. Positive identification of a new element based only on detection of fissions and half-life and systematics is extremely uncertain.

The discovery of element 106 was reported by an LBL-LLL group in 1974 from the bombardment of californium-249 with oxygen-18 ions. The 0.8-sec 106-263 was identified by its alpha decay to the known daughter 3-sec 104-259 and granddaughter no-255. About the same time the Dubna group reported the discovery of a 4 to 10 ms fission activity in bombardments of lead-207,208 with chromium-54 ions.

A 1.2-ms spontaneous fission activity attributed to 107-261 was reported by Oganessian et al. in 1976. Again, the same difficulties with identification occur. However, the development of new "on-line" techniques at the Heavy Ion Acclerator in Darmstadt, West Germany has permitted Munzenberg et al. to identify isotopes of elements 107, 108, and 109 having half-lives of only a few-thousandths of a second by the alpha genetic relationship technique. They could not find the spontaneous fission activity reported by Oganessian. Munzenberg et al. used similar techniques to identify elements 108 and 109. The original claim to the discovery of element 109 was based on the observation of the decay chain from only a single atom of element 109! However, a second experiment was conducted in 1988 in which two more time-correlated decays similar to the first event were detected, lending additional support to their claim for discovery of element 109. In accordance with the suggestion made in the criteria paper names have not yet been proposed for elements 106 and heavier.

Oganessian and co-workers in 1986 and 1987 reported evidence for discovery of element 110 based on detection of two spontaneously fissioning species with half-lives of the order of a thousandth to a hundredth of a second. These were observed in reactions of calcium-44 ions with thorium-232 and argon-40 ions with uranium 235 and 236, but the evidence does not meet the criteria for the discovery of a new chemical element.

In summary then, there is now good evidence for the discovery of elements through 109. However, elements 106 through 109 still await confirmation by other groups.

IV. FUTURE

Although theoretical calculations have predicted the existence of an island of relatively stable superheavy elements in the region of 114 protons and 184 neutrons (see Fig. 5), numerous searches in nature and in accelerator bombardments of curium-248 with a wide variety of heavy ions have so far proved fruitless. Recent calculations indicate that the half-lives of these elements are probably too short for them to exist in nature, but attempts to produce them at accelerators are still being proposed. Extra stability is also predicted around 110 to 111 protons for neutron numbers of 162-164 and this region might be reached in bombardments of stable lead or bismuth targets with nickel or cobalt ions, or radioactive targets such as einsteinium or californium with sodium or magnesium ions. Einsteinium-254 plus calcium-48 might also permit reaching the region of the superheavy elements. As new techniques are developed for providing ever more exotic beams and targets it seems likely that 6 to 10 new elements may ultimately be produced.

Table I. Discovery of transuranium isotopes: A. neptunium through mendelevium

DISCOVERY OF TRANSURANIUM ELEMENTS

Z	Symbol	Date	Source	Isotope	Half Life	Decay	Method
92	U	1789	Natural	238	4.5×10^9 y	α	Chem.
93	Np	1940	^{238}U(n, γ)	239	2.3 d	β^-	Chem.
94	Pu	1941	^{238}U(d,n) [cyclotron]	238	87.7 y	α	Chem.
95	Am	1944	^{239}Pu(n, γ)^2 [reactor]	241	432 y	α	Chem.
96	Cm	1944	^{239}Pu(α,n) [cyclotron]	242	162.8 d	α	Chem.
97	Bk	1949	^{241}Am(α,2n) [cyclotron]	243	4.5 h	E.C.	Chem.
98	Cf	1950	^{242}Cm(α,n)	245	44 m	E.C.	Chem.
99	Es	1952	^{238}U(n, γ)^{15} [hydrogen bomb]	253	20.5 d	α	Chem.
100	Fm	1952	^{238}U(n, γ)^{17} [hydrogen bomb]	255	20.1 h	α	Chem.
101	Md	1955	^{253}Es(α,n) [cyclotron]	256	76 m	E.C.	Recoil, Chem.

Table II. Discovery of transuranium isotopes: B. nobelium through element 109

Z	Symbol	Date	Source	Isotope	Half Life	Decay	Method
102	No	1958	$^{246}Cm(^{12}C,4n)$ [HILAC, LBL]	254	1m	α	α-ID
		1971	$^{249}Cf(^{12}C, α2n)$	255	3m	α	α-X Coinc.
103	Lr	1961	$^{249}Cf(^{10,11}B,n)$ [HILAC, LBL]	258,259	4.2s,5.4s	α	E_x,cross bomb.
104	Rf	1969	$^{249}Cf(^{12}C,4n);(^{13}C,3n)$	257,259	4.5s,3s	α	α-ID
	--	1973	$^{249}Cf(^{12}C,4n)$[ORNL]	257	4.5s	α	α-X Coinc.
	Ku?	1964	$^{242}Pu(^{22}Ne,4n)$	260?	300ms	SF	E_x,cross bomb.
	--	1976	$^{246}Cm(^{18}O,4n)$ [Cyclotron, Dubna]	260?	80ms	SF	
105	Ha	1970	$^{249}Cf(^{15}N,4n)$[LBL]	260	1.6s	α	α-ID;
		1975	Same [ORNL]	260	1.5s	α	α-X Coinc.
	Ns?	1968	$^{243}Am(^{22}Ne,4n)$[Dubna]	260,261?	0.01-3s	α	9.4-9.7 MeV
106 (unnilhexium)	Unh	1974	$^{208}Pb(^{54}Cr,3n)$[Dubna]	259	≈7ms	SF	E_x,cross bomb.
		1974	$^{249}Cf(^{18}O,4n)$ [LBL-LLL]	263	0.9s	α	α-ID
107 (unnilseptium)	Uns	1976	$^{209}Bi(^{54}Cr,2n)$[Dubna]	261	≈2ms	SF, α	E_x,cross bomb.
		1981	$^{209}Bi(^{54}Cr,n)$[GSI]	262	4.7ms	α	SHIP, α-ID
108 (unniloctium)	Uno	1983	$^{208}Pb(^{58}Fe,n)$ [GSI]	265	ms	α	SHIP, α-ID
109 (unnilennium)	Une	1982	$^{209}Bi(^{58}Fe,n)$ [GSI]	266	3 ms	α	SHIP, α-ID

PERIODIC TABLE - BEFORE WORLD WAR II

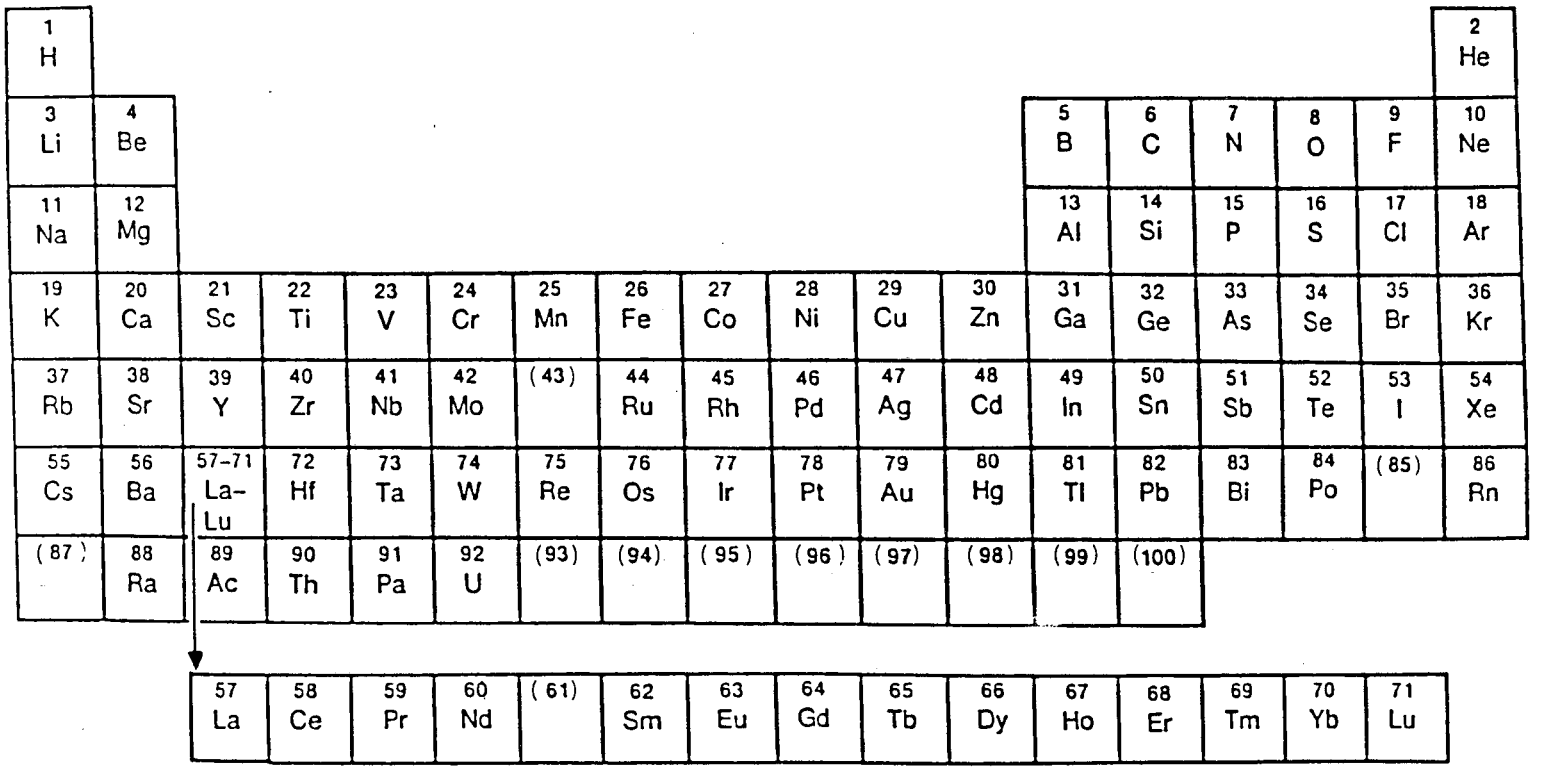

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Fig. 1. Periodic table of the elements from the 1930's.

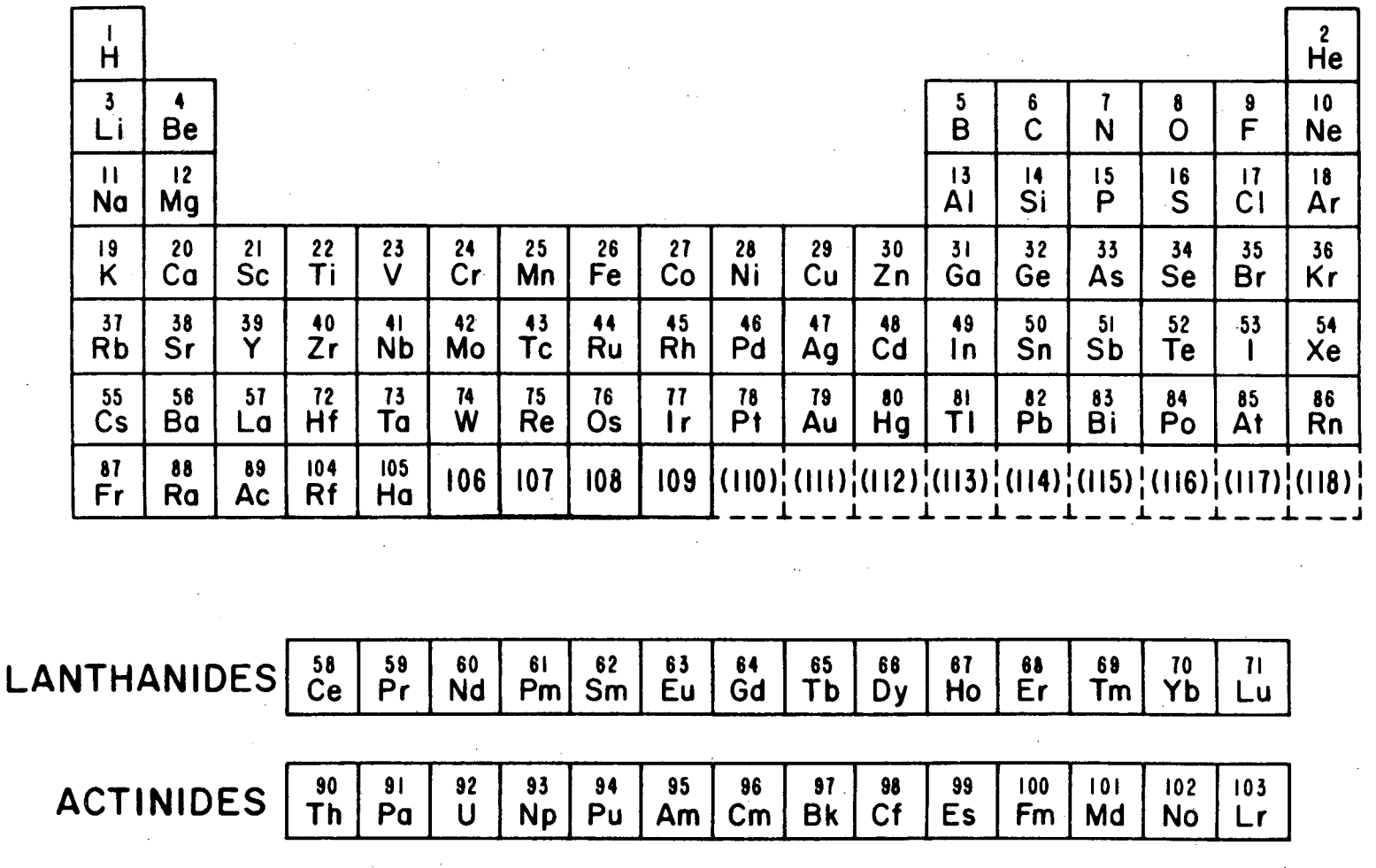

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Fig. 2. Modern periodic table of the elements (atomic numbers of undiscovered elements are shown in parentheses)

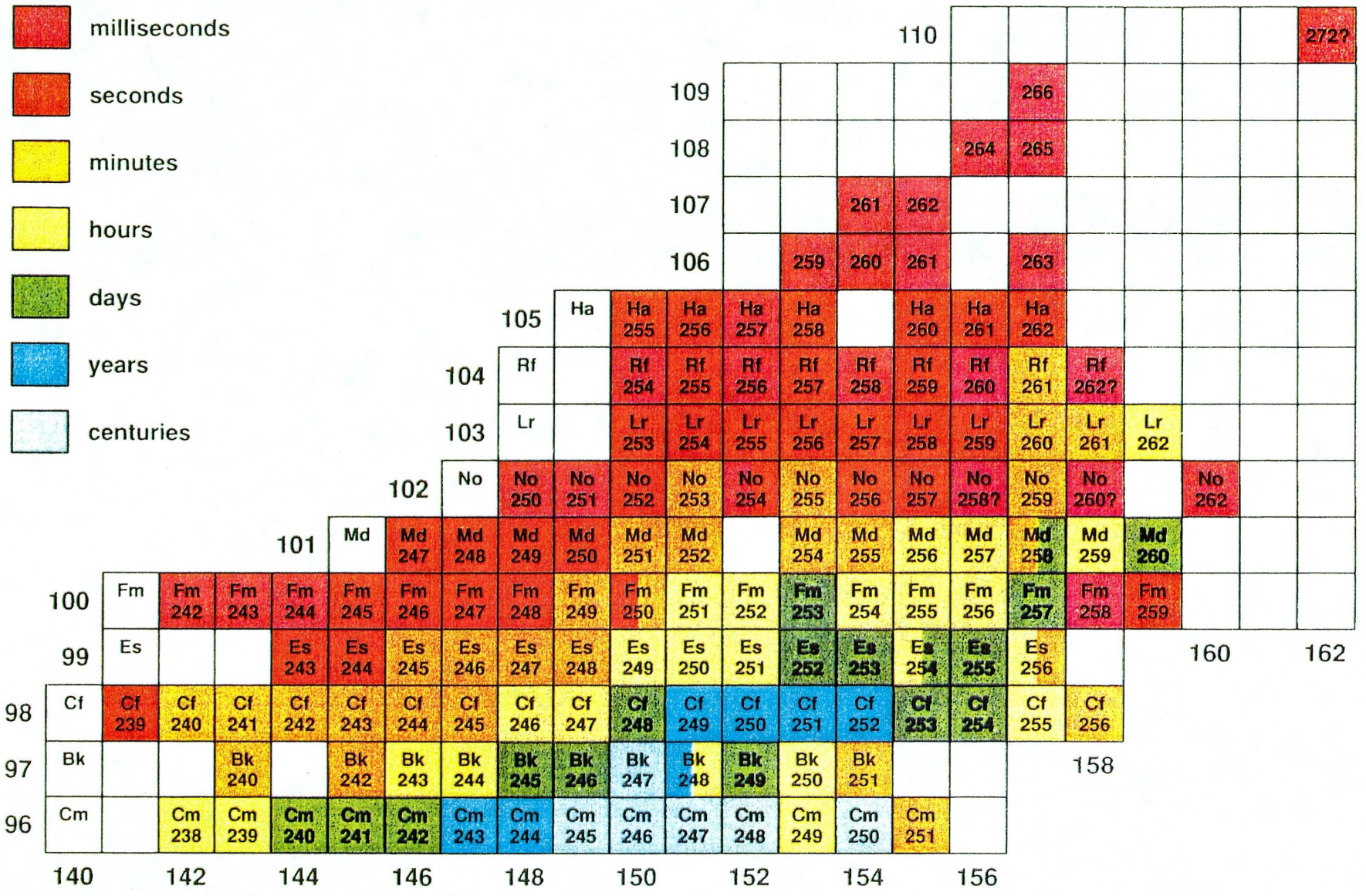

Fig. 3. Chart of transamericium isotopes
(From E. K. Hulet)

CRITERIA

BY DEFINITION A NEW ELEMENT = A NEW Z (OR PROTON NUMBER)

1. PROOF MUST BE SHOWN THAT THE Z OF THE NEW ELEMENT IS DIFFERENT FROM THAT OF ANY PREVIOUSLY KNOWN ELEMENT. IN GENERAL, THIS MEANS THAT Z MUST BE IDENTIFIED BY SOME TECHNIQUE -- THE MORE CLOSELY THE IDENTIFICATION TECHNIQUE IS LINKED TO Z, THE MORE DEFINITIVE IT IS. (MASS NUMBER IS NOT NECESSARILY REQUIRED, UNLESS RELATED DIRECTLY TO THE METHOD USED.)

2. THE DISCOVERY MUST BE COMMUNICATED TO THE SCIENTIFIC COMMUNITY AND PUBLISHED WITH SUFFICIENT DETAIL AND SUPPORTING DATA TO PERMIT CRITICAL EVALUATION AND VERIFICATION BY OTHER SCIENTISTS.

3. MERE FIRST OBSERVATION OF AN ACTIVITY (OR ELEMENT) WITHOUT PROOF OF ITS ATOMIC NUMBER HAS NOT HISTORICALLY BEEN BEEN CONSIDERED SUFFICIENT TO CONSTITUTE DISCOVERY.

4. CONFIRMATION.

Fig. 4. Criteria for discovery of new elements from Harvey et al., Science 193, 1271 (1976)

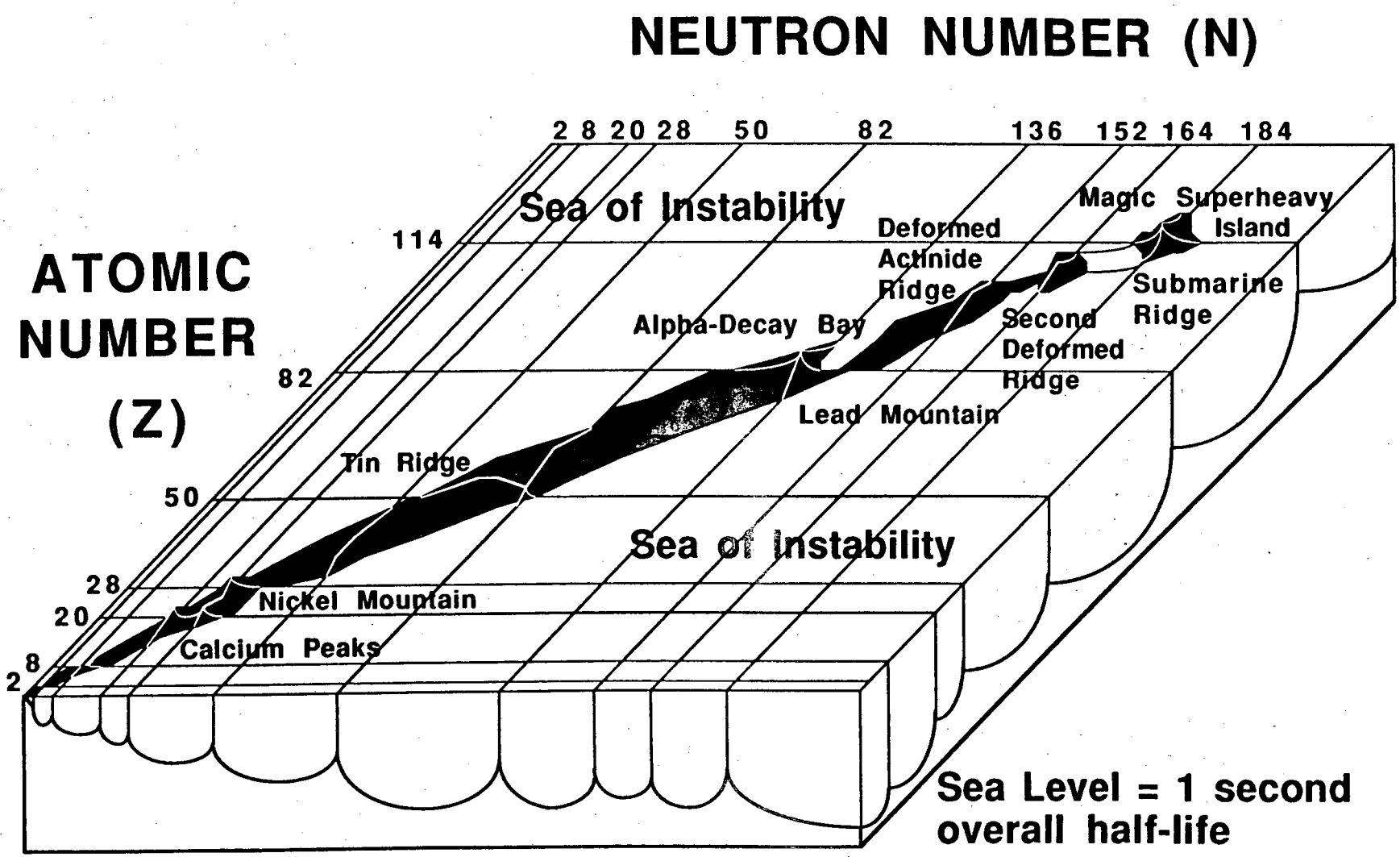

Fig. 5. Schematic drawing of the limits of nuclear stability

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