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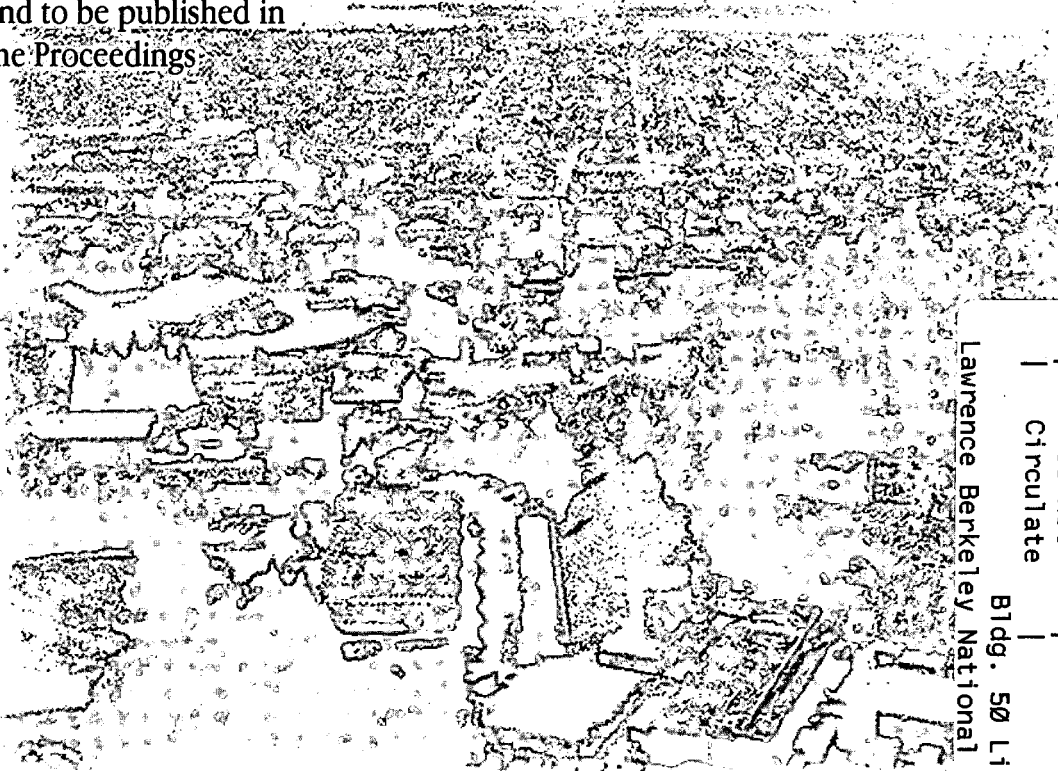
Frontiers of Heavy Element Nuclear and Radiochemistry

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Frontiers of Heavy Element Nuclear and Radiochemistry

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Abstract

The production and half-lives of the heaviest chemical elements, now known through $Z=112$, are reviewed. Recent experimental evidence for the stabilization of heavy element isotopes due to proximity to deformed nuclear shells at $Z=108$ and $N=162$ is compared with the theoretical predictions. The possible existence of isotopes of elements 107-110 with half-lives of seconds or longer, and production reactions and experimental techniques for increasing the overall yields of such isotopes in order to study both their nuclear and chemical properties are discussed. The present status of studies of the chemical properties of Rf, Ha, and Sg is briefly summarized and prospects for extending chemical studies beyond Sg are considered.

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1. Introduction

Over the past ten years there has been a renaissance of interest in experimental investigations of the chemical properties of the heaviest elements as well as in studies of the nuclear properties and attempts to extend the periodic table still further. In this paper some of the experimental results on the chemistry of the transactinide elements, i.e., those with $Z > 103$ (Lr) will be briefly reviewed. The periodic table as of mid-1997 is shown in Fig. 1. Although 112 elements are now known, chemical studies have only been extended through seaborgium (element 106, Sg). The influence of relativistic effects on the chemical properties of the chemical elements increases as Z^2 . Consequently, both experimental and theoretical studies of relativistic effects become especially important for the transactinide elements and are among the frontier research areas which offer exciting opportunities for further exploration. The discovery of new elements and new heavy element isotopes has made these chemical studies of three “transactinide” elements possible, just as our new knowledge of their chemistry has made possible chemical separations prior to studies of their nuclear properties.

The “time line” for the discovery of the transuranium elements is shown in Fig. 2. Seaborgium (Sg, element 106) was produced and discovered [1] at Berkeley in 1974 using the “hot fusion” reaction, $^{249}\text{Cf}(^{18}\text{O}, 4n)^{263}\text{Sg}$ (0.9 s). This discovery was confirmed some 20 years later by a different Berkeley group [2] using the same reaction, but with a different accelerator and experimental system. However, Sg was the last element to be discovered using a “hot fusion” reaction and elements 107 through 109 were not discovered until researchers at GSI in Darmstadt, Germany led by P. Armbruster exploited the use of “cold” fusion reactions and their newly constructed Separator for Heavy Ion reaction Products (SHIP) to discover 107 in 1981 [3],

109 in 1982 [4], and 108 [5] in 1984. The “cold” fusion reaction using target nuclei near the doubly magic ^{208}Pb with appropriate neutron-rich heavy ion projectiles around Fe ($Z=26$) had been suggested by Y. Oganessian of Dubna as a way to form a much “colder” compound nucleus which might then de-excite by emitting only 1 or 2 neutrons with resulting much smaller losses to fission. As the cross sections for production of still heavier elements and their expected half-lives dropped still further, it became necessary to improve the efficiency and discrimination of the existing on-line separator systems, and it was not until 1991 that A. Ghiorso *et al.*[6] found possible evidence for $^{267}110$ based on the partial decay chain of one event from the cold fusion reaction $^{209}\text{Bi}(^{59}\text{Co},n)^{267}110$. The measured lifetime was 4 μs .

In experiments conducted at GSI during November and December of 1994, S. Hofmann *et al.* [7], using an improved SHIP, reported identifying two isotopes of element 110 of mass 269 and 271 using cold fusion reactions between ^{208}Pb targets and ^{62}Ni and ^{64}Ni projectiles. Their half-lives were estimated to be only 0.17 ms and 1.1 ms, respectively. A combined Dubna-Lawrence Livermore National Laboratory (LLNL) team then reported [8] evidence for one event of element 110 in experiments performed during September to December, 1994 at the Dubna Cyclotron using the Dubna gas-filled recoil separator. But they used the “hot” fusion reaction $^{244}\text{Pu}(^{34}\text{S}, 5n)^{273}110$. Elements 111 and 112 were reported [9, 10] shortly thereafter in 1995 and 1996 by the GSI group, again using cold fusion reactions with ^{209}Bi and ^{208}Pb targets. The cross sections for these “cold” fusion reactions to produce isotopes of elements 111 and 112 with masses of 272 and 277, and half-lives of 1.5 ms and 0.24 ms, respectively, were only about 3 pb, but for the “hot” fusion reaction to produce $^{273}108$, the cross section is estimated to be still lower, only ~ 0.4 pb. Fig. 3 shows the trans-nobelium isotopes known as of early 1997.

So it is now apparent that many isotopes of elements heavier than hahnium (element 105) can be produced.

The discovery in 1994 by a joint Dubna-Livermore group [11,12] of the α -decay of longer-lived isotopes of Sg of masses 265 and 266 with half-lives they estimated to be from 2-30 s based on α -decay systematics tended to confirm theoretical predictions [13-17] of enhanced stability against SF and α -decay of heavy element isotopes near the predicted doubly magic deformed shell at $Z=108$ (Hs) and $N=162$. Although this doubly magic nucleus, ^{270}Hs , has not yet been detected, the Dubna-Livermore group [18] reported detection of 19 ms ^{270}Hs , an α -decaying odd mass isotope of element 108, and the GSI group [10] observed ^{269}Hs with a half-life estimated to be ~ 9 s as a product of the α -decay chain of $^{277}112$. Again, these results seem to support the predictions of enhanced stability toward SF in this region as well as the extra stability from the odd neutron. Previously it was believed that the even-even heavy element isotopes such as ^{266}Sg would decay via SF with half-lives of the order of milliseconds as reported for ^{260}Rf and ^{262}Rf . However, a 2.1-s SF activity has now also been assigned [19] to ^{262}Rf .

It appears that many of these heavy element isotopes will have sufficiently long half-lives to permit chemical studies as well as more detailed studies of their SF properties such as fragment kinetic energies, total kinetic-energy distributions, and mass-yield distributions. The reports of the longer-lived Sg isotopes almost immediately prompted an international group to plan for chemical studies of Sg and preliminary results of these experiments have just been reported by Schädel *et al.* [20] in Nature. Now the real challenge to the extension of the chemical studies to elements beyond 106 will be to find the best production reactions and devise

methods for optimizing the production rates, perhaps by using multiple targets and multiple transport systems together with the most efficient chemical and physical separation systems.

2. Nuclear properties

One of the most fundamental properties of the heavy and superheavy nuclei (and the most important to us) is their stability. In 1996, Sobiczewski [16] published a short review of current theoretical studies based on the macroscopic-microscopic description of the heaviest nuclei with the aim of predicting the stability of as yet undiscovered nuclides as well as describing existing experimental data. Very recently, Smolanczuk [17] has described and reported the results of theoretical calculations of the ground-state properties for spherical superheavy nuclei for $Z=104-120$. He also draws some conclusions about odd-A [e-o (even Z-odd N); o-e (odd Z-even N)]; and o-o (odd Z-odd N) superheavy nuclei. Earlier results for e-e (even-even) deformed nuclei with $Z=104-114$ are included for comparison. Nuclear masses, alpha-decay energies and half-lives, SF half-lives and beta stability are discussed. The calculations are based on the macroscopic-microscopic model using a multi-dimensional deformation space describing axially symmetric nuclear shapes. Especially noteworthy is that SF half-lives are calculated individually (with no averaging) using a four-dimensional deformation space describing axially and reflection-symmetric shapes. The fission trajectory is determined by minimizing the action integral in the multidimensional deformation space. Resistance to shape changes are described by the effective inertia for motion along the one-dimensional trajectory. The inertia has been found to be more reliable than a “phenomenological” mass parameter. Use of the larger deformation space gives larger potential energy barriers. For calculation of masses and α -decay

energies in four-dimensional space, 3 of 5 parameters are readjusted to recent data for e-e nuclei with $Z > 81$ and $N > 125$.

The doubly magic deformed nucleus ^{270}Hs ($Z=108$, $N=162$) is predicted to have an α -half-life of ~ 6 s with an SF half-life of 1.8 h, while the doubly magic spherical nucleus $^{298}114$ is predicted to have a 12-min α -half-life and an SF half-life of 4.4×10^5 y. The calculated dynamic fission barriers for these isotopes are shown in Fig. 4.

The experimentally determined partial α -decay half-lives for even-neutron nuclides with Z from 95 (Am) through 108 (Hs) are shown in Fig. 5. The stabilizing effect of the $N=152$ subshell can be seen until elements 103 and 104 where it begins to disappear. For 104, 105, and 106, a lengthening of the half-lives is even observed, contrary to earlier predictions, but consistent with stabilization due to the approach to the postulated $Z=108$, $N=162$ doubly magic deformed region. The experimentally determined partial SF half-lives for the same region for e-e isotopes again show stabilization of Rf, Sg, and Hs. (No SF half-lives are available for element 110 because only odd- N isotopes have been measured and the SF branches for these are not known, presumably because they are small due to hindrance from the odd neutron.) In Fig. 6, the experimental SF half-life values for e-e isotopes beginning with $Z=104$ are plotted together with the theoretical predictions of Smolanczuk, Skalski, and Sobiczewski [21] and the agreement is excellent. The calculated SF partial half-lives for nuclides up to $N=174$ show the stabilizing influence of the predicted deformed shells at $N=162$ and $Z=108$ which results in the longest SF half-lives for $Z=106$ and 108 with 162 neutrons. Fig. 7 shows the calculated partial half-lives for SF and α -decay for even-even isotopes of elements from 104-114 together with the currently known experimental values. The calculations predict that for element 106, SF decay will not

predominate until $N > 164$, for 108 SF will not take over until $N > 166$, and for $Z = 110, 112,$ and 114 , α -decay will dominate until around $N = 170$ when the α - and SF half-lives become comparable. This would be a good region for more detailed studies of SF properties if these isotopes can be made in sufficient yield and can be positively identified. Information about the kinetic energies and mass distributions of the fragments would be especially interesting in order to see if the abrupt change to symmetric mass division observed in the heavy fermium isotopes [22] persists above element 104, and if there are special features associated with the region around the deformed shells at $Z = 108, N = 162$.

The SF half-lives again increase above $N = 170$ and it was suggested [23] that due to these deformed shells there will be a peninsula of relatively stable nuclides extending up to the relatively stable region around the doubly magic spherical nucleus $^{298}114$. However, in direct disagreement with this, other calculations using the fermion dynamical symmetry model (FDSM) [24] indicate that the newly discovered isotopes of 110, 111, and 112 are near the “true” island of spherical superheavies which has been shifted down in neutron number. Other calculations [25] indicate that some of the predicted superheavies may be proton unstable, but the half-lives for this mode are believed to be sufficiently long that they should not affect the total half-lives appreciably.

New experiments are being planned to synthesize spherical superheavy nuclei in the region of $Z = 114$ and $N = 184$, but it is not possible to reach neutron numbers near 184 with stable targets and beams. However, attempts will be made to produce nuclei with the largest possible neutron number using long-lived neutron-rich actinide targets and neutron-rich projectiles. The reaction $^{244}\text{Pu}(^{48}\text{Ca}, xn)^{292-xn}114$ is one of the better possibilities. Another is the reaction

$^{248}\text{Cm}(^{48}\text{Ca},\text{xn})^{296-\text{xn}}116$ which was investigated earlier [26] with negative results, but the cross section limits which were set then were far above the sensitivity that could now be achieved and the reaction should be reinvestigated.

3. Chemical properties of the transactinides

Theoretical studies. The study of the chemical properties of the heaviest elements is extremely challenging both experimentally and theoretically. Challenges for the theoretician include making fully relativistic multiconfiguration atomic calculations for complex atoms such as the transactinide elements—a transition series beginning with element 104 which is expected to end with the heaviest element now known, element 112. It is placed as eka-Hg in the periodic table (see Fig. 1), although Pitzer [27] as early as 1975 reported that initial results from Hartree-Fock (DHF) calculations led to the striking conclusion that elements 112 and 114, as well as 118, should be volatile, relatively inert gases. An even more difficult additional challenge is to predict the properties of the chemical compounds of these elements and only relatively recently (1990-92) did calculations of the electronic structure of Rf halides appear. More systematic theoretical studies were begun by Pershina and co-workers in 1990 [28] in conjunction with the international collaboration formed to perform experimental studies of the chemical properties of the compounds of the transactinide elements which to date have included elements 104, 105, and 106. Related publications from other groups [29-34] have been published as well, indicating the quickly growing interest in this new field, sparked by the recent availability of experimental data on Rf, Ha, and Sg and the discoveries of the elements through 112. V. Pershina [28] has reviewed the results published through early 1996 on theoretical studies of transactinide compounds based on molecular-orbital calculations, on very recent

atomic calculations and on different qualitative or quantitative theories concerning the electronic structure and properties of transactinide-containing compounds.

Since relativistic effects for atomic electronic shells increase proportionally with Z^2 , the transactinide elements provide the optimum opportunity for evaluating the influence of relativistic effects on chemical properties. As pointed out by P. Pykkö [35] in his 1988 review, when the charge of the nucleus becomes very large, it causes a decrease in the effective Bohr radius for the inner s and p shells, making them more stable. This effect is felt by the s and p electrons in the outer valence shells causing them to contract which more effectively screens the d and f orbitals, causing their destabilization and an increase in their radial extension. Spin-orbit splitting of the p , d , and f electron energy levels may also occur with the lower angular momentum orbitals such as the $p_{1/2}$ being strongly stabilized. As outlined by Pershina [28], large changes in properties such as electronic configurations, ionization potentials, ionic/atomic radii, oxidation states (redox potentials), and complexing ability can occur. In some cases these can lead to considerable deviations from the trends predicted based on simple extrapolation of trends found for the lighter homologs in the same periodic table group. The plot in Fig. 9 of the non-relativistic vs. relativistic Dirac-Fock calculations [34] of the valence orbital eigenvalues for the group 6 elements, Mo, W, and Sg shows the large differences due to relativistic effects.

Experimental Studies. The challenges for the experimentalist are extremely formidable and include low production rates, half-lives of a minute or less for the transactinide isotopes (Fig. 3), the necessity for detection and positive identification of the element being studied, and discrimination against the many unwanted activities which are produced. In addition, an accelerator capable of delivering high intensity beams which also has a protected beam line

where irradiation of sometimes extremely radioactive targets can be carried out is needed. Facilities and expertise for fast radiochemical separations and detection techniques, and for preparation of radioactive targets are necessary. Furthermore, atom-at-a-time chemistry on site or even on-line at the accelerator is required for studies of the transactinide elements, and appropriate chemical separation techniques must be used in which equilibrium is reached very rapidly and the atoms or ions involved undergo many interactions, thus ensuring statistical chemical behavior. Typically, chromatographic systems have been used for both aqueous- and gas-phase systems. These have included liquid-liquid extractions or solid-liquid extractions and gas-phase thermochromatography or isothermal chromatography.

In 1970, Silva *et al.*, [36] conducted the first study of the solution chemistry of Rf and showed that its properties were similar to those of Zr and Hf and different from trivalent actinides including Lr. The element Rf was positively identified by measuring the characteristic well known α -decay of ^{261}Rf . This experiment established Rf as a heavy member of group 4 and confirmed that Lr ended the actinide series as predicted by the actinide hypothesis. Studies of the halides of elements 104 and 105 were also conducted in the gas phase in the 1960's. They indicated increased volatilities compared to the actinides and suggested that they were probably members of groups 4 and 5, respectively, of the periodic table. However, these studies depended on interpretations and models based on the half-lives of the observed spontaneous fission activities. Positive identification of the 104 and 105 nuclides under investigation was not made, and detailed studies of the differences in their behavior relative to their lighter homologs in groups 4 and 5 were not possible. These early results are reviewed in Refs. [37-40].

No investigation of the solution chemistry of Ha, nor any detailed comparisons of the behavior of Rf relative to Zr and Hf were performed prior to the late 1980's when a renaissance of interest began in performing more experimental detailed studies of the chemical properties of the heaviest elements in order to compare their behavior with that of their lighter homologs in the same group. The major impetus for this was the prediction by Keller [38] based on relativistic calculations that Rf might have the valence electronic configuration $7s^2 7p^2$ rather than $6d^2 7s^2$ by analogy to the $5d^2 6s^2$ configuration of its lighter homolog, Hf. Similarly, Ha might have a $6d 7s^2 7p^2$ configuration rather than the $6d^3 7s^2$ configuration analogous to that of $5d^3 7s^2$ of its lighter homolog, Ta. In fact, if the $7s^2$ electrons were sufficiently stabilized due to relativistic effects, it was even conceivable that Ha unlike its lighter Group 5 homologs might exhibit a more stable 3+ rather than a 5+ oxidation state in aqueous solutions.

Reactions now typically used to produce the longest-lived isotopes of the transactinide elements 104 and 105 for chemical studies are: $^{248}\text{Cm}(^{18}\text{O}, 5n)^{261}\text{Rf}$ (78 s) and $^{249}\text{Bk}(^{18}\text{O}, 5n)^{262}\text{Ha}$ (34 s). (See Table 1.) The reaction products recoiling from the relatively thin ($<1\text{mg}/\text{cm}^2$) targets are transported from the reaction chamber to a suitable collection station or instrument outside the accelerator. The reactions to produce ^{261}Rf and ^{262}Ha have cross sections of the order of 5 nb which results in the production of about 2 atoms per minute, but after the transport efficiency, chemical yield, detection efficiencies, and 50% decay are folded in, only about 0.1 alpha decay per minute is actually detected. Thus the procedure must be repeated many, many times and the first aqueous chemistry on element Ha [41] conducted in 1987 involved a 50-s manual procedure which was repeated some 800 times. Since then a variety of automated systems have been developed and used for both aqueous and gas-phase chemistry of

the transactinides and Wierczinski and Hoffman [42] have written a review of instrumentation for atom-at-a-time chemistry.

It was not until 1987 that Gregorich *et al.* [41] performed the first aqueous chemistry experiments on element 105 using 35-s ^{262}Ha produced at the 88-Inch Cyclotron at Lawrence Berkeley National Laboratory (LBNL). The energy and time distribution of the α -decay and the detection of time-correlated pairs of α -particles from the decay of ^{262}Ha and its 3.9-s daughter, ^{258}Lr , provided positive identification of the Ha. These manual separations showed that, indeed, Ha sorbed on glass surfaces after fuming with nitric acid as did its group 5 homologs, Nb and Ta, while the group 4 elements, Zr and Hf, and the trivalent actinides did not sorb under these conditions. However, additional manual liquid-liquid extraction experiments unexpectedly showed that Ha did not extract into methylisobutylketone from mixed nitric/hydrofluoric acid solutions as does Ta, but behaved like Nb which does not extract. This was the first indication of differences in the behavior of Ha from its lighter homolog Ta.

A series of chromatographic separations of element 105 using the Automated Rapid Chemistry Apparatus (ARCA II) [43] was then conducted at the LBNL 88-Inch Cyclotron jointly by the GSI-Mainz-LBL groups. It was shown that Ha was eluted from cation exchange columns with 0.05 M α -hydroxyisobutyric acid (α -HIB) as were Nb, Ta, and Pa, but in elutions from triisooctylamine (TIOA) columns with HCl/dilute HF mixtures Ha again exhibited non-Ta-like behavior indicating formation of oxygen-containing halide complexes similar to those of Pa and Nb and different from $[\text{TaX}_6]^-$. These results showing extractability of $\text{Ta} > \text{Nb} > \text{Ha} > \text{Pa}$ were consistent with calculations of complex formation, but predictions of extractability using the Born theory gave the reverse order to that observed. The discrepancy was attributed [44] to

multiply charged F^- or mixed F-Cl complexes; new experiments with single halide systems were suggested for easier comparison with theoretical predictions [45] based on considerations of hydrolysis vs. complex formation from electronic structures calculated with an improved Dirac-Slater discrete variational (DSDV) code. These calculations indicated the extraction order should be Pa>Nb~Ha>Ta. Chromatographic separations using ARCA-II were just conducted at LBNL by Paulus *et al.* [46] with 1 M to 12 M HCl [46] and Aliquat 336 and confirm these predictions; more experiments will be done in the future with HBr and HF.

Our group at LBNL has also performed manual studies to compare the extraction of ^{261}Rf with its lighter homologs Zr and Hf and the pseudohomologs Th(IV) and Pu(IV) into tributylphosphate (TBP), TIOA, and thenoyltrifluoroacetone (TTA). These experiments showed [47] that Rf generally behaves as a group 4 element. However, in extractions from HCl solutions with $[\text{H}^+] = 8 \text{ M}$ into TBP which extracts neutral complexes, at low Cl^- concentrations Rf extracts well like Zr and Hf, but at $[\text{Cl}^-] > 10 \text{ M}$ Rf extraction decreases rapidly, similarly to Pu(IV). Presumably, this is because Rf and Pu(IV) form stronger anionic chloride complexes at high $[\text{Cl}^-]$ concentrations than do Zr, Hf, and Th.

The On-Line Gas Chemistry Apparatus (OLGA II), developed at the Paul Scherrer Institute in Switzerland by Gaggeler *et al.* [48], and the Heavy Element Volatility Instrument (HEVI), developed by Kadkhodayan *et al.* [49] at LBL, have been used to perform isothermal chromatographic gas phase studies of the volatilities of the halides of Rf and Ha. Again, these studies have shown marked deviations in the behavior of Rf and Ha from predictions based on simple extrapolations of the properties of their lighter group 4 and 5 homologs. Fig. 9 shows the adsorption enthalpies on SiO_2 calculated from a Monte-Carlo fit to the measurements of relative

yield as a function of temperature between about 100 to 600° C for the tetrachlorides and tetrabromides of Rf, Hf, and Zr. A dramatic break in the sequence is observed for both chlorides and bromides: Hf is the least volatile while Zr and Rf are nearly the same. This is presumably due to relativistic effects. The bromides are less volatile than the chlorides as expected. Data [50] for the bromides of Ha, Nb, and Ta seem to show very low volatility for Ha, in disagreement with relativistic molecular calculations [51] which predicted that HaBr_5 should have the highest covalency and lowest effective charge of the group 5 bromides which should make it the most volatile. It may be that a less volatile oxybromide was formed and additional experiments on the oxybromide are needed.

There are several recent reviews of the chemistry of the transactinides [52-54] comparing experimental results for elements 104 and 105 with theoretical predictions and discussing the prospect of extending the studies to heavier elements. Schädel's 1995 review [54] was particularly comprehensive and discussed possibilities for performing chemical studies of Sg using the longer-lived isotopes of mass 265 and 266 reported to have been produced [11,12] via the reaction: $^{248}\text{Cm}(^{22}\text{Ne}, 4n, 5n)^{266,265}\text{Sg}$ (2-30s).

Preliminary results of the first chemical separations of Sg conducted with OLGA and ARCA in 1995 and 1996 have just been reported [20, 55]. Isothermal gas chromatography experiments on the oxychlorides were conducted with OLGA followed by unambiguous detection of $^{266,265}\text{Sg}$ via its α -decay chain. Based on 15 atoms of $^{266+265}\text{Sg}$, it was possible to show that Sg formed a volatile oxychloride, presumably SgO_2Cl_2 , of lower or equal volatility than WO_2Cl_2 , consistent with Dirac-Slater discrete-variational calculations [56]. This is consistent with predictions based on macroamounts which also show MO_2Cl_2 to be the most

volatile. The half-lives of ^{265}Sg and ^{266}Sg (SF<80%) were found to be $\sim 7\text{s}$ and $\sim 21\text{s}$, with cross sections estimated to be ~ 440 and ~ 60 pb at 121 MeV.

From detection of the α -daughters of 3 atoms of ^{265}Sg , the ARCA experiments showed that Sg is eluted promptly as a negative (or possibly neutral) species from cation exchange columns with 0.1 M HNO_3 /0.0005 M HF like its group 6 homologs, W(VI) and Mo(VI), but unlike U(VI) which is retained on the column, presumably as UO_2^{2+} .

Experiments with the SISAK system, a micro-centrifuge system for performing liquid-liquid extractions on the second-time scale, coupled to a continuously flowing liquid scintillation system (LISSY) [42] to allow detection of α - α correlations were also performed to extract Sg from 1 M α -HIB into trioctylamine (TOA) but the detection limit at that time of ~ 1 nb was not sufficient for detection of Sg.

4. Future

More Sg studies. Plans for additional experiments on Sg are being made in order to investigate the chemistry in more detail to see if there are unexpected differences within the group 6 elements as there have been within the group 4 and 5 elements. In addition, techniques for studying shorter-lived isotopes with ARCA are envisioned so that the parent Sg itself, rather than its daughters, can be measured directly.

Improvements to the overall production rates and possible multiple target systems are being considered. Better limits on the SF branch of ^{266}Sg would be extremely valuable for comparison with theoretical predictions. OLGA coupled with a detection system to permit measurement of coincident fission fragments would be ideal for this investigation.

Improvements to SISAK-LISSY are continuing, and in experiments conducted in 1996 at LBNL [57], 0.85-s ^{224}Pa was separated and measured by detection of α - α correlations from its decay chain as shown in Fig. 10. However, the overall yield was only about 10% after correction for the estimated yields for the gas transport system, detection system, decay prior to measurement, etc. This is lower than observed in off-line tracer experiments and the reasons for this are not yet clear but are being investigated [58].

Elements beyond Sg. In order to produce longer-lived isotopes for chemical studies of elements heavier than Sg, attempts will be made to synthesize isotopes with N near 162. Some of the best reactions for elements 107 through 109 are included in Table 1, together with those commonly used to produce elements 103 through 106 for chemical studies.

The longest known isotope of element 107 is 0.44-s, ^{264}Ns but it is predicted that ^{267}Ns which has 160 neutrons will have a half-life of about 10 s and decay by α -emission. ^{266}Ns which has only one less neutron should also have a similar half-life and could be made by a 5n reaction using the same ^{249}Bk target as shown in Table 1 with a similar cross section. The chemistry is expected to be similar to the group 7 elements Tc and Re. Preliminary on-line tracer experiments have been performed with OLGA on volatile oxy- and hydroxy-compounds of $^{182,184}\text{Re}$, and it seems that the sensitivity of the present OLGA system should be adequate, but the sensitivity of SISAK is not yet at the 30 pb level and the half-life may be too short for ARCA.

The longest known isotope of element 108 is 9-s ^{269}Hs , which could be produced by a 5n reaction on the same targets as shown in Table 1 for ^{270}Hs with a similar cross section of a few pb. The $^{248}\text{Cm}(^{26}\text{Mg}, 4n, 5n)^{270,269}\text{Hs}$ reactions could also be used, but again, the cross sections

are estimated to be only a few pb. ^{270}Hs is the predicted [17] doubly magic deformed nucleus with 108 protons and 162 neutrons and should decay via α -emission with a half-life of ~ 6 s [17]. It is expected to have a volatile tetroxide as do the group 8 elements Ru and Os.

In addition to the reactions to produce element 109 as ^{271}Mt shown in Table 1, the reaction $^{254}\text{Es}(^{22}\text{Ne},4n)$ to produce ^{272}Mt (~ 1 s) has a larger estimated cross section of 1 pb and should be considered if a target of even 20 or 30 μg of the rare 276-day ^{254}Es can be produced. In order to perform chemical studies of Hs and Mt, significant improvements in the production rates and efficiencies of the various techniques are required.

The Berkeley Gas-Filled Separator. A new separator is currently being built at Berkeley, called the Berkeley Gas-Filled Separator or BGS which can be used as a “pre-separator” for subsequent chemical studies in addition to its proposed broad-based physics program. Some of the advantages of the BGS over current separators and the early heavy element experiments which are being planned are outlined in Table 2. One of the most exciting experiments will be to look for the doubly deformed ^{270}Hs to see if, indeed, the theoretical predictions are correct. If so, a whole new vista of longer-lived isotopes opens before us. The challenges will be to find suitable production reactions and ingenious ways to increase production rates with the use of multiple targets, more efficient collection and transport systems, and to devise efficient chemical separation techniques in order to enter this frontier region.

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References

1. A. Ghiorso, J. M. Nitschke, J. R. Alonso, C. T. Alonso, M. Nurmi, G. T. Seaborg, E. K. Hulet, and R. W. Lougheed, *Phys. Rev. Lett.*, 33 (1974) 1490.
2. K. E. Gregorich, M. R. Lane, M. F. Mohar, D. M. Lee, C. D. Kacher, E. R. Sylwester, and D. C. Hoffman, *Phys. Rev. Lett.*, 73 (1994) 1423.
3. G. Münzenberg *et al.*, *Z. Phys.*, A300 (1981) 107.
4. G. Münzenberg *et al.*, *Z. Phys.*, A309 (1982) 89; A315 (1984) 145.
5. G. Münzenberg *et al.*, *Z. Phys.*, A317 (1984) 235.
6. A. Ghiorso *et al.*, Fifth Internatl. Conf. On Nucleus-Nucleus Collisions, Taormina, Italy, May 1994, Published in *Nucl. Phys. A583* (1995) 861; *Phys. Rev. C (Rapid Communications)*, 51 (1995) R2293.
7. S. Hofmann *et al.*, *Z. Phys.*, A350 (1995) 277.
8. Yu. A. Lazarev *et al.* *Phys. Rev. C* (1996) (110 ref)
9. S. Hoffman *et al.*, *Z. Phys.*, A350 (1995) 281—ref. 53
10. S. Hoffman *et al.*, *Z. Phys.*, (Short Note), A350 (1996) 229. Ref. 54
11. R. W. Lougheed *et al.*, *J. Alloys and Comp.*, 213/214 (1994) 6.
12. Yu. A. Lazarev *et al.*, *Phys. Rev. Lett.*, 73 (1994) 624. (106 paper)
13. A. Sobiczewski, *Phys. Particles and Nuclei*, 25 (1994) 295.
14. P. Möller and J. R. Nix, *J. Phys.*, 20 (1994) 1681.
15. A. Sobiczewski, R. Smolanczuk, J. Skalski, *J. Alloys and Comp.*, 213/214 (1994) 38.
16. A. Sobiczewski, *Physics-Uspekhi*, 39 (1996) 885.
17. R. Smolanczuk, *Phys. Rev. C*, 56 (1997) 812.
18. Yu. A. Lazarev *et al.* *Phys. Rev. Lett.*, 75 (1995) 1903.
19. M. R. Lane *et al.* *Phys. Rev. C*, 53 (1996) 2893.
20. M. Schädel *et al.*, *Nature (Letters)*, 388 (1997) 55.
21. R. Smolanczuk, J. Skalski, and A. Sobiczewski, *Phys. Rev. C*, 52 (1995) 1871.
22. D. C. Hoffman and M. R. Lane, *Radiochimica Acta*, 70/71 (1995) 135
23. A. Sobiczewski, Z. Patyk, and S. Cwiok, *Phys. Lett.*, B186 (1987) 6.
24. C.-L. Wu, M. Guidry, and D. H. Feng, *Phys. Lett.*, B392 (1996).
25. S. Cwiok *et al.*, *Nucl. Phys.*, A611 (1996) 211.
26. P. Armbruster *et al.*, *Phys. Rev. Lett.*, 54 (1985) 406.
27. K. S. Pitzer, *J. Chem. Phys.*, 63 (1975) 1032.

28. V. Pershina, *Chem. Rev.*, 96 (1996) 1977.
29. M. Dolg *et al.*, *J. Phys Chem.*, 97 (1993) 5852.
30. G. Malli *et al.*, *Phys. Rev. A*, 47 (1993) 143; *J. Chem. Phys.*, 101 (1994) 10736; *ibid.*, 104 (1996).
31. M. Seth *et al.*, *Chem. Phys. Lett.*, 250 (1996) 461
32. E. Eliav *et al.*, *Phys. Rev. Lett.*, 73 (1994) 3203.
33. C. S. Nash and B. E. Bursten, *New J. Chem.*, 19 (1995) 669.
34. C. S. Nash and B. E. Bursten, "Computational comparisons of $\text{Sg}(\text{CO})_6$, $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ ", to be published, private communication (1997).
35. P. Pykkö, *Chem. Rev.*, 88 (1988) 563.
36. R J. Silva *et al.*, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 871.
37. E. K. Hyde, Darleane C. Hoffman, and O. L. Keller, Jr., *Radiochimica Acta*, 42 (1987) 57.
38. O. L. Keller, Jr., *Radiochimica Acta*, 37 (1984) 169.
39. O. L. Keller, Jr., and G. T. Seaborg, *Ann. Rev. Nucl. Sci.*, 27 (1977) 139.
40. E. K. Hulet, in *Actinides in Perspective*, ed., N. M. Edelstein, Pergamon Press, Oxford (1981), p. 453.
41. K. E. Gregorich *et al.*, *Radiochimica Acta*, 43 (1988) 223
42. B. Wierczinski and D. C. Hoffman, in *IANCAS' Frontiers in Nuclear Chemistry*, Eds. Sood, Reddy, Pujari, (1996) Perfect Prints, Thane, India, p. 171.
43. M. Schädel *et al.*, *Radiochimica Acta*, 48 (1989) 171.
44. V. Pershina *et al.*, *Radiochimica Acta*, 64 (1994) 37.
45. V. Pershina, *Radiochimica Acta*, (1997) In Press.
46. W. Paulus *et al.*, "Extraction of the Fluoride-, Chloride-, and Bromide-Complexes of Elements Nb, Ta, Pa, and 105 into Aliphatic Amines", *Proc. Actinides-97*, Baden-Baden, Germany, Sept. 21-27, 1997 (to be published in *J. Alloys and Comp.*).
47. K. R. Czerwinski *et al.*, *Radiochimica Acta*, 64 (1994) 23; *Ibid.*, 29; C. D. Kacher *et al.*, *Radiochimica Acta* 75, (1996) 127; *Ibid.*, 135.
48. H. W. Gäggeler *et al.*, *Nucl. Instrum. Methods in Phys. Res.*, A309 (1991) 201.
49. B. Kadkhodayan *et al.*, *Nucl. Instrum. Methods in Phys. Res.*, A317 (1992) 254..
50. H. Gäggeler *et al.*, *Radiochimica Acta*, 57 (1992) 93.
51. V. Pershina *et al.*, *J. Chem. Phys.*, 97 (1992) 1116.
52. D. C. Hoffman, *Radiochimica Acta*, 61 (1993) 123; *Ibid.*, 72 (1996) 1.
53. J. V. Kratz, *J. Alloy and Comp.*, 213/214 (1994) 20.
54. M. Schädel, *Radiochimica Acta*, 70/71 (1995) 207.
55. H. Gäggeler, "Chemistry Gains a New Element: Z=106", Paul Scherrer Institut report PSI-R-97-19, August 1997, *Proc. ACTINIDES-97*, Baden-Baden, Germany, Sept. 1997, to be published in *J. Alloys and Comp.*
56. V. Pershina and B. Fricke, *J. Phys. Chem.*, 100 (1997) 8748.
57. B. Wierczinski *et al.*, manuscript in preparation (1997).
58. J. Alstad, G. Skarnemark, N. Trautmann, *et al.*, (1997) private communication.

Figure Captions

Fig. 1. Periodic Table as of mid-1997.

Fig. 2. "Time line" for the discovery of the transuranium elements.

Fig. 3. Trans-nobelium isotopes as of early 1997.

Fig. 4. Calculated dynamical fission barriers for ^{270}Hs and $^{298}114$ from Ref. 17.

Fig. 5. Experimentally determined partial α -decay half-lives for even-neutron nuclides with Z from 95(Am) through 108 (Hs).

Fig. 6. Experimental SF values (solid symbols, dashed line) of even-even isotopes beginning with Z=104, plotted together with the theoretical predictions (open symbols) from Ref. 21.

Fig. 7. Experimental partial half-lives for SF and α -decay of even-even isotopes (solid symbols) plotted together with the theoretical predictions for even-even isotopes of elements 104-114 from Ref. 21.

Fig. 8. Valence orbital eigenvalues for the group 6 elements, Mo, W, and Sg [Ref. 34].

Fig. 9. Adsorption enthalpies on SiO_2 for chlorides and bromides of the group 4 elements, Zr, Hf, and Rf.

Fig. 10. SISAK separation of 0.85-s ^{224}Pa .

Table 1. Best Actinide-Target Reactions for Chemical Studies

<u>Z</u>	<u>Reaction</u>	<u>σ(pb)</u>	<u>Half-life (s)</u>	<u>Decay Signature</u>
103	$^{249}\text{Bk}(^{18}\text{O},\alpha 3\text{n})^{260}\text{Lr}$	9000	180	α 8.0 MeV
104	$^{248}\text{Cm}(^{18}\text{O},5\text{n})^{261}\text{Rf}$	5000	75	α 8.3 - 8.2
105	$^{249}\text{Bk}(^{18}\text{O},5\text{n})^{262}\text{Ha}$	6000	34	α 8.4 - 8.6
106	$^{248}\text{Cm}(^{22}\text{Ne},5\text{n})^{265}\text{Sg}$	250	25	α 8.6 - 8.3 - 8.2
	$^{249}\text{Cf}(^{18}\text{O},4\text{n})^{263}\text{Sg}$	300	0.9	α 9.1 - 8.8 - 8.0
	$^{250}\text{Cf}(^{18}\text{O},4\text{n})^{264}\text{Sg}$	200	2	α 8.9 - SF
107	$^{249}\text{Bk}(^{22}\text{Ne},4\text{n})^{267}\text{Ns}$	30	10	α 8.9 - 8.3 - 8.5
108	$^{252}\text{Cf}(^{22}\text{Ne},4\text{n})^{270}\text{Hs}$	2	5	α 9.0 - 8.6 - SF
	$^{238}\text{U}(^{36}\text{S},4\text{n})^{270}\text{Hs}$	2	5	α 9.0 - 8.6 - SF
109	$^{249}\text{Bk}(^{26}\text{Mg},4\text{n})^{271}\text{Mt}$	0.3	0.2	α 9.4 - 8.9 - 8.3 - 8.5
	$^{252}\text{Cf}(^{23}\text{Na},4\text{n})^{271}\text{Mt}$	0.1	0.2	α 9.4 - 8.9 - 8.3 - 8.5

Table 2. BERKELEY GAS-FILLED SEPARATOR (BGS)

WORLD-CLASS FACILITY AT THE LBNL 88-INCH CYCLOTRON

- High-Intensity Beams: Small Cross Sections Accessible
- Large Angular Acceptance: Better Efficiency for Asymmetric Reactions
- Large Bending Angle: Better Separation
- Large Momentum Acceptance: High Efficiency, Thick Targets

HEAVY ELEMENT EXPERIMENTS WITH BGS

$^{248}\text{Cm}(^{26}\text{Mg},4n)^{270}\text{Hs}$	N= 162, Z= 108 deformed shells
$^{238}\text{U}(^{36}\text{S},4n)^{270}\text{Hs}$	What are α - and SF-half-lives?
$^{248}\text{Cm}(^{48}\text{Ca},4n)^{292}\text{116}$	Spherical Superheavies?
$^{244}\text{Pu}(^{48}\text{Ca},4n)^{288}\text{114}$	(100 times more sensitive)
$^{209}\text{Bi}(^{24}\text{Mg},3n)^{230}\text{Am}$	Electron-Capture Delayed Fission
$^{209}\text{Bi}(^{28}\text{Si},3n)^{234}\text{Bk}$	(QEC > Fission Barrier)
$^{238}\text{U} + ^{86}\text{Kr}$	Binary Transfers for Production of New
$^{248}\text{Cm} + ^{76}\text{Ge}$	Neutron-Rich Nuclides Prior to Chemistry

Periodic Table of the Elements

GROUP

																	18
1											2						
H											He						
												13	14	15	16	17	
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	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	112	(113)	(114)	(115)	(116)	(117)	(118)
Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt									

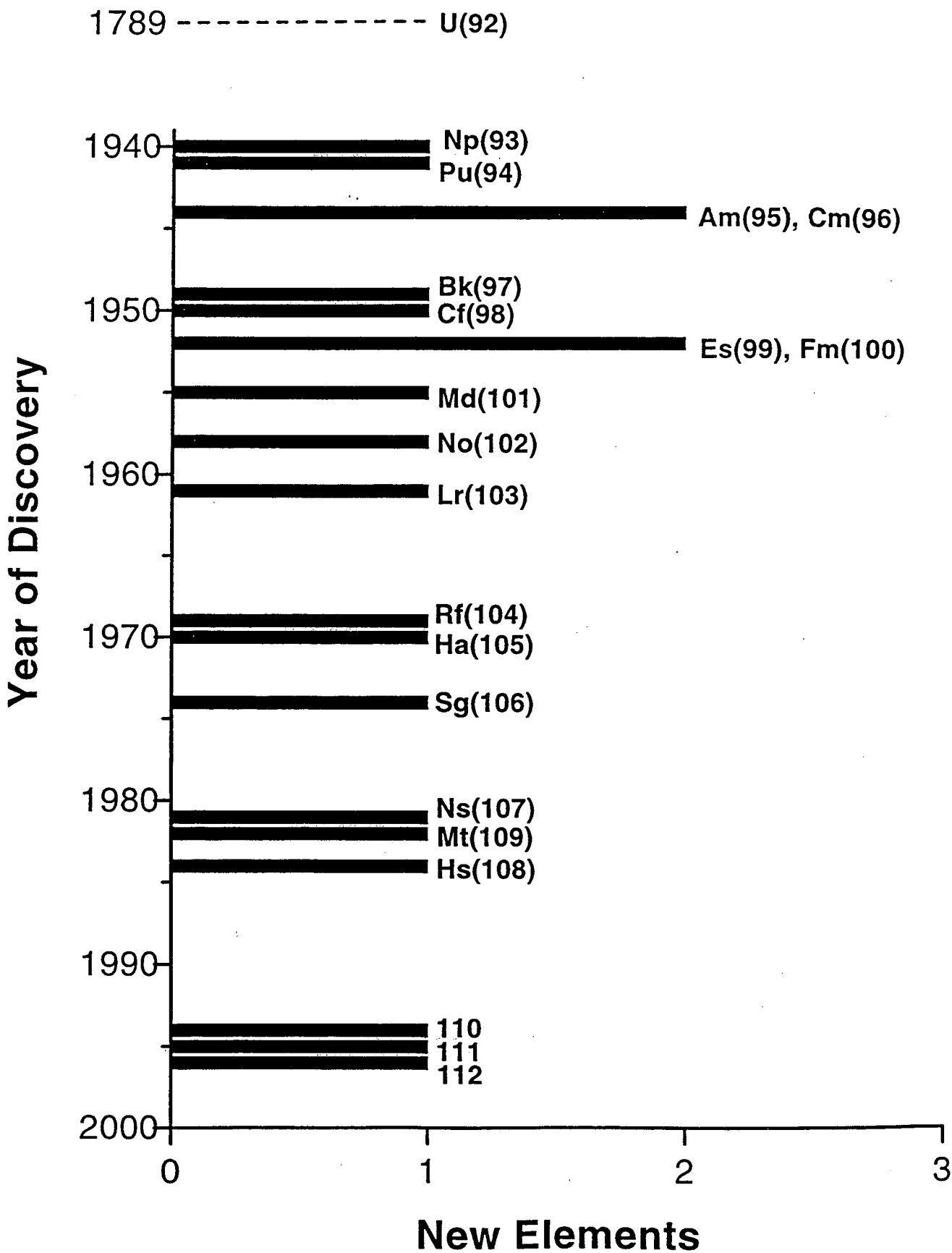
Lanthanides

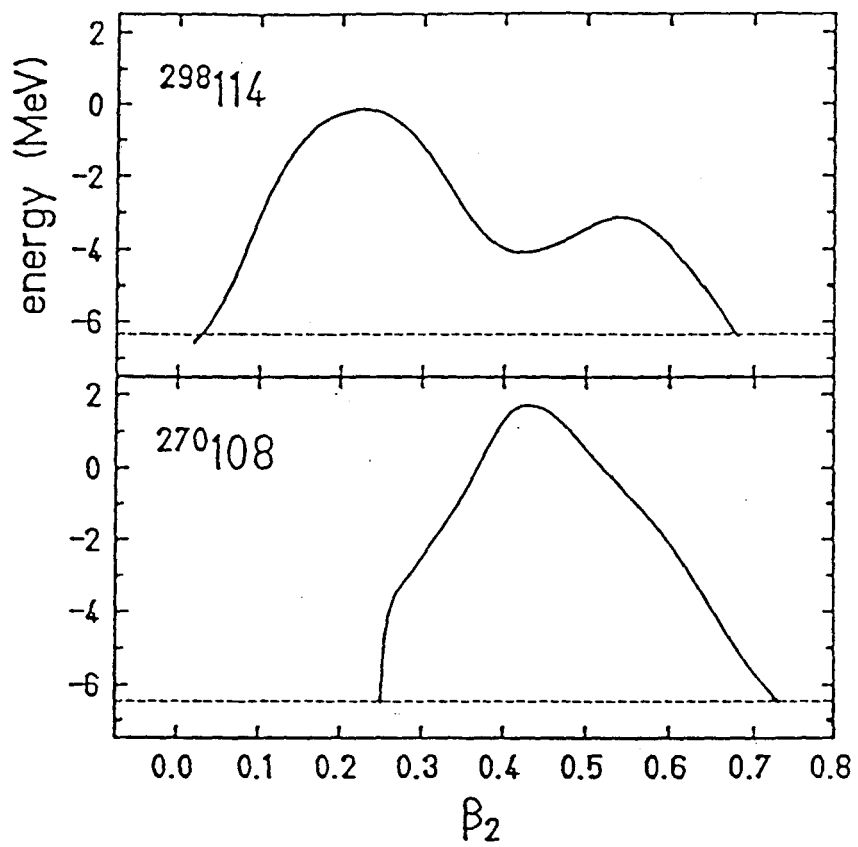
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

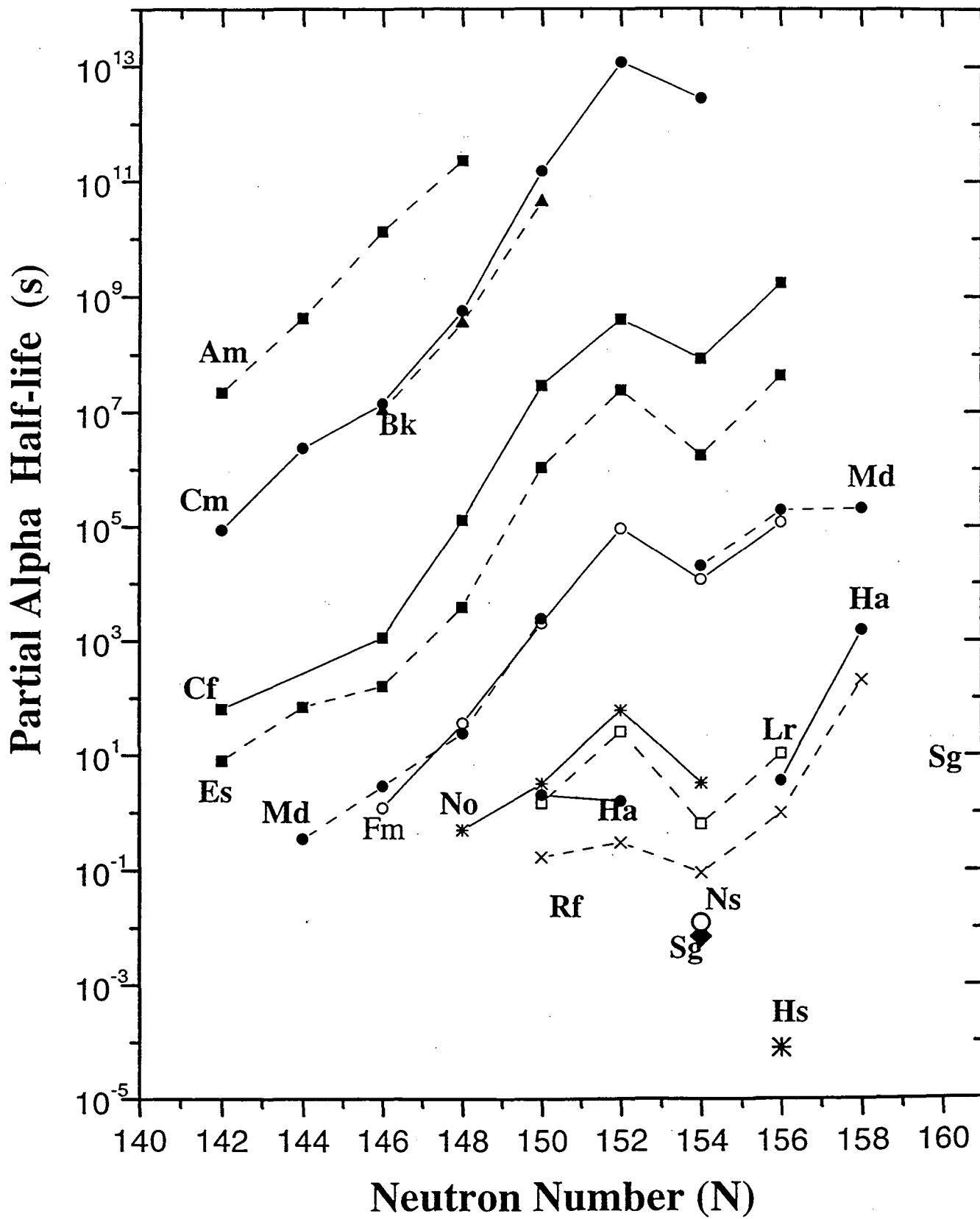
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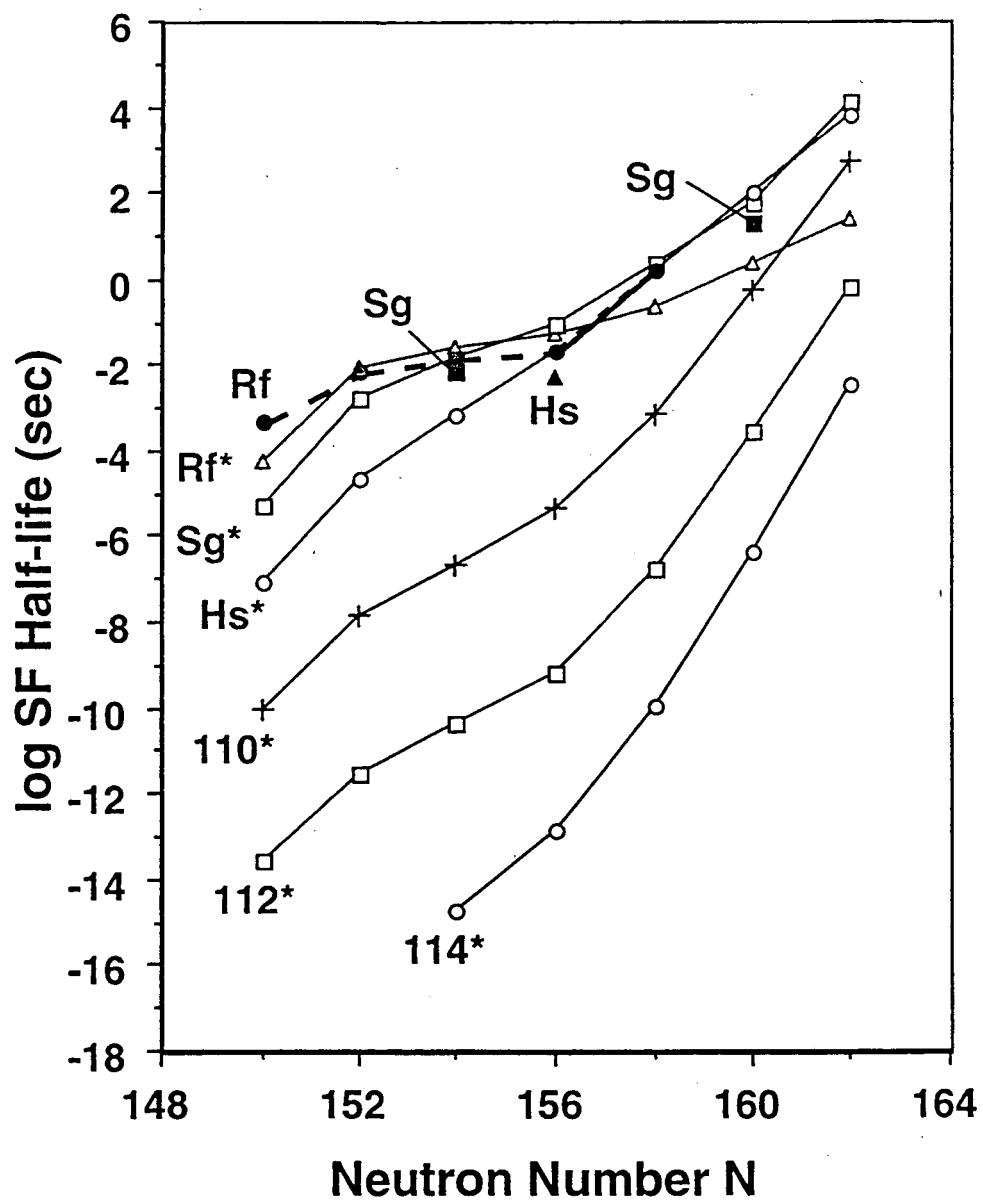
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

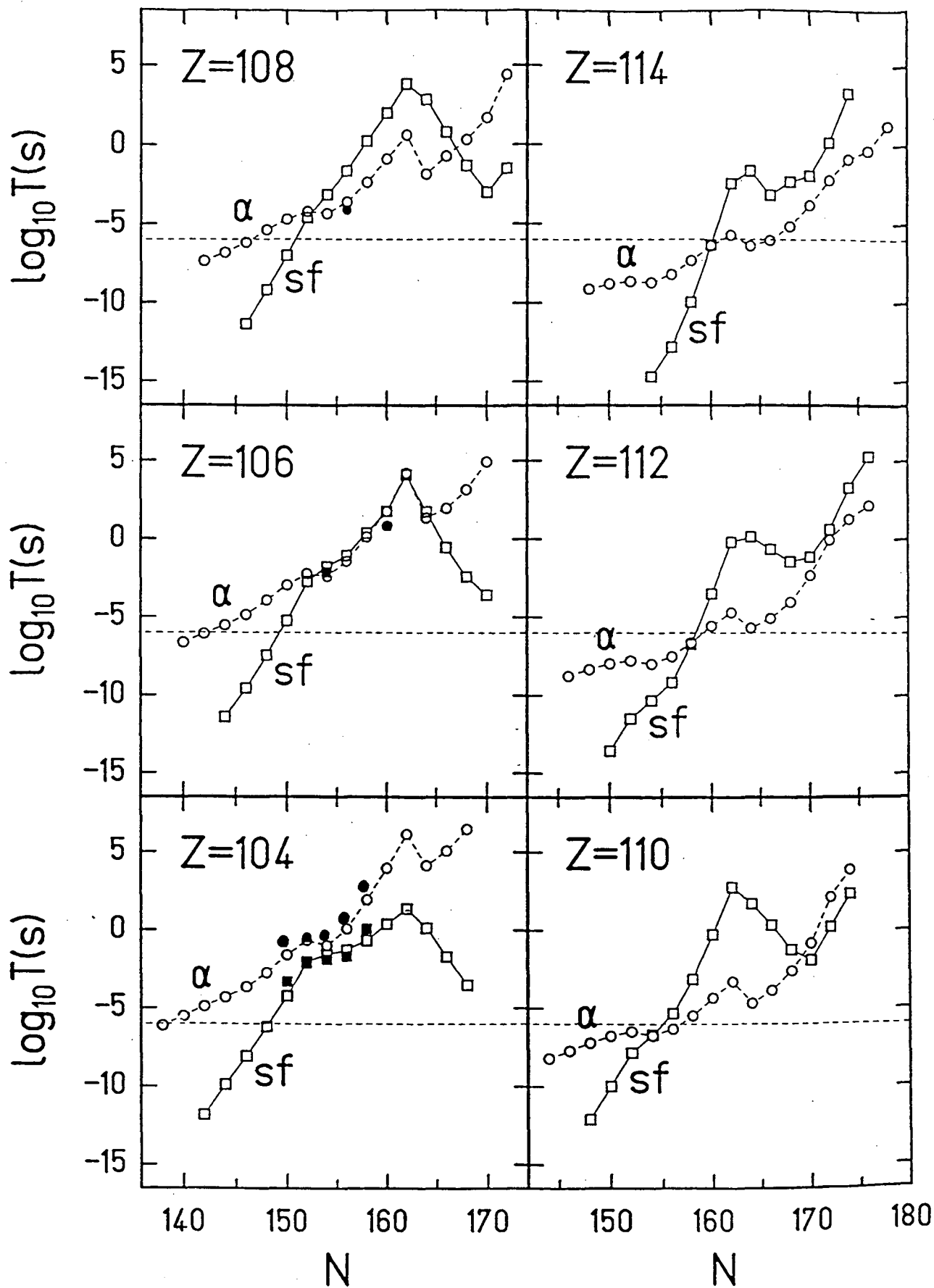
Discovery of Transuranium Elements²⁴



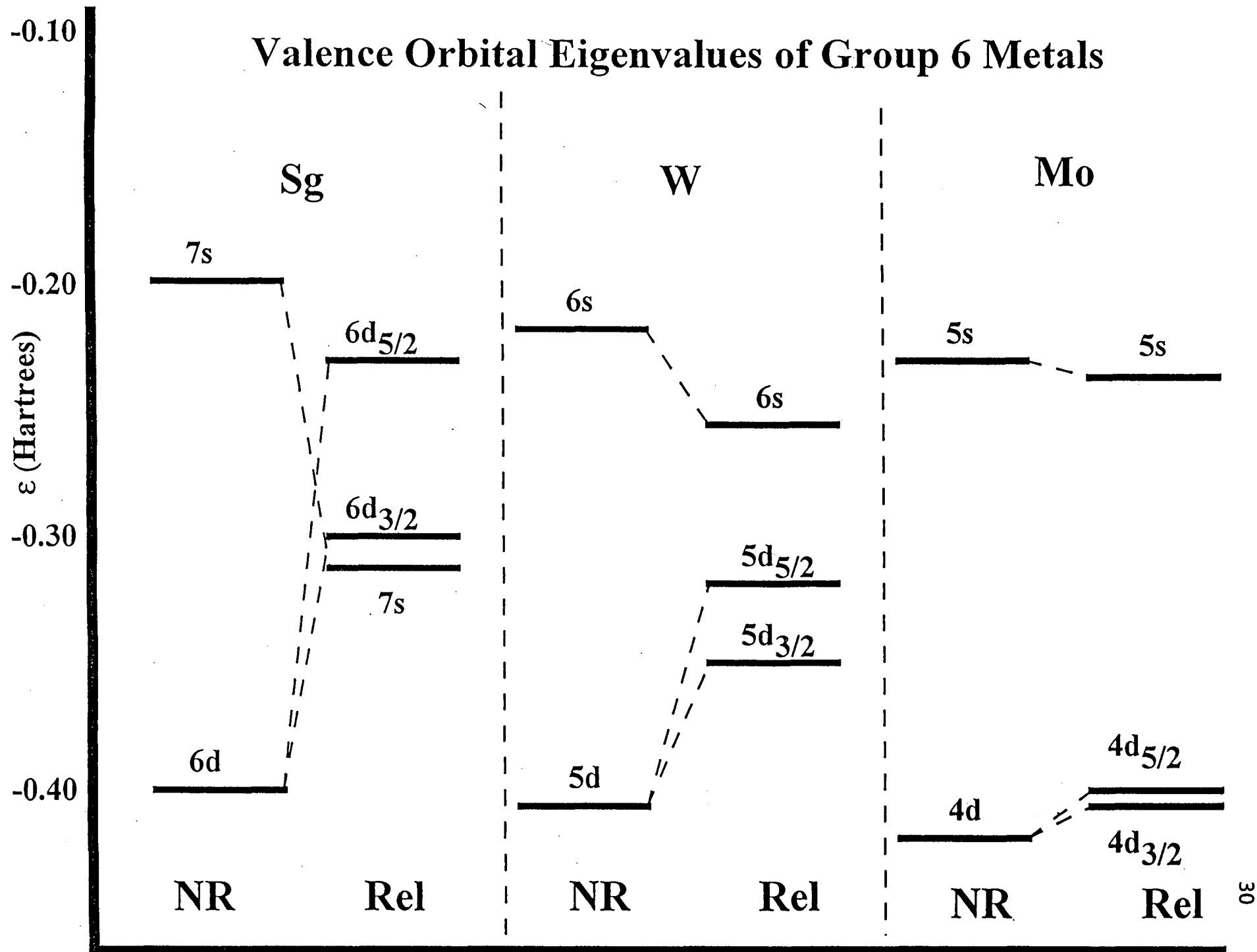


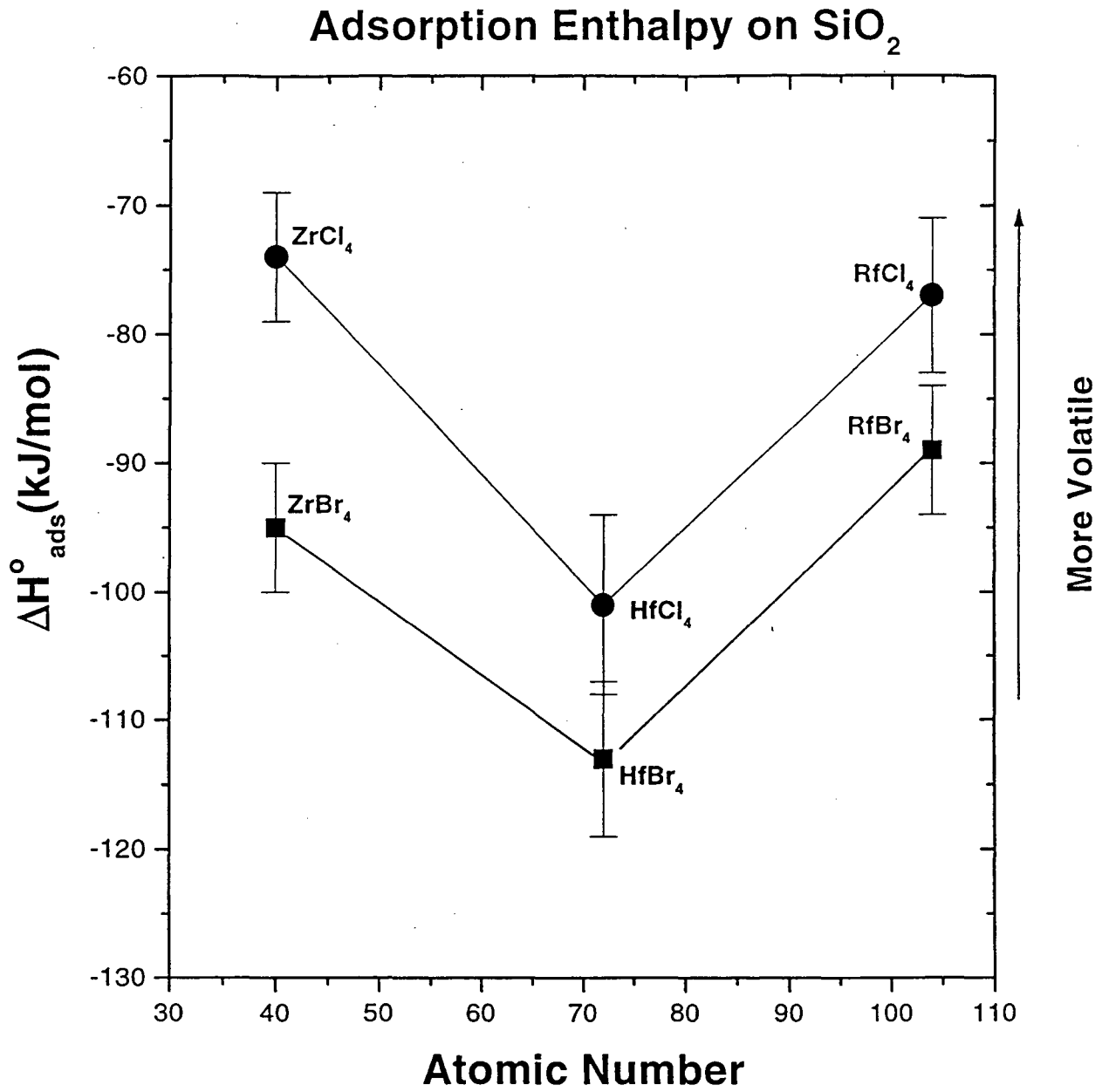






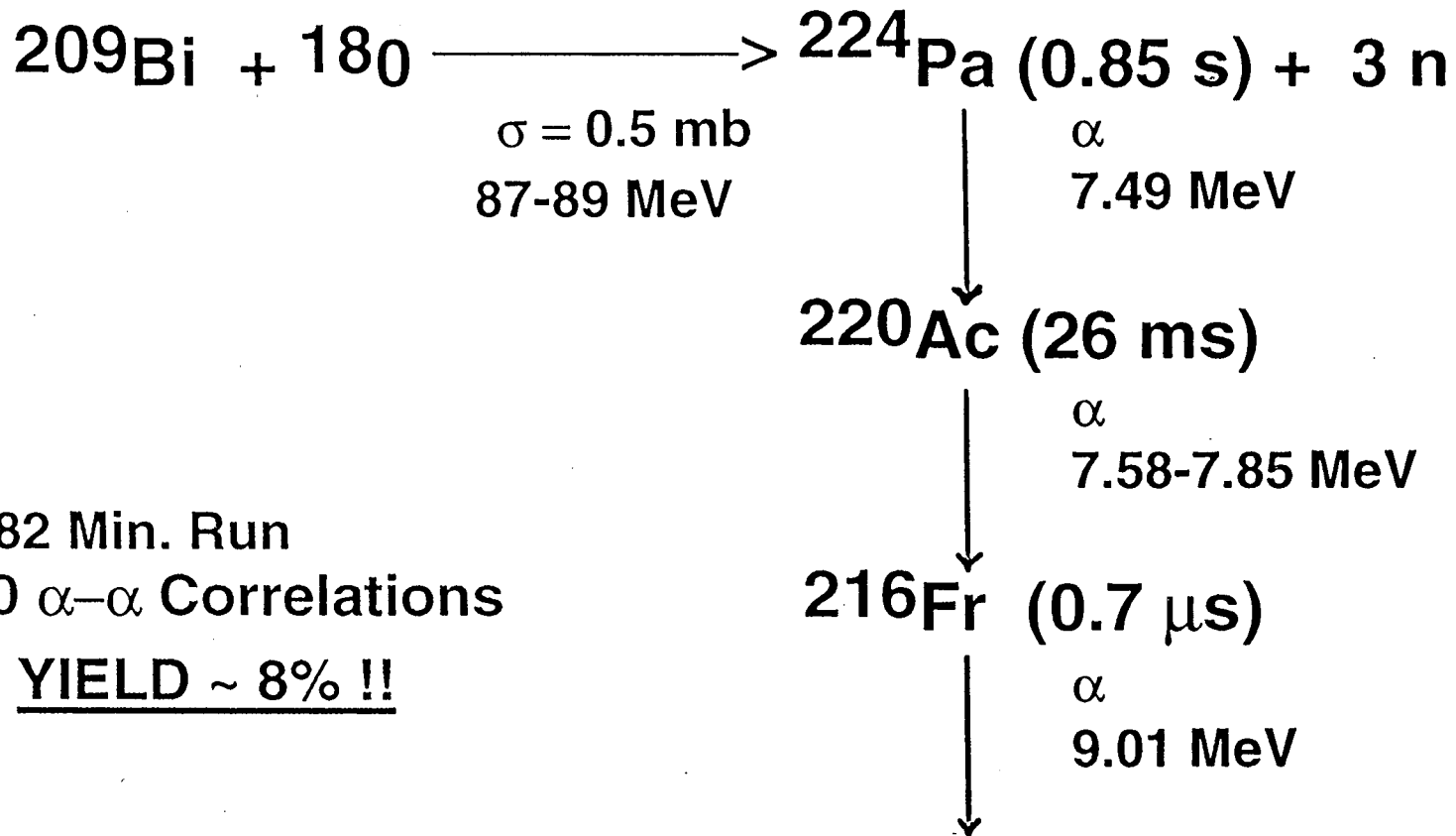
Valence Orbital Eigenvalues of Group 6 Metals





SISAK SEPARATION: Pa

1 M Lactic Acid: TOA/toluene & Dimethyl POPOP:
Flow rate 0.3-1.0 ml/s



82 Min. Run
650 α - α Correlations
YIELD ~ 8% !!

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