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CHEMISTRY OF THE HEAVIEST ELEMENTS--ONE ATOM AT A TIME

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In keeping with the goal of the Viewpoint series of the Journal of Chemical Education, this article gives a 75-year perspective of the chemistry of the heaviest elements, including a 50-year retrospective view of past developments, a summary of current research achievements and applications, and some predictions about exciting, new developments that might be envisioned within the next 25 years. A historical perspective of the importance of chemical separations in the discoveries of the transuranium elements from neptunium (Z=93) through mendelevium (Z=101) is given.   The development of techniques for studying the chemical properties of mendelevium and still heavier elements on the basis of measuring the radioactive decay of a single atom ("atom-at-a-time" chemistry) and combining the results of many separate experiments is reviewed. The influence of relativistic effects (expected to increase as Z^2) on chemical properties is discussed. The results from recent atom-at-a-time studies of the chemistry of the heaviest elements through seaborgium (Z=106) are summarized and show that their properties cannot be readily predicted based on simple extrapolation from the properties of their lighter homologues in the periodic table. The prospects for extending chemical studies to still heavier elements than seaborgium are considered and appear promising.

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Chemistry of the Heaviest Elements—One Atom at a Time

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Historical Perspective

Ever since ancient times, humans have been fascinated with trying to understand the composition of the world around them. The Greek philosophers considered the problem "theoretically" and as early as the 4th century B. C., Aristotle proposed that all matter consisted of varying proportions of the four "elements"—air, earth, fire, and water. Within the next few hundred years humans isolated and used a number of elements such as gold, silver, and tin, which were found relatively pure in nature, and removed others such as sulfur, lead, and mercury from their ores. In medieval times, the alchemists isolated and discovered additional elements and dreamed of turning lead into gold using secret formulas and incantations, but to no avail. With the development of experimental science and the scientific method in the 18th century, the pace of discovery of new elements accelerated rapidly. But uranium, discovered in 1789 in pitchblende from Saxony, Germany by Martin Klaproth, was to remain the heaviest known chemical element for more than 150 years.

Beginning in the mid-1930's, the new breed of nuclear scientists, including both chemists and physicists, became intrigued with the possibility of synthesizing new "artificial" elements not found in nature. The ancient alchemists' dream of transmutation was finally realized in 1937 when the first man-made element, technetium (Z=43), was synthesized by C. Perrier and E. Segrè *(1)*. In experiments initially designed to investigate the newly discovered (1939) phenomenon of nuclear fission, E. M. McMillan and P. H. Abelson *(2)* chemically isolated and identified the new element neptunium (93) in 1940 at Berkeley in the products of neutron irradiation of uranium. Shortly thereafter, in December 1940, G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl *(3)* identified an isotope of plutonium, and in February 1941 the first chemical separation of plutonium was performed *(4)* by Seaborg's first graduate student, Art Wahl. Although these experiments were conducted as part of the investigators' academic research and without governmental financial support, the discoverers voluntarily withheld publication until 1946 because of wartime security concerns about the fissionability of plutonium.

By 1961 the elements through lawrencium (103) had been discovered, thus completing the actinide series. Since that time, nine transactinide elements have been produced and identified so the elements through 112 are now known. Figure 1 shows the 1998 periodic table—the 24 elements discovered since 1936 are shaded. Table 1 gives the names and symbols for the transfermium elements approved by the International Union of Pure and Applied Chemistry (IUPAC) in August 1997, ending a long period of dissent and confusion. It also ended use of the unwieldy "provisionary" names unnilquadium (unq), unnilpentium(unp), unnilhexium (unh), etc. which had begun to appear on periodic tables in our classrooms, though they were never used by researchers in the field! IUPAC is now considering claims to priority of discovery of elements 110, 111, and 112, and will then request suggestions from the discoverers for names for these elements. To avoid confusion, we shall continue to use hahnium (Ha) for element 105 in this article as hahnium has been used in all of our previous publications on the chemistry of element 105, having been approved by the American Chemical Society in 1994 prior to the IUPAC approval of the compromise names shown in Table 1.

A time-line for the discovery of the transuranium elements is shown in Fig. 2. "Gaps" in the time-line can be noted, usually due to the need to develop the new techniques and concepts needed for the production, separation, and identification of each successive group of new elements. For example, before Seaborg's proposal of the actinide concept and his proposed periodic table (Fig. 3) published *(5)* in Chemical & Engineering News in 1945, it was believed that thorium, protactinium, uranium, neptunium, plutonium, and the next elements, 95, 96, should be placed as the heaviest members of groups 4 through 10. But, based on the actinide concept, the new series should start with actinium as a prototype and end with the filling of the 5f electron shell at element 103. The heavier actinides should then be extremely difficult to oxidize and according to Seaborg *would be trivalent homologues of the lanthanide series in which the 4f orbitals are being filled*. At the time it was believed to be a "wild" hypothesis, but Seaborg's group was unsuccessful in identifying elements 95 and 96 until they performed chemical separations designed to separate them as trivalent homologues of the lanthanides europium and gadolinium.

Another example of the actinide concept in the description of heavy element chemistry is the so-called "actinide contraction", analogous to the lanthanide contraction in which the radii of the M^{3+} (and M^{4+}) ions are observed to decrease as the positive charge on the nucleus increases with increasing atomic number. This is because, as successive electrons are added to the inner f shell, the imperfect screening of the nuclear charge by these added f electrons gives rise to a contraction of the valence shell. The trivalent actinides and lanthanides are generally eluted from a cation exchange column in order of the radii of the hydrated ions with the largest hydrated ions eluting first. Thus Lr is eluted first, Md next, etc. and similarly for the

lanthanides–Lu, Yb being first and the rest following in order. This concept was utilized to perform separations of the individual actinides from each other by elution from cation exchange columns with a variety of complexing agents, one of the best being ammonium α–hydroxyisobutyrate (HIB). In the 1955 Md discovery experiment, 1.6-h ^{256}Md was separated and chemically identified *(6)* by its elution with HIB from a carefully calibrated cation-exchange resin column in the predicted position for trivalent element 101.

By the end of 1970, the actinide concept had been further validated by chemical studies of the properties of No, Lr, and Rf. According to the actinide hypothesis it was expected that No^{2+} might exist, by analogy to its homologue Yb which can be reduced from 3+ to 2+ with strong reducing agents. However, it was among the early surprises that not only was the 2+ state of No achievable, it was actually the *most stable* oxidation state in aqueous solution! Thus the earliest report of the discovery *(7)* of nobelium, based on separating it as a trivalent actinide, could not have been correct because the chemical separations used would have separated No^{3+}, but not No^{2+} which would have been present under the conditions of the experiment.

First studies of the solution chemistry of Lr and Rf, performed in 1970 by Silva *et al. (8,9)*, showed that for Lr the trivalent state was again the most stable. The experiments with Rf showed that the 4+ state was the most stable in aqueous solution. Its properties were shown to be similar to those of Zr^{4+} and Hf^{4+} and different from Lr^{3+} and the other trivalent actinides. These experiments thus confirmed that Lr actually did complete the actinide series, and that Rf was the first transactinide element and the first member of a new 6d transition series. The Rf was positively identified by measuring the radioactive alpha (α) decay and half-life of about a minute of the well known isotope, ^{261}Rf.

Later experiments, conducted in 1980 by Hulet *et al. (10),* showed that, in elutions from anion exchange columns, the chloride complexes of Rf also behaved like those of the tetravalent group 4 elements rather than like those of the trivalent actinides. Some early gas-phase experiments were conducted on both Rf and Ha, but the atomic number of the species whose radioactivity was being measured was not definitively established so the results are somewhat suspect. No studies of the chemical properties of Ha in aqueous solution were reported until 1988.

Recent experimental evidence has shown that although elements 104 and 105 generally seem to belong to groups 4 and 5, they also show unexpected deviations in chemical properties from trends based on extrapolation from their lighter homologues in the periodic table. In fact, Rf and Ha have been found to behave more like the psuedo-homologues Th (IV) and Pa(V) under some conditions. On the other hand, preliminary studies of Sg show that it behaves like the group 6 elements, Mo and W, and not like the psuedo-homologue, U(VI). Recently, periodic tables similar to the one shown in Fig. 4 have been proposed *(11-13)*. The first five actinides are

shown in a stairstep arrangement leading from Rf down to the trivalent actinides, Am and Cm, to reflect the similarities in chemical behavior between the early actinides and the elements in groups 4 to 8. This arrangement shows Th and Pa as pseudo-homologues of the group 4 and 5 elements, and, to a lesser extent, shows U, Np, and Pu as pseudo-homologues of the group 6, 7, and 8 elements. Assessment of the validity of such a representation must await the results of more detailed studies of the chemical behavior of the transactinide elements.

As illustrated in Fig. 2, the definition of "heaviest elements" changes with time as new, still heavier elements are discovered. In discussing the atom-at-a-time chemistry of the heaviest elements, Md is a natural place to begin. It was discovered in 1955 and is the last of the heavy elements to be identified initially by direct chemical separation techniques, and it is the first of the transuranium elements to be identified using "one-atom-at-a-time" chemistry (6). That is, it was chemically identified by performing many chemical separations in which a total of only 7 atoms of ^{256}Md (half-life about 30 minutes) were detected on a one atom at a time basis by measuring the radioactive decay of single atoms. An additional 8 atoms of its radioactive decay product, ^{256}Fm, were also separated and measured. The ^{256}Md was produced at the 60-Inch Cyclotron at Berkeley by helium-ion bombardment of only about 10^9 atoms of the very radioactive target, 20-day ^{253}Es.

The heavier elements from nobelium (Z=102) through 112 must be produced in irradiations with heavier projectiles than helium ions and were identified first by physical techniques. Many controversies developed concerning the discoveries of elements 102, 103, 104, and 105 because of the very low production rates, the half-lives of minutes or less, and the necessity for developing new techniques for positive identification of atomic number other than chemical separations. The currently known isotopes of Md through Sg are shown in Fig. 5a. Atom-at-a-time chemical studies have now been performed on all of these elements—the first studies on Sg were reported by Schädel *et al. (12,13) in* 1997. The chart of the known isotopes of Sg through element 112 is given in Fig. 5b and clearly shows that the half-lives are rapidly decreasing with increasing atomic number and that the candidates for chemical studies beyond Sg are relatively few and will depend on the discovery of longer-lived isotopes.

The production and study of the heaviest elements require special facilities and capabilities and present unique challenges to the chemist. These include: special facilities for preparation and use of radioactive targets; an accelerator that can furnish high intensity beams of light to heavy ions; provision for preventing contamination of the accelerator should a radioactive target rupture; methods for rapidly and efficiently transporting the desired products from the hostile radiation environment associated with the production site in the accelerator beam line to a facility outside the radiation field where chemistry can be performed; selective and efficient chemical separations for measurement and identification of isotopes whose half-lives are minutes

or less and have very small production rates. A single atom must be detected by measuring its known radioactive decay properties. For example, in the chemical studies of Rf, only one atom was detected in about every ten one-minute chemical separations, resulting in detection of several atoms per hour, while in recently reported studies of the 7- and 21-second ^{265,266}Sg isotopes, only 15 atoms were detected over weeks of running time. Consequently, chemical separation procedures which come to equilibrium rapidly, and are valid on an "atom-at-a-time" basis must be used. Personnel trained in the techniques of handling radioactivity and in nuclear and radiochemistry are essential. Such facilities and capabilities exist at only a few laboratories around the world. These include the: Lawrence Berkeley National Laboratory (LBNL)[a]; Gesellschaft für Schwerionenforschung (GSI) near Darmstadt, Germany; the Joint Institute for Nuclear Research (JINR), Dubna, Russia; and the Paul Scherrer Institute (PSI) in Villigen, Switzerland.

With all the difficulties and challenges involved, why should we go to so much effort to study the chemical properties of the heaviest chemical elements? These investigations are among the most fundamental in all of chemistry in that they are the only means for obtaining the information required to place the heaviest elements in the appropriate group or series in the periodic table, and to compare their properties with those of their proposed lighter homologues. It was recognized rather early that the increasingly strong "relativistic effects" *(14-17),* predicted to increase proportionally as Z^2, would lead to ever larger deviations from the periodicity of the chemical properties of the heavier elements based on simple extrapolation of their properties from those of their lighter homologues. As the atomic number, and hence the positive charge on the nucleus, increases, there is a contraction of the s and p electronic orbitals which can give rise to changes in the electronic orbital configurations, even extending out to the valence electrons. Consequently, changes in ionic/atomic radii, ionization potentials, most stable oxidation states (redox potentials), and complexing ability are predicted.   Experimental studies of the heaviest elements provide the unique opportunity to compare actual experimental results with the theoretical predictions in order to assess the magnitude of the influence of relativistic effects on chemical properties at the very highest atomic numbers, where the effects should be largest and could drastically change chemical properties.

Theory

Studies of the chemical properties of the heaviest elements are extremely challenging for the theorists as well as for the experimentalists. The Schrödinger equation is no longer applicable

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[a] The name of the Lawrence Berkeley Laboratory (LBL) was officially changed to the Ernest Orlando Lawrence Berkeley National Laboratory (LBNL) in June, 1995.

and fully relativistic calculations must be performed. Fundamental predictions of the properties of the elements up through Z=172, based on atomic relativistic calculations, were reported more than 25 years ago *(14-17)* and indicated the deviations in atomic properties that might be expected due to relativistic effects. For example, in 1975, Pitzer *(18)* reported the striking conclusion, based on initial results from Hartree-Fock relativistic calculations, that elements 112 and 114, as well as 118 (eka-Rn), might be volatile, relatively inert gases. Relativistic atomic calculations also led to predictions that the transactinides would be members of a 6d transition series and show similarities to the 4d and 5d transition series elements.

In a 1988 review of relativistic effects on structural chemistry, P. Pyykkö *(19)* summarized the primary relativistic effects on atomic orbitals as: 1) contraction of the radius and energetic stabilization of s and p electronic orbitals; 2) spin-orbit splitting of the l>0 orbitals; 3) a resulting increase in the radii and energetic destabilization of the outer d and all f orbitals. As mentioned earlier, these effects can give rise to drastic changes in the chemical properties of the heaviest elements. The diagram shown in Figure 6 of the non-relativistic *vs*. relativistic Dirac-Fock calculations *(20)* of the valence orbital eigenvalues for the group 6 elements, Mo, W, and Sg, illustrates the large differences due to relativistic effects.

In recent reviews, Pershina (*21,22)*, has given excellent summaries of the development and recent improvements in the various computational methods for making more accurate relativistic atomic calculations of heavy element atomic properties. However, she points out that although these atomic calculations give some general guidance for experimental research, they do not predict the behavior of molecular species, especially under particular experimental conditions. This is a still more difficult and complex theoretical problem which was undertaken by Pershina and co-workers in conjunction with our initial international collaboration of scientists from the U. S., Germany, Switzerland, and Russia to perform experimental studies of the compounds of the heaviest elements. Systematic theoretical studies of heavy element compounds using relativistic quantum-chemical calculations were combined with fundamental physico-chemical considerations, to make detailed predictions *(23,24)* of the volatilities of the halides and of the partitioning of the transactinides and their lighter homologues between aqueous and organic solvents for specific experimental conditions.

Pershina and Fricke *(25)* have just completed a review of the theoretical studies of molecular properties of the transactinides. Except for a very few early publications, most of these theoretical studies were initiated in the 90s, indicating the increasing interest of theorists in this new field which was sparked by the recent availability of experimental data on Rf, Ha, and Sg. Relativistic molecular codes have been successful in describing the electronic structure of compounds and predicting molecular properties for the gas-phase compounds of the transactinides and their complexes in aqueous solutions. Especially promising are predictions of

actual equilibria of reactions. The agreement between calculations *(24)* and experiment *(26,)* "confirmed the necessity for doing relativistic molecular orbital calculations and the unreliability of the straightforward extrapolations of properties within the chemical groups"—4, 5, 6 of the periodic table. Additional theoretical calculations and new methods must be developed in order to treat the still more complex chemistry expected for elements 107 (Bh) and 108 (Hs), which like their lighter group 7 and 8 homologues, should exhibit a much larger variety of oxidation states, but with preferential stability of the lower ones.

Experimental Techniques
Production of Heavy Element Isotopes for Chemical Studies

Although Md and No were initially produced and identified in atom-at-a-time studies, they can now be produced in much larger, although still not weighable, quantities by irradiations of larger targets of radioactive isotopes such as ^{253,254}Es and ^{249}Cf.   But beginning with Lr, due to the very short half-lives of the isotopes and/or low production rates, all the chemical experiments have been conducted on a one-atom-at-a-time basis. Normal chemical analysis techniques are usually not applicable and the atoms must be detected by measuring the radioactive decay of a single atom at a time.

Typically, the longest-lived known isotope of the element is used for chemical studies, if the isotope can be made with a "reasonable" production cross section[b] and if the appropriate target material and projectiles are available. The isotopes used for the first chemistry performed on each of the transfermium elements, together with their half-lives, production reactions, and the year of the experiments, are given in Table 2.

Insert Table 2 here.

These are all "compound" nucleus reactions which means that the incoming projectile and the target atom completely fuse to form a highly excited nucleus which then can de-excite in a variety of ways−−fission being one of the most probable for the heavy elements. The desired reactions constitute only a small fraction of the large variety of unwanted reactions which occur.

Insert Fig. A here.

As can be seen from Fig. 5a, considerably longer-lived isotopes of some of these elements have now been synthesized. In the case of the transnobelium isotopes, the production cross

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[b]The probability of the occurrence of a specific nuclear reaction is expressed in terms of the concept of cross section. Interactions of the projectile (neutron, accelerated He ion or heavy ion) take place with individual target nuclei independently of each other, so it is useful to refer the probability of a nuclear reaction to a given target nucleus. The cross section (σ) gives a measure of the reaction probability per single target nucleus. It is a fictitious area which is customarily expressed in units of the barn (b) $=10^{-24}$ cm^2 which is approximately the geometrical section of a nucleus of mass number (A) $=100$. The prefixes pico (10^{-12}), nano (10^{-9}), micro (10^{-6}), etc. are used as appropriate.

sections are nanobarns or less, while those for fission or other competing reactions may be barns or millibarns.

In some later studies, "transfer" reactions, in which only a portion of the projectile is transferred to the target nucleus and fuses with it, have been used to produce neutron-rich products near the atomic number of the target in high yield

Insert Fig. B here.

For example, studies of Lr chemistry were conducted with ^{259,260}Lr produced by transfer of ^{5,6}Be fragments from ^{22}Ne projectiles to the rare (currently available only in microgram quantities) target nucleus, 276-d ^{254}Es.

In current studies of chemical properties, 3-min ^{260}Lr, 75-s ^{261}Rf, and 34-s ^{262}Ha produced in reactions of ^{18}O projectiles with ^{249}Bk (320 d) and ^{248}Cm (3.5 x 10^5 y) targets are normally used. These reactions have cross sections of a few nanobarns.

Detection and Analysis

Beginning with Md, methods were devised for removing the desired reaction products from the hostile irradiation site in the accelerator, rather than removing the highly radioactive and difficult to prepare targets and chemically dissolving and processing them to remove the desired isotope. Due to the momentum imparted to them during the nuclear reaction, the desired reaction products (along with many of the unwanted recoiling reaction products) will recoil out of the relatively thin targets and can be collected in a variety of ways

In the earliest studies, they were deposited on a thin "catcher" foil placed directly behind the target in the production chamber of the accelerator. The foil can then be removed manually or remotely shuttled to a detection system, without disturbing the accelerator vacuum, and analyzed directly for its α and spontaneous fission (SF) activity with appropriate radiation detectors. Or, alternatively, the collector foil can be removed and chemically processed. In any case, the valuable target is not destroyed, and considerable decontamination from all of the activity remaining in the target itself is achieved.

Later, gas transport systems using a variety of different gases and aerosols were developed and utilized by many investigators to rapidly and efficiently transport reaction products attached to various aerosols, including water vapor, NaCl, KCl, MoO$_3$, and C clusters, to collection foils or automated systems for subsequent chemistry or direct measurements of the radioactivity. A schematic diagram of the target system and the helium (KCl aerosol) gas transport system used by our Heavy Element Nuclear and Radiochemistry Group at the LBNL 88-Inch Cyclotron is shown in Fig. 7. It can be used to transport reaction products to a manual collection site as shown, or to automated chemical processing systems, directly to gamma- or X-ray spectrometer

systems, or to our rotating wheel system, the Merry Go-Around (MGA) shown in Fig. 8 for measurement of α and SF activity.

One of the major problems in the determination of chemical properties is to make sure that the detection method can provide positive identification that the activity being measured actually belongs to the desired element. A technique which can provide this positive proof and has been widely used in the identification of new heavy elements is that of measuring the known half-life and the energies of the α-particles of the isotope being studied and the time relationships between its α-particles and those emitted from its known daughter and even granddaughters. Since the atomic number (Z) and mass number (A) of the daughter nuclides are known, the parent atomic number and mass number will simply be that of the daughter plus an α-particle, i.e., Z=2, A=4. This technique was used in the initial discovery and identification of Sg (Element 106) in 1974 by Ghiorso *et al. (29),* and in the subsequent confirmation of that discovery by Gregorich et al. *(30)* in 1994 using the production reaction: ^{249}Cf + ^{18}O → ^{263}Sg + 4n. The α-decay sequence shown schematically below was used to positively identify ^{263}Sg using this method which is usually referred to as the "α−α correlation technique".

Insert Fig. C here.

Although the fragments from spontaneous fission (SF) can be measured with great sensitivity, such measurements do not provide positive identification of the element which fissioned because the process itself destroys the original nucleus. The nucleus divides into two large fission fragments which then de-excite by emitting neutrons, photons, and β-particles until they reach a long-lived or stable nucleus.

Insert Fig. D here.

A wide variety of different mass "splits" is possible and the Z of each of the two original fission fragments must be determined for each different split in order to determine the Z of the atom being studied. It has so far not been possible to measure the Z and A of the fission fragments to infer the Z and A of the fissioning nucleus from atom-at-a-time measurements. Half-life measurements are insufficient to provide positive identification because the SF half-lives of the various elements overlap and cover an extremely wide range of values from 4.5 x 10^9 years for ^{238}U to milliseconds and microseconds for many of the isotopes of the trans-fermium elements shown in Fig. 5. In early measurements, SF activity was detected from the "tracks" made by the fragments in mica or glass plates, but especially designed solid-state silicon detectors are now typically used for measurement of the energies and decay of both SF and α−activities.

Chemical Separation Methods

The chemical procedures used in atom-at-a-time studies must be rapid enough to be accomplished in times comparable to the half-lives of the isotopes used in the studies. Furthermore, the chemistry must give the same results for only a few atoms as for tracer and macro amounts. This typically limits the techniques to ion exchange and gas chromatography, solvent extraction, and other procedures with fast kinetics in which the atoms rapidly undergo many identical chemical reactions between two-phase systems in which equilibrium is attained rapidly. Adloff and Guillaumont (31) have given a thorough discussion of the validity of conclusions about chemical behavior obtained from very small numbers of atoms. They defined an equilibrium constant for such reactions in terms of the probabilities of finding the species in one phase or the other and concluded that it is valid to combine the results of many separate one-atom-at-a-time experiments in order to get statistically significant results (32,33).

Both manual and automated systems have been used to perform atom-at-a-time chemical separations of the heaviest elements. In the manual separations, after deposition of the activity-laden aerosol on one of the disks positioned on the collection wheel shown in Fig. 7, the wheel is rotated and the disk is manually removed. Subsequently, rather standard chemical procedures, usually liquid-liquid extractions or ion-exchange column separations, are performed very rapidly with 5 to 10 microliter volumes of solutions. The photo of the rather ordinary looking chemical fume hood and equipment given in Fig. 9 shows the lucite housing containing the collection station for the aerosols in the corner. This hood is located outside the Cyclotron vault and shielding, some 10 meters away from the radiation field of the production chamber and beam line; the simple equipment shown was used in the first studies of the aqueous chemistry of Ha which established that it behaved similarly to the pentavalent group 5 elements and that its most stable oxidation state in aqueous solution was 5+. A similarly simple setup with the addition of stoppered mini-test tubes and a centrifuge was used in liquid-liquid extraction studies of Rf. The success of such "manual" studies depends on the dexterity, speed, and endurance of the graduate students and staff who perform them, rather than on expensive, computer-controlled automated systems. However, although the automated systems are not necessarily faster, they usually give more reproducible results and are more appropriate for around the clock experiments lasting weeks at a time.

New Instrumentation

A comprehensive review of the instrumentation for atom-at-a-time chemistry of the heavy elements up to 1996 is given in Ref. 34. Among the systems used in studies of the aqueous chemistry of the heaviest elements is the Automated Rapid Chemistry Apparatus (ARCA II, mini-ARCA) developed by scientists at the Insitut für Kernchemie, Johannes Gutenberg-Universität Mainz and the Gesellschaft für Schwerionenforschung (GSI), Darmstadt, Germany.

The photo in Fig. 10 illustrates the complexity of the equipment compared to that for the manual experiments! ARCA II is used to perform rapid, repeated, high pressure liquid chromatography column experiments on the seconds time scale. The flow of various solutions is directed through small chromatography columns by microcomputer control of a series of pumps, valves, and mechanical sliders. It is equipped with two "magazines", each containing 20 mini-chromatography columns (1.6-mm i.d. x 8-mm long). The activity-laden KCl aerosols from the gas transport system are collected by pumping the carrier gas through a glass frit. After a suitable collection time, the KCl aerosol is dissolved in a small volume of solution and the flow is directed to one of the columns. The eluting solution is pumped through and the desired fraction is collected on Ta or Pt plates held in positions on the hot plate. A heat lamp and gas stream are also used to speed evaporation, but it still takes approximately 35 seconds before the samples are dried and ready for α-spectroscopy measurements.

Both thermochromatographic and isothermal methods have been used to study gas-phase properties. These are especially suitable for studies of short-lived isotopes because the time-consuming step of evaporating a liquid sample is avoided. I. Zvara *et al.* (35, 36) at Dubna pioneered the use of the thermochromatographic method to study the halides of Rf and Ha. Unfortunately, in these early studies only SF activity was measured, so the identity of the element being studied is uncertain and the results cannot be considered definitive. The use of automated isothermal systems, such as the On-Line Automated Gas Analyzer (OLGA) for studies of the volatilities of the halides of the heaviest elements was pioneered by Gäggeler and his group *(37)* at the Paul Scherrer Institute in Switzerland. In thermochromatographic systems, the chromatography column has a temperature gradient to deposit different species along the column according to their volatilities. By contrast, in an isothermal system, the entire quartz column after the high-temperature halogenation position, is kept at a constant temperature. A series of different temperatures is then run and the amount of the given species passing through the column at each temperature is determined. An improved isothermal system, the Heavy Element Volatility Instrument (HEVI) was built at LBNL by B. Kadkhodayan *et al. (38)* and gave better separations and more uniform isothermal temperature profiles. A schematic diagram of the HEVI isothermal gas-phase chemistry system is shown in Fig. 11 and a photo of HEVI, just after its completion, is shown in Fig. 12. Recently, in OLGA III *(39),* further improvements have been made to reduce the time between production of the isotope and final detection by miniaturizing and cooling the aerosol reclustering chamber so that isotopes with half-lives as short as 1 to 4 s can be studied.

A schematic diagram *(34)* of the SISAK apparatus *(40,41)*, a micro-centrifuge system for performing liquid-liquid extractions on the seconds-time scale, coupled to a continuously flowing liquid scintillation system (LISSY) for detection of $\alpha-\alpha$ correlations is shown in

Fig.13. This system has been used in studies of the transactinides, but improvements in sensitivity are needed in order to make measurements of nuclides produced with cross sections of nanobarns or less.

Studies of Chemical Properties
Earliest Studies

A review of the results of studies of chemical properties of the transeinsteinium elements as of 1983 was given by E. K. Hulet *(42)*. By the late 70s chemical studies had established that the most stable oxidation states of the transfermium elements in aqueous solution were: Md (3+); No (2+); Lr (3+), Rf (4+), and the redox potentials shown in Table 3 had been measured. The volatility of Md metal had been compared with that of other actinide metals and because of its high volatility it was believed to be a divalent metal. No experimental verification of the electronic structure of Md had been attempted, but it was calculated to be $[Rn]5f^{13}7s^2$.

Although early gas-phase studies of the halides of Rf and Ha had been conducted *(35, 36)*, suggesting that they behaved like their lighter group 4 and 5 homologues, only SF activity was detected and, therefore, the identity of the species being measured could not be positively attributed to elements 104 or 105. No studies of the aqueous properties of Ha (Z=105) had been performed at all. The longest-lived known isotope of Sg was ^{263}Sg which had a half-life of only 0.9 s and no chemical studies had yet been attempted.

Renaissance and New Results

After the pioneering early studies of the chemical properties of Md, No, Lr, and Rf, there was a rather long hiatus, extending from the 1970s until the late 1980s, when a "renaissance" of interest began in studying Lr and the transactinides. This was sparked in part by predictions summarized by Keller *(43)* in 1984 that relativistic effects might cause qualitative changes in the electronic configurations such that the valence electron structure of Lr might be $7s^2 7p_{1/2}$ rather than $6d7s^2$ as expected by analogy to the $5d6s^2$ valence configuration of its homologue Lu. Similarly, Rf and Ha might also be expected to exhibit stabilized $7p_{1/2}$ orbitals. As discussed earlier, these relativistic effects might result in significant differences in chemical properties from those predicted from simple extrapolation of periodic table trends. Our Heavy Element Nuclear and Radiochemistry Group at LBL and the Chemistry Department of the University of California, Berkeley subsequently set out to investigate these effects at the end of the actinide series and the beginning of the transactinide elements.

Although 3-min ^{260}Lr had been discovered in 1971, no subsequent studies of Lr chemistry were performed until 1987 when we decided to use it in manual studies designed to determine the ionic radius of Lr^{3+} by comparison of its elution position relative to the trivalent

lanthanides in ammonium HIB elutions from cation exchange resin columns. Although only 7 α–events were detected, we showed *(44)* that Lr^{3+} eluted in nearly the same position as Er^{3+}. Later, a long-lasting GSI-University of Mainz/LBNL-University of California collaboration was formed to conduct more experiments at LBNL using the GSI/Mainz automated system, mini-ARCA. Our first result was corroborated and its statistical significance was improved *(45)*. From these experiments, Lr^{3+} was inferred to have an ionic radius of 0.0881 nm. This result was rather unexpected because it gives a difference of only 0.0015 nm between Md^{3+} (0.0896 nm) and Lr^{3+}, which differ by 2 Z. This difference is much smaller than the 2 Z separation of 0.0021 nm between the homologous lanthanide ions, Tm^{3+} and Lu^{3+}. Attempts to reduce Lr^{3+} with V^{2+} and Cr^{2+} in dilute HCl were unsuccessful *(46)*, and the resulting limit for the reduction potential of the $Lr^{3+}/ Lr^{1(2)+}$ couple was found to be more negative than -0.44 V.

Discovery by a Lawrence Livermore National Laboratory/LBL collaboration in 1988 *(47)* of 40-min ^{261}Lr and 3.6-h ^{262}Lr permitted longer chemical procedures to be performed. Attempts to reduce Lr^{3+} with Sm^{2+} and coprecipitate Lr^{1+} with Rb^{1+} tetraphenylborate or chloroplatinate were unsuccessful. The Lr^{3+}/ Lr^{1+} couple was estimated to be more negative than -1.56 V, making it unlikely that Lr^{1+} can exist in aqueous solutions.

Since no experiments on Ha in aqueous solution had been performed, we began experiments in 1987 simply to determine its most stable oxidation state in aqueous solution. It was postulated that Ha might have a $7s^2 6d7p^2$ valence configuration rather than the $6d^3 7s^2$ valence configuration analogous to the $5d^3 7s^2$ valence configuration of its lighter homologue, Ta. It was conceivable that the $7s^2$ electrons might be sufficiently stabilized due to relativistic effects that the most stable state of Ha in aqueous solution might be 3+ rather than 5+, unlike its lighter pentavalent Group 5 homologues, Nb and Ta. Gregorich et al. *(28)* performed the first aqueous chemistry experiments on element 105 using 35-s ^{262}Ha produced at the 88-Inch Cyclotron at LBL. 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 4.3-s daughter, ^{258}Lr, provided positive identification of the Ha. The procedure involved removing the glass cover slip, on which the KCl aerosols were deposited, from the collector wheel (Fig. 7), placing the cover slip on a hot plate where 3 μl of concentrated nitric acid were added to dissolve the KCl, fuming to dryness, fuming again to dryness with more nitric acid, washing with dilute nitric acid, drying, and then transferring the cover slip to a detector for measurement of its radioactivity. From 801 such manual separations (Fig. 11), taking 51 s each, 26 α decays from ^{262}Ha were positively identified, showing that, indeed, Ha sorbed on glass surfaces after fuming with nitric acid as did its pentavalent group 5 homologues, Nb and Ta. The tetravalent group 4 elements, Zr and Hf, and the trivalent actinides did not sorb under these conditions. These experiments confirmed the

group 5 character of Ha and indicated that it should be placed in the periodic table as the heaviest known member of group 5.

However, additional manual liquid-liquid extraction experiments unexpectedly showed that Ha did not extract into methylisobutylketone from mixed nitric/hydrofluoric acid solutions as did Ta(V), but behaved like Nb(V) which does not extract. This was the *first indication* of differences in the behavior of Ha from its lighter homologue Ta(V) and was the impetus for a long series of experiments to elucidate the chemical behavior of Ha.

Chromatographic separations of Ha using ARCA II *(48)* were then conducted at the 88-Inch LBL Cyclotron jointly by the GSI/Mainz-PSI/Bern-LBL/Berkeley groups in 1988 and 1990. It was shown that Ha was eluted promptly from cation exchange columns with HIB together with pentavalent Nb, Ta, and Pa, while tri- and tetravalent ions were retained. Again, this provided proof that pentavlent Ha is the most stable oxidation state in aqueous solution. However, in elutions of pentavalent Ha, Nb, and Pa sorbed on columns composed of the liquid anion exchanger triisooctylamine on an inert support, Ha again exhibited non-Ta-like behavior, behaving more like the psuedo-homologue, Pa (V). Nearly 2200 collection and separation cycles on a one-minute time scale were carried out with ARCA II! These results showing extractability in the order Ta>Nb>Ha>Pa were consistent with calculations of complex formation, but calculations of extractability *(23)* gave the reverse order. The discrepancy was attributed *(23)* to multiply charged F$^-$ or mixed F-Cl complexes; new experiments with single halide systems were suggested for easier comparison with theoretical predictions *(24)* based on considerations of hydrolysis vs. complex formation from electronic structures calculated with an improved relativistic code and Born's theory of metal-ion extraction. These calculations indicated the extraction order should be Pa>>Nb~Ha>Ta. First experiments conducted at LBNL by Paulus *et al.* (*26*) with a pure HCl system and anion exchange chromatographic separations using ARCA II confirm these predictions of an inversion of the trend in properties in going from the 5d to the 6d elements. More experiments will be performed with HBr and HF.

Our group at LBNL has also performed manual studies to compare the extraction into tributylphosphate (TBP), triisooctylamine (TIOA), and TTA from aqueous solutions of ^{261}Rf with its lighter homologues Zr and Hf, and the pseudo-homologues Th(IV) and Pu(IV),. These experiments show *(49,50)* that Rf generally behaves as a group 4 element. However, in extractions into TBP (which extracts neutral complexes) from HCl solutions with [H$^+$]=8 M, Rf extracts well at low Cl$^-$ concentrations as do Zr^{4+} and Hf^{4+}, but at [Cl$^-$]>10 M, Rf extraction decreases rapidly, similarly to Pu(IV). Presumably, this is because Rf (IV) and Pu(IV) form stronger anionic chloride complexes at high [Cl$^-$] concentrations than do tetravalent Zr, Hf, and Th.

The isothermal gas systems, OLGA and HEVI described earlier (Figs. 11,12), have been used to perform isothermal chromatographic gas phase studies *(51-53)* of the volatilities of the halides of Rf and Ha. Again, these studies have shown marked deviations in their behaviors from predictions based on simple extrapolations of the properties of their lighter group 4 and 5 homologues. The adsorption enthalpies on SiO_2 calculated from Monte-Carlo fits to the measurements *(52,53)* of relative yields as a function of temperature between about 100 ^{O}C to 600 ^{O}C for the tetrachlorides and tetrabromides of Rf, Hf, and Zr are shown in Fig. 14. A dramatic break in the sequence for the adsorption enthalpies of the tetrachlorides is found while that for the bromides is more modest. In general, the adsorption enthalpies[c] calculated for the chlorides are less negative (indicating greater volatility) than the bromides as predicted by Pershina. The volatilities of the halides of Zr^{4+} and Rf^{4+} are nearly the same for both series and more volatile than the Hf species. Data from Gäggeler *et al.(54)* for the bromides show very low volatility for Ha relative to Nb(V) and Ta(V), in disagreement with relativistic molecular calculations *(55)* 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 the less volatile oxybromide was formed, and additional experiments on the oxybromides are needed to clarify this.

Preliminary results of the first chemical separations of Sg conducted with OLGA and ARCA in 1995 and 1996 have now been reported *(12, 13)*. Isothermal gas chromatography experiments on the oxychlorides were conducted with OLGA followed by unambiguous detection of $^{265+266}$Sg via the α-decay chains. Based on 15 atoms of $^{265+266}$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 also consistent with predictions based on macro-amounts which show the species, MO_2Cl_2, to be the most volatile. The half-lives of ^{265}Sg and ^{266}Sg (SF<80%) were found to be ~7s and ~21 s. Their production cross sections were estimated to be ~440 and ~60 picobarns for the reaction of 121-MeV ^{22}Ne projectiles with ^{248}Cm.

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

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[c]In experiments in which only single molecules can be studied, the sublimation enthalpy, ΔH_s, cannot be determined directly. The adsorption enthalpy, ΔH_a, on the chromatographic surface is deduced from the gas chromatographic experiments using a Monte Carlo code which generates the yield of the volatile species as a function of temperature and includes the influence of the carrier gas flow, the half-lives and molecular weights of the investigated species, etc. For each isothermal temperature, the transport through the column is modeled for a large number of sample molecules. Curves of yield vs. temperatures for each value of ΔH_a are obtained and the value which best fits the experimental volatility curves is obtained by a least-squares method. A linear correlation between ΔH_a and ΔH_s has been developed empirically. Thus, ΔH_a is the quantity used to compare the volatilities of the transactinide compounds with those of their lighter homologs.

columns with 0.1M HNO3/0.0005 M HF. This behavior is similar to the group 6 homologues, W(VI) and Mo(VI), but unlike the psuedo-homologue, U(VI), which forms $[UO_2]^{2+}$ ions under these conditions, and also unlike 2+, 3+, 4+ cations. Experiments with the SISAK-LISSY system, were also performed to extract Sg from 1 M HIB into trioctylamine, but the sensitivity was not sufficient for detection of ^{265,266}Sg.

There are several recent reviews of the chemistry of the transactinides *(57-59)* and an extremely comprehensive, very recent review by Kratz *(60)* which compare experimental results for elements 104, 105, and 106 with theoretical predictions and discuss the prospects for extending studies to heavier elements. These should be consulted for additional, more detailed information.

Future

More "In-depth" Chemical Studies

Additional more detailed investigations of the chemistry of Sg should be undertaken 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 being developed so that the parent Sg itself, rather than its daughters, can be measured directly. Improvements to SISAK-LISSY are continuing in order to increase its sensitivity so that nuclides with production cross sections lower than nanobarns can be investigated. General methods for increasing overall production rates, such as possible multiple-target and gas-transport systems must be devised.

Experiments should also be performed to make more detailed investigations of the elements lighter than Sg for comparison with the theoretical predictions which are now much better developed. For example, additional attempts should be undertaken to prepare No^{3+} (Z=102), perhaps in non-aqueous solvents, in order to measure its ionic radius. It would be of great interest to see how its radius fits in between Lr^{3+} (Z=103) and Md^{3+} (Z=101) whose radii differ by only 0.0015 nm.   More studies of the complexing ability of Rf with a variety of ligands need to be undertaken to clear up some ambiguities in the results and to compare them with the theoretical predictions. Although these experiments may not appear as glamorous as pushing on past Sg, they are certainly worthy of attention.

Chemistry Beyond Seaborgium?

In order to discuss the prospects for chemical studies beyond Sg, the possibilities for longer-lived isotopes of those elements need to be considered. A topological map of the known isotopes as of about 1978 and the doubly magic spherical region of long-lived SuperHeavy

Elements (SHEs) predicted at that time, which has never yet been reached, is shown in Fig. 15. The heavy isotopes beyond the known region discovered since then have been added to the plot. Recent theoretical calculations of nuclear stability predict [61,62] stabilization of nuclei near ^{270}Hs, the doubly magic deformed nucleus with 108 protons and 162 neutrons. It is predicted to decay via α−emission with a half-life of ~6 s which should permit chemical studies. In order to produce longer-lived isotopes for chemical studies, attempts will be made to synthesize isotopes with neutron number near the predicted deformed nuclear shell at 162 neutrons. It was also suggested that due to these deformed shells there will be a peninsula of relatively stable nuclides extending up to the region of stability around the doubly magic spherical nucleus ^{298}114. Smolanczuk *(63)* has recently calculated that it should decay by α-emission with a half-life of only about 12 min, but that ^{292}110 will decay predominantly by α-emission with a half-life of about 50 y. The isotopes discovered since then seem to confirm the existence of an intermediate region of deformed stability and give us hope that there may be isotopes of elements at least through Mt (Z=109) which will live long enough to permit chemical studies.

Some of the reactions predicted to be best for production of elements 107 through 109 for chemical studies are shown in Table 4, together with those commonly used today to produce elements 103 through 106 for chemical studies. The longest-lived known isotope of element 107 is 0.44-s ^{264}Bh, but it is predicted that ^{266}Bh and ^{267}Bh will have half-lives of about 10 s and decay by α-emission, and could be made with similar cross sections using a ^{249}Bk target. as shown in Table 4. The cross sections for ^{254}Es targets are much higher, but it is doubtful that the required 30-40 μg will be available for target preparation. In addition, special precautions for handling this highly radioactive target are required. The chemistry of Bh 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}Re. It appears that the speed and sensitivity of the present OLGA III system should be adequate, but the sensitivity of SISAK is not yet sufficient to make measurements of products whose production cross sections are only 30 picobarns.

The longest-lived known isotope of element 108 is 9-s ^{269}Hs, which could also be produced from the same targets as shown in Table 4 for ^{270}Hs with a similar cross section of a few picobarns. The ^{248}Cm(^{26}Mg, 4n,5n) ^{270,269}Hs reactions could also be used, but again, the cross sections are estimated to be only a few picobarns. It is expected to have a volatile tetroxide as do the group 8 elements, Ru and Os.

The reaction ^{254}Es (^{22}Ne,4n) would be the best for producing ^{272}Mt (~1 s) for chemical studies as it has the largest estimated cross section, but, again, requires ^{254}Es. The cross sections for the other reactions shown are much smaller and the half-lives of the products are even shorter. The newly constructed Berkeley Gas-filled Separator (BGS) will be used to investigate

the best production reactions and determine the half-lives and nuclear properties of Mt isotopes prior to attempting chemical studies. Another possibility under consideration is to use the BGS as a pre-separator to quickly separate the desired species from a host of unwanted activities prior to chemical studies. It might also permit access to some of the predicted longer-lived isotopes which could be separated and "stock-piled" on a collector for future chemical separation experiments. However, in order to perform chemical studies of Bh, Hs, and Mt, significant increases in the production rates, perhaps by using multiple targets and gas transport systems, and in the efficiencies and speed of the various chemical separation techniques must be achieved.

It appears that chemical studies can be extended beyond Sg to Bh, Hs, and Mt since it seems clear that isotopes which have half-lives of seconds or longer can exist for these elements, provided they can produced in sufficient quantity. Smolanczuk *(63)* also predicts half-lives as long as years for isotopes of element 110, months for 112, and minutes for 114 with neutron numbers near the spherical shell of 184 neutrons. It is no longer expected *(62)* that these spherical nuclei around the doubly magic spherical nucleus $^{298}114$ form an island in a sea of instability, but rather that they belong to an extended peninsula of relatively long-lived nuclides. One of the most exciting future experiments will be to look for the doubly deformed, lighter isotope ^{270}Hs to see if, indeed, the theoretical predictions are correct. If so, a whole new vista of longer-lived isotopes opens up before us.

Some potential compound nucleus reactions with ^{48}Ca projectiles and targets of the neutron-rich, very long-lived isotopes, ^{244}Pu, ^{248}Cm, and ^{250}Cm for gaining access to the doubly magic superheavy element (SHE) region are shown in Fig. 15. Discussions of some of these reactions, as well as reactions with ^{26}Mg and ^{36}S projectiles are given in Refs. 64, 65. Transfer and deeply inelastic reactions in which only a portion of the projectile is transferred to the target, resulting in a nucleus with lower excitation energy which is less likely to fission, are also being reconsidered. Among the new techniques being proposed for production of SHEs is the use of extremely neutron-rich, unstable ("radioactive") beams *(66)*, but increases in the intensities of these beams are still needed.

It appears quite likely that we will be able to study the chemistry of the elements through Mt. It also seems probable that a host of isotopes can exist which are sufficiently long-lived for chemical studies of elements 110 through 114. But, the challenge remains to devise suitable production reactions and ingenious ways to increase production rates in order for us to enter this frontier region beyond Mt.

Acknowledgements

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Table 1. Comparison of Predictions of Robert Smolańczuk for the $^{293}118$ Decay Chain with Experimental Results Obtained Later with BGS for the Irradiation of ^{208}Pb targets with 449-MeV ^{86}Kr projectiles.

$^{A}Z_{N}$	Q_{α} (MeV)		Half-Lives	
	Predicted	BGS	Predicted	BGS
$^{293}118_{175}$	12.23	(12.4)	$31 - 310$ µs	(0.12 ms)
$^{289}116_{173}$	11.37	(11.6)	$0.96 - 9.6$ ms	(0.60 ms)
$^{285}114_{171}$	11.18	(11.4)	$0.80 - 8.0$ ms	(0.58 ms)
$^{281}112_{169}$	11.00	(10.7)	$0.61 - 6.1$ ms	(0.89 ms)
$^{277}110_{167}$	10.77	(10.2)	$0.62 - 6.2$ ms	(3.0 ms)
$^{273}\text{Hs}_{165}$	9.69	(9.7)	$0.12 - 1.2$ s	(1.2 s)
$^{269}\text{Sg}_{163}$	8.35	(8.7)	$8.0 - 80$ min	(~20 s)
$^{265}\text{Rf}_{161}$			$T_{SF} \sim$ 41 min	