ACTINIDE

THE INC-4 REUNION CONFERENCE

☀ Actinide Research Quarterly

The INC-4 Reunion Conference

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THE DEVELOPMENT OF INORGANIC AND STABLE ISOTOPE CHEMISTRY CAPABILITIES AT LOS ALAMOS

Los Alamos has a long and rich tradition in inorganic and stable isotope chemistry that started in the early 1950s and continues to this day. The early motivation for inorganic chemistry was to develop actinide separations, purification, and materials-handling technologies that directly impacted the development of nuclear weapons. Over the years this capability has evolved to include main-group, transition-metal, bioinorganic, actinide-fluoride, lanthanide, and organometallic-actinide chemistries that are critical to a number of missions, including stockpile maintenance, alternate energy, and nuclear forensics.

The development of stable isotopes began later in the Laboratory's history as a spin-off of separations technologies developed for tritium. The separation of stable isotopes of carbon, oxygen, and nitrogen led to the development of entirely new probes of the structure and dynamics of biological and inorganic molecules through the use of nuclear magnetic resonance, vibrational spectroscopy, mass spectrometry, and related measurement techniques. Stable isotopes also found use as tracers for atmospheric and geological transport and related fields of study.

Both inorganic and isotope chemistry started, flourished, and remained in a single group (INC-4 and its predecessors and progenitors) for more than four decades until the mid-1990s when these capabilities began to be distributed into several different groups and divisions within the Laboratory.

The INC-4 "reunion" conference, held at Los Alamos in May 2009, explored the evolution of these two important capabilities. The conference was dedicated to the careers of four of the early Laboratory pioneers who first formed INC-4: Robert (Bob) Penneman, Llewlleyn (Lew) Jones, and B. B. McInteer—all of whom recently turned 90—and the late Larned (Larry) Asprey. This issue of *Actinide Research Quarterly* covers highlights from the conference on the early origins and the progression of science within INC-4.

—*Basil Swanson, Chemistry Division, and Nan Sauer, Institutes Office*

Members of INC-4 past and present gather for a photo at the reunion conference. Honorees Bob Penneman and Lew Jones are fifth and fourth from right, respectively; Marge Asprey, widow of honoree Larry Asprey, is at far left in the white sweater. B. B. McInteer was unable to attend.

THE OLD WEST

Built back in 1946, the buildings inside DP West were the site of many scientific breakthroughs over the decades. It was there, for example, that chemists developed the Plutonium Uranium Extraction process, or PUREX, which separates plutonium and uranium from fission products. Researchers also gained a better understanding of americium chemistry at TA-21. Americium is a by-product in the production of plutonium.

This area is where a process was developed that separates plutonium from various waste streams. Renowned scientists such as Robert Penneman, Larned Asprey, [B. B. McInteer,]and Llewellyn Jones were behind these and many other accomplishments.

—LOS ALAMOS REFLECTIONS
MARCH 1998

A view of DP West at TA-21 during construction (above) and after opening (below). DP West (DP stands for Delta Prime) was home to uranium and plutonium research from the mid-1940s until 1978. Bob Penneman recalled that in the early years there were a few women in Building 1 but none in the plant itself.
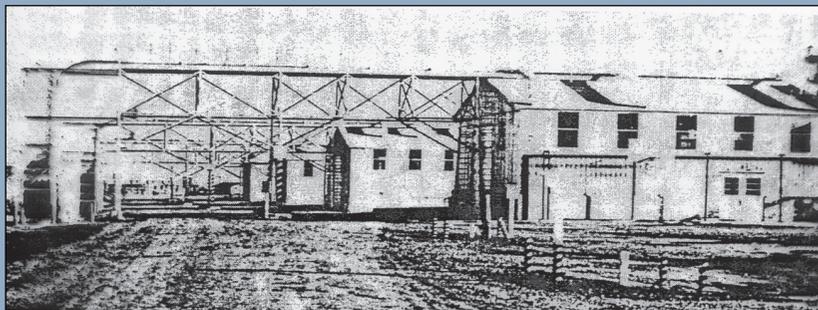
ROBERT "BOB" PENNEMAN
(CIRCA 1962)
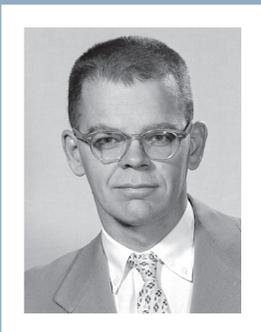
LLEWELLYN "LEW" JONES
(CIRCA 1962)

B. B. MCINTEER
(CIRCA 1957)

LARNED "LARRY" ASPREY
(CIRCA 1959)

THE EARLY DAYS OF INC-4

A RETROSPECTIVE BY BOB PENNEMAN

The discovery of plutonium

After James Chadwick's 1932 discovery of the neutron, researchers used cyclotrons to generate neutrons to irradiate ordinary elements, normally yielding beta emitters to form elements of the next-higher atomic number but of the same atomic weight. However, when they irradiated uranium they got a bewildering ton of activities, which could not be then explained and which we now know came from uranium fission products.

In 1940 Edwin McMillan and Philip Abelson of the University of California, Berkeley exposed a foil of uranium (element 92) to neutrons and caught the recoil fragments on a piece of cigarette paper. They showed chemically that a new element, neptunium-239 (element 93), had been formed. However, its daughter product—plutonium-239—was too long-lived for them to detect. (The half-life of plutonium-239 is 24,000 years). So Glenn Seaborg and collaborators used a cyclotron to irradiate uranium-238 and got the shorter half-life (90-year) plutonium-238 isotope and were able to expand its chemistry.

Both new element discoveries were written up but not published until after World War II. Seaborg gifted to the Smithsonian the platinum disk on which the original plutonium-239 sample was deposited. He kindly invited me to the ceremony and I have that program signed by Seaborg and Emilio Segrè.

Before December 1942, researchers irradiated a hundred pounds of uranyl nitrate (hydrate) at the St. Louis cyclotron, day after day after day and finally were able to separate a few micrograms of plutonium-239. On Dec. 2, 1942, Enrico Fermi established a sustained chain reaction in the squash courts under the west stand of Stagg Field at the University of Chicago; thus plutonium-239 could eventually be made in quantity. The first yield of plutonium from the Clinton Pile at Oak Ridge didn't occur until early 1944. By late 1943 a total of two and a half milligrams of plutonium was available. Now there are tons of excess plutonium. It boggles the mind.

Ancient history

I was born in 1919. People of that era were shaped by two major events: the Depression and World War II. One of my early jobs in 1938–1939 was as a high school stringer for the Springfield, Ill., *Journal-Register*. A stringer is a reporter who doesn't get paid a salary but instead is paid by the column inch; I think I got 5 cents an inch. In 1940 I became a Popsicle production manager for a salary of 25 cents an hour. Some wag in my group at Los Alamos said it was the height of my career!

By the time I was a college senior in 1941, I had a technical job working for an Illinois highway department lab as a chemist analyzing cement. We analyzed
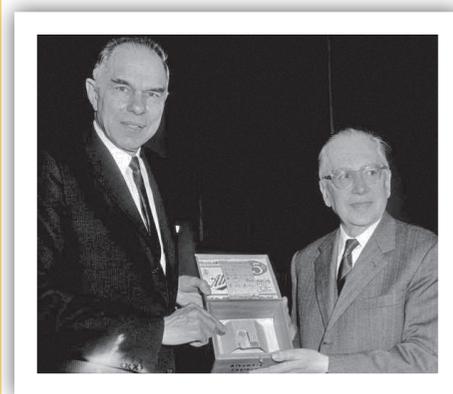
Glenn Seaborg (left) and Emilio Segrè hold the cigar box that was used to store the first half-microgram sample of plutonium-239. They presented the box and sample carrier to the Smithsonian Institution on the 25th anniversary of the discovery of the isotope. Bob Penneman attended the ceremony.
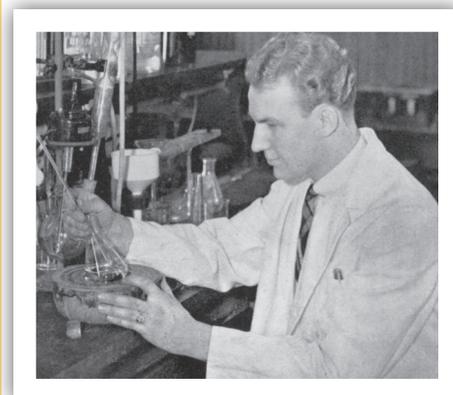
College senior Bob Penneman.
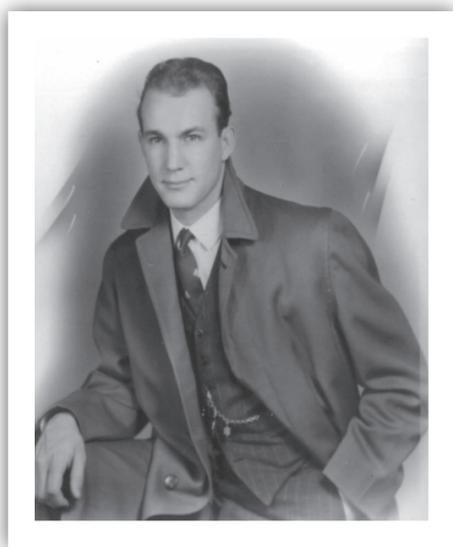
Bob Penneman in the spring of 1942, about the time he received his master's degree in chemistry from the University of Illinois.

a collapsed bridge and discovered that the tank car of water used to mix the cement had retained enough molasses from a previous use to severely weaken the cement from the sugar which complexes calcium.

In the summer of 1942 I had a master's degree in chemistry from the University of Illinois, having received a sum of $50 a month from a University of Illinois Presidential Fellowship. On July 15, 1942, I joined the Metallurgical Lab at the University of Chicago. On July 25, 1942, I married my wife, Mary; we've now been married 68 years.

The war years at Met Lab and Oak Ridge

In mid-August 1942, the Met Lab sent me to the Metal Hydrides plant in Beverly, Mass., to get uranium metal for Fermi's first reactor. We used Canadian uranium oxide and heated it with calcium hydride to reduce the uranium oxide to uranium metal. It was then compressed into briquettes, cooled in dry ice, and was motored to Cambridge, where it was vacuum cast into metal at MIT. Fermi's reactor went critical in Chicago in December 1942, and I returned to Chicago in January 1943.

The expected radiation levels from the expected fission products far exceeded any previously known. One day I was talking to Aristid von Grosse [atomic chemist who became President of the Temple University Research Institute in Philadelphia], and he said that they had collected a gram of radium, presented it to Madame Curie, and she put it in her vest pocket. [Penneman shakes his head at this recollection, saying "Hard to believe."]

The best human examples of radiation effects in those days were dentists, who used their fingers to hold the X-ray films against your tooth. They no

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GARY ELLER: PENNEMAN'S MANHATTAN PROJECT YEARS

One notable thing about Bob [Penneman]: he really got around during the Manhattan Project: Chicago Met Lab; Oak Ridge; Massachusetts Uranium Processing Facility; R&D on the radiation effects on graphite, chemicals, plastics, and wires; R&D on stored energy in irradiated graphite. He packed a lot into those years. And for every one of these stops in the road, he can regale you with great stories; really wonderful stories. I believe he understates the significance of the radiation-effects work in that period.

This was the time when the Clinton pile and the Hanford reactors were being brought online, and they were carbon-based, graphite-based reactors.

There were "minor" details like fuel rods getting stuck in swollen graphite, or perhaps massive releases of stored energy in the graphite; in fact these were really significant practical problems—potential show-stopping and dangerous problems

Editor's note: P. Gary Eller came to the Lab in 1974 and retired in 2004. His areas of expertise are actinide, environmental, and fluorine chemistry. He presented the retrospective on Larry Asprey; it begins on page 25.

longer do that, of course. In 1943 I had a Chicago dentist who did just that, but I was sworn to secrecy and could not caution him.

At Chicago, Nobel Prize winners and future Nobelists were commonplace. I worked for Eugene Wigner on measuring what's called the "Wigner effect," i.e., the displacement of carbon atoms in a graphite reactor, or pile, by the slowing of high-speed (high-energy) neutrons. Wigner raised the specter of a catastrophic energy release, which would destroy the pile. I made the first measurements of the Wigner effect by copying a device that a man named Charles Sykes had made to measure the work-hardening of copper metal. (As you know, if you take a piece of flexible copper and you bend it a few times, you displace the copper atoms, the copper wire gets stiff, and the wire eventually breaks.) I used the device to study irradiated graphite and determined the temperature of safe releases of stored energy and quantified it.

James Franck, a Nobel Prize winner, oversaw my work on determining radiation effects on ion-exchange resins. Some damage occurred to the organic skeleton, and you got some brown exodus from the column, but plenty of ion-exchange properties remained unchanged. Much later, I irradiated some Los Alamos americium-241 at Chalk River, Canada, to form curium-242. We used ion exchange to remove the fission products. You could turn off the lights in the room and watch the brilliantly illuminated curium band moving down. With the americium, you have to run a counter down the column to follow its progress; with the curium, in contrast, all you had to do was watch it.

At the University of Chicago from 1942 to mid-1945 and then at Oak Ridge from July 1945 to January 1946, we irradiated at the anticipated high levels everything you can possibly imagine—glass, electrical wires, insulation, solutions, any materials suspected to be used and exposed to radiation—and quantified the deterioration properties whenever possible. For radiation sources we used the cyclotron at Chicago for the alpha radiation, the 2-million-electronvolt machine at Notre Dame for beta radiation, and the reactor at Oak Ridge in Tennessee. I was able to quantify the breaking strength of glass rods upon exposure to radiation at the anticipated levels. All of you who work with old residues know the extreme fragility of centrifuge cones and glass containing dried radiation residues; the glass just crumples in your hands.

To close this discussion of my wartime experiences at Chicago, it is simple courtesy to thank one of the cyclotron operators, a guy named Harold. He later became director of Los Alamos [referring to Harold Agnew].

In January 1946, I went back to the U. of Illinois as a Ph.D. candidate, where I had an extraordinary bit of luck. My thesis advisor was a consultant to Western Cartridge Co., later Olin Industries. They obtained a tank car of the German V-2 rocket fuel (hydrazine hydrate), and part of my thesis assignment was to make anhydrous hydrazine from its constant boiling hydrate.

Bob Penneman poses with members of Milton Burton's Chemistry Group at the University of Chicago Met Lab, circa 1944. Penneman is at the far left of the second row from the top; Burton is third from right in the top row.
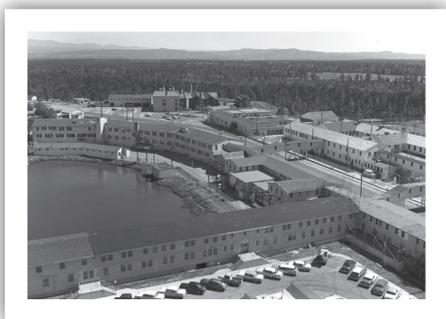
My first idea was to add just enough sodium hydroxide to form a hydrate, heat it up, cool it down, and dump off the hydrate—but that didn't work. But what really did work—and it was my good fortune to discover it—was a two-phase liquid system; one that was extraordinarily hydrazine-rich. Thus, a few-plate distillation column could make anhydrous hydrazine. Before that I'd built a hundred-plate distillation column, but we didn't have to use it. In an act of extraordinary kindness on the part of my thesis advisor, I was allowed to separately patent the preparation of anhydrous hydrazine.

The Los Alamos years

I came to Los Alamos at exactly the right time. There was considerable thought regarding closing the Lab, as it had accomplished its wartime job. However, Norris Bradbury [the director following Robert Oppenheimer] had the contrary opinion: He wanted the Lab to continue and especially to broaden chemical studies from those dealing solely with plutonium. Later, he also wanted to fund a postdoctoral program, and we were able to attract a large share of top-level postdoctoral candidates. Many of them stayed within the group [which became known as INC-4], and others branched out elsewhere in the Lab. War-time salaries at the Lab ranged from $200 a month for a B.S. to $400 a month for a Ph.D. I hired on in 1947 at $490 a month.

Trinity Road went directly through the town, and all the theoreticians were located around Ashley Pond. George Kistiakowski [Manhattan pioneer who headed the implosion department] once remarked that he ran a thousand pounds of high explosive over this road every day. If it had ever detonated at the wrong time, it could have wiped out the theoretical brains in Los Alamos.

I was hired by Rod Spence to separate parts per million of americium-241 from machining scraps from the Clementine fast reactor, and if successful, to explore and expand its little-known chemistry. A lab was established in a vacant

Trinity Road went directly through the original technical area, and all the theoreticians were located around Ashley Pond. George Kistiakowski (Manhattan pioneer who headed the implosion department) said he ran a thousand pounds of high explosive over this road every day: "If it had ever detonated at the wrong time, it could have wiped out the theoretical brains in Los Alamos."

Tom Keenan: A Complimentary Letter

I came across a letter to Bob Penneman from R. G. Weimer, who used to be director of the Oak Ridge Chem Tech Division. He said this about Bob: "There are few people that could match what you did as a chemist, and in the field of actinide chemistry there are none. Young scientists could learn a great deal from you about what it really means to be a chemist, the intellectual challenge, the excitement and the fun."

When you think about Bob Penneman, words like inspirational and encouraging and instructive and exciting come to mind—because those really were days that fulfilled all of those adjectives.

Editor's note: Tom Keenan, now retired, joined Bob Penneman's group as a summer student in 1950.

warehouse at DP West. It had 18-foot ceilings, so you could build a high appa-ratus if you really wanted to. We dissolved plutonium turnings in nitric acid—a lively reaction!—and precipitated plutonium peroxide, leaving some milligrams of americium(III) plus grams of lanthanum(III) behind in the supernatant.

When we turned our plutonium back to the plant, they found that it yielded a better oxalate precipitate than did the plutonium directly from Hanford in Richland, Wash. Soon thereafter, the plutonium plant inserted a peroxide step and gave us the supernatant (liquid) that they concentrated. Thus, we had a constant supply of americium, but with a lot of junk in it. In contrast, today's plutonium is so pure that, precipitated as the peroxide, it leaves a very pure americium fraction in the supernatant liquid.

In the early years—some 65 years ago—all the plutonium was at Los Alamos, and hence, all the americium-241, the daughter of plutonium-241. Once it became known that I had americium, Seaborg came around with his hand out, so naturally we gave him some. They used that americium as a target to obtain the next heavy element to be discovered and isolated, berkelium, Z = 97. Albert Ghiorso credited our discovery of fluoride-soluble americium(VI), which enabled them to remove the bulk of americium target and thus concentrate the smaller berkelium-containing residue and more readily isolate the new element.

In the early days, so few of us at DP worked together to separate ameri-cium and curium that it's difficult to separate individual contributions. This is especially true of the elucidation of early americium chemistry, including americium(V), americium(VI), and curium(IV). Tom Keenan first found a gadolinium(III)-like spectrum of curium(III). As the group expanded, individual contributions could more easily be determined. Larry Asprey made many contributions, some of which can be read about in *Actinide Research Quarterly,* 1st Quarter, 2005.

Lew Jones alone suggested the use of micron thin films of the aqueous uranyl ion placed between two optical flats to study the infrared "asymmetric stretch" of uranium. I prepared the rest of the "yl"-type ions for him: neptunium, plutonium, and americium. He deserves sole credit for that powerful technique. Noting that uranyl-type ions, XO_2^{2+} represented a general class of MX_2 ions, I suggested the study of other complex ions, such as cyanides. Lew got a wonder-ful letter from Sten Ahrland, [Lund University, Sweden] that said in part: " . . . and now people have to believe that there are step-wise formation constants in solution."

I was at Los Alamos for 37 years and have chosen to discuss a few contribu-tions that I actually originated. One was the preparation of soluble tetravalent americium. The americium(III/IV) potential is so high (over 2 volts) that we weren't able to prepare it, and americium(IV) eluded all chemists for a long time. In W.M. Latimer's book [*The Oxidation States of the Elements and Their Potentials in Aqueous Solution,* published in 1938], I noticed the enormous differences between the solubility products of the rare-earth tri-hydroxides and

GARY ELLER: ATOMS FOR PEACE

Bob Penneman served as a delegate to first Atoms for Peace Conference, held in Geneva in 1954. It's hard to overestimate the significance of the first Atoms for Peace Conference. It was the first international conference in which our scientists were allowed to openly mix it up with folks abroad. And that established a set of interactions that Bob had with Russian, German, and other scientists in the area that still exists today. I was always very impressed that Bob was the only chemist from Los Alamos for that first international actinide science conference.

Gary Eller:
Gift Horses

Bob Penneman coauthored the americium and curium chapters for the second edition of The Chemistry of the Actinides. One thing I learned from Bob was that sometimes you need to look at gift horses carefully. At some point he said to me: "Have I got a deal for you." I should have known what was going to happen, but bit anyway. And so I got on the hook to upgrade the curium chapter for the 1986 2nd edition of the actinide book (co-edited by Glenn Seaborg). I got my name on that chapter (along with Penneman, who is heard remarking to Eller from the audience: "You did all the work.").

Bob always put people who were working for him out on the front stage probably earlier than we ever had any right to take that stage. And so I had opportunities of meeting the Seaborgs of the world long before I was fit to polish their boots.

that estimated for the thorium tetra-hydroxide, or the hydrous oxide. If that would be applicable to americium(III) and (IV), it could substantially lower the threshold of oxidation in base.

My first treatment of pink $Am(OH)_3$ with hypochlorite immediately produced the intense black precipitate of $Am(OH)_4$ or the hydrous oxide of americium(IV). I used concentrated ammonium fluoride to sequester the hydroxide, which was then replaced by a fluoride. The black precipitate dissolved cleanly to form a red fluoride solution, which gave the spectrum characteristic of a new valence state, that of americium(IV).

X-ray diffraction structural studies were made primarily by our expert Bob Ryan, using Don Cromer's equipment until we got our own. Uranium penta-fluoride is insoluble in anhydrous hydrofluoric acid. However, when I added just enough water to doubly hydrate the proton, a sky-blue solution resulted, from which $H_5O_2UF_6$ was crystallized. Ryan showed that it contained the doubly hydrated proton with the characteristically short oxygen–oxygen distance

Under the aegis of Norris Bradbury and his support to broaden chemistry, we made an extensive study of the actinide fluorides. Extensive preparations of complex fluorides were made, often with Asprey's assistance. My contribution was synthesizing many of the compounds.

Much later, the plutonium isotope separations group needed an estimate of the refractive index of plutonium(V) fluoride. By graphing the molar refractivity values of our entire series of $MPuF_6$ compounds (M = cesium to lithium), I was able to extrapolate to alkali-metal-free PuF_5 itself and thus derive a good estimate for the value of the desired PuF_5 molar refractivity.

Because of the relativistic tight binding of s electrons, some argued that the very high Z elements would be rare gases. To the contrary, we predicted that there would be significant chemical consequences. Indeed, as a direct result of increased relativistic binding of s electrons and some p electrons in the heaviest elements, there was concomitant promotion of other p electrons to ionization levels. With Joe Mann and Klixbüll Jørgensen, I predicted that the next alkali element [the hypothetical element 119] would show a valence higher than one (unity) for the first time.

As an aside, to help enliven my talk, I entitled this observation "Split Peas." To explain, electron levels were originally assigned names due to the appearance of their elemental spectra: s for sharp, p for principal lines, etc. In elements of very high atomic number, relativistic effects split the six p electrons into two groups. Part of the p electrons are very tightly bound. The remaining p electrons are raised in energy to within the range of chemical ionization.

One discovery occurred when the laser isotope separations group was trying to do isotope separation using PuF_6, which contains several percent of the shorter-lived isotope, plutonium-238. They intended to use laser excitation to precipitate a pure plutonium-239 fluoride from the PuF_6 gaseous feed. Unfortunately, the gaseous PuF_6 coated the entire apparatus with unseparated

feed, thus diluting any of the desired pure plutonium isotope that had been laser precipitated.

So I suggested adding oxygen and fluorine to the mixture and letting it stand overnight, hoping the alpha radiation would activate it. We had found early on in our pulse-analysis work that if you had oxygen present it would suck up the electrons to form heavy ions. And sure enough, adding oxygen and fluorine worked. The alpha radiation activated the mixture to react with the surface deposit to re-form gaseous PuF_6. This back reaction was confirmed, possibly leading to the patent and use of O_2F_2—or "FOOF"—for that purpose.

My last scientific contribution impacted safe storage of tons of plutonium dioxide. In a remarkable discovery, Los Alamos authors [John Haschke, Thomas Allen, and Luis Morales, in their article, "Reaction of Plutonium Dioxide with Water: Formation and Properties of $PuO_{2+}x$ Reaction of Plutonium Dioxide with Water: Formation and Properties of $PuO_{2+}x$," which appeared in *Science*, Volume 287, 2000] showed that PuO_2 reacted at modest temperatures with water vapor, yielding hydrogen gas, an increased oxygen content of the solid but essentially unchanged cell constants. They suggested the addition of a centered oxide ion to the PuO_2 lattice, balanced by plutonium(VI).

Inserting an oxide ion in the cube center of four surrounding oxide ions in the PuO_2 lattice seemed unlikely to me. I recommended addition of hydroxyl, with concomitant formation of plutonium(V). Using the prior authors' data to substantiate the change, I predicted the plutonium(V)–O distance, later confirmed. (The great crystallographer) William Zachariasen's bond strength/bond length rules underpinned my prediction.

Wrapping it up

The most enduring of my life achievements was certainly being the head for more than 37 years of a chemistry group that had wide-ranging capabilities. I was fortunate to come when the Lab was re-forming after World War II, and especially to have good finances and substantial freedom of actions. I had immediate access to Director Bradbury and his single deputy, who unfailingly supported the wide range of work. These factors allowed me to slowly build a group that became a de facto chemistry department; not a group devoted to a single area of study as was previously the custom.

I close with a quotation from a former leader of the critical assembly group, Hugh Paxton. After I retired, Gary Eller called me back to look into some one-point detonation work that had been done at Los Alamos in the 1960s under great, great secrecy. I was able to get most of that declassified and I went to Paxton to ask him about my version of the "maximum credible event." He was very helpful, and so I offered to get him paid—not only for his time but also especially for his lifetime of expertise.

Paxton declined payment, making a comment so typical of Los Alamos at that time: "You and I come from the time when it was our *job* to help each other."

GARY ELLER: BOB'S FINAL PAPER

Just before I retired I was working on long-term plutonium storage and questions arose about long-term radiation damage, stored energy, and all that. I was able to bring Bob back on a consulting basis to help sort out the wheat from the chaff. This constituted his going full-circle to his pioneering materials radiation-damage work in the Manhattan Project. Bob helped us sort out what was significant and what wasn't significant regarding long-term damage effects on safe long-term plutonium storage. Bob's final publication, "An alternative structure of Pu_4O_9 ("$PuO_{2.25}$") incorporating interstitial hydroxyl rather than oxide," appeared in the *Journal of Solid State Chemistry* in 2005. Isn't this interesting; Bob was right back to solid-state chemistry. There was a highly visible dustup six or eight years ago. A publication speculated that maybe PuO_2 is somewhat soluble after all, because it might contain some plutonium(V) or (VI)—and everybody knows compounds with those valences are soluble. And so Bob did a reinterpretation of that paper with Mark Paffett, showing that the concerns were unwarranted, and the flap went away.

GETTING PUBLISHED IN PHYSICS TODAY

AS RECOUNTED BY DARLEANE HOFFMAN, FORMER INC DIVISION LEADER

Accomplishments and promise of transplutonium research

The 16 new elements added to the periodic table beyond uranium not only have contributed to our understanding of nuclear and atomic physics, but some have practical uses as well.

O. Lewin Keller Jr., Darleane C. Hoffman, Robert A. Penneman and Gregory R. Choppin

Editor's note: Basil Swanson credits Darleane Hoffman with helping INC Division expand its scope. "Darleane helped us get into programs—the weapons program and other kinds of programs—that began to balance our portfolio so that we were not just fundamental but also had a more applied research base. That was tremendously important for the success of the division." Hoffman was INC Division's first leader, taking the helm of the newly formed division in 1981 after serving for several years as head of the Chemistry and Nuclear Chemistry (CNC) Division. In 1984, the same year that Bob Penneman retired, Hoffman left Los Alamos to become a professor of nuclear chemistry at the University of California, Berkeley. She is a frequent visitor to Los Alamos and was the charter director of the Seaborg Institute (see *ARQ,* 2nd Quarter, 2009).

In February 1983, Bob and I attended a workshop on Opportunities and Challenges in Research with Transplutonium Elements. The workshop was sponsored by the National Research Council's Committee on Nuclear and Radiochemistry, Board on Chemical Sciences and Technology. This workshop spawned an article in *Physics Today* on "Accomplishments and Promise of Transplutonium Research" (March 1984), which Bob and I coauthored along with O. Lewin Keller, Jr., and Gregory Choppin.

I quote from that issue of Physics Today: "The recent discoveries of element 107 and especially 109 at Darmstadt make the island of stability seem tantalizingly close. If relatively stable superheavy elements are eventually discovered at Berkeley, Darmstadt, Dubna or one of the other laboratories working in the field, their chemical properties will certainly be dominated in an unprecedented way by relativistic effects. The spontaneously fissionable spherical nuclei in this region will also offer properties that are not simple extensions from the known fissionable elements, whose nuclei are deformed."

Physics Today also mentioned the Transplutonium Production Program, which Glenn Seaborg started after he became chairman of the Atomic Energy Commission. The High Flux Isotopes Reactor and the Transplutonium Processing Plant, both at Oak Ridge National Laboratory, were furnishing key isotopes. Look at the quantities involved here: curium-248, 150 milligrams per year; berkelium-249, 60 milligrams; californium-252, 500 milligrams; einsteinium-253, 2 milligrams; einsteinium-254, 3 micrograms; fermium-257, 1 picogram. At that time we wanted to make a lot of einsteinium-254 and bombard it with calcium and other things like that to try to make more heavy elements.

Gerhard Friedlander of Brookhaven National Laboratory, who was the workshop chair, summarized some of the conclusions of the workshop: "The operation of these facilities should be continued for at least several years and their status should be reviewed again three to five years from the date of the workshop's report. … In the meantime, the highest priority in research with transplutonium material should be given to the support of those experimental programs identified in the panel reports as particularly interesting, promising, and crucially dependent on products of the HFIR/TRU [the facilities at Oak Ridge]."

B. B. McInteer and Isotope Separation

A Retrospective by Tom Mills

B. B. McInteer was instrumental in pioneering Los Alamos' research in the use of cryogenic distillation columns to produce stable isotopes. The process involves using tall columns (up to 700 feet) to cool naturally occurring gases to the point of liquefying. When heat is applied at a column bottom, the isotopes stratify—with the lighter isotopes at the top and the heavier isotopes at the bottom—and are collected.

B. B. and the beginning

Berthus Boston McInteer, Jr., was named for his father, a noted professor of botany at the University of Kentucky. The story goes that his grandfather wanted to name his daughter Bertha, but the child was a boy. The grandfather, being somewhat of a Latin scholar, knew that the masculine form of Bertha would be Berthus, thus B. B.'s father was named such. As one might guess, this name was sufficiently unusual to deal with easily, and the initials B. B. became the name everyone was used to.

B. B. went to the University of Minnesota for his graduate work in physics and received his Ph.D. under Alfred O. C. Nier, who is well known in the world of mass spectrometry. I believe B. B. was doing some work on tritium isotope separation as a graduate student. Certainly that was one of his main focuses when he came to the Lab.

When one thinks of B. B.'s contribution to science, his leadership in isotope separation stands out immediately. There was great interest in the 1950s in using tritium for thermonuclear weapons. B. B.'s first assignment was to develop a process for enriching large amounts of tritium. The separation was done by a process called gaseous thermal diffusion. The hardware includes, typically, a


B. B. McInteer (right) and Bob Potter look over a drilling bit developed by CMF-4. The bit, heated electrically to 1200 degrees Celsius, drilled through basalt at the rate of 50 feet per day in experiments at Los Alamos. Development of the bit was the outgrowth of an academic discussion about geophysics, according to an article in the January 1965 issue of The Atom.
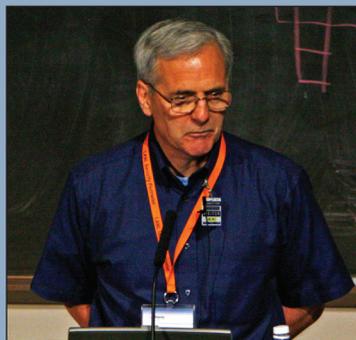
About the author: Tom Mills received a B.S. in chemical engineering from the University of Illinois in 1966 and a Ph.D. in chemical engineering from the University of California, Berkeley, in 1971. He came to Los Alamos in 1971 as a postdoc under B. B. McInteer and became a technical staff member in 1972. Mills designed, built, and operated isotope separation systems from 1972 to 1989 and conducted research in isotope separation, fluorine chemistry, and plutonium chemistry from 1987 to 2001. He held various group-level management positions in INC-4 and NMT Division. After retiring in 2001, he consulted with and assisted Spectra Gases Inc. in restarting the 700-foot carbon monoxide (CO) isotope column, 2001–04.
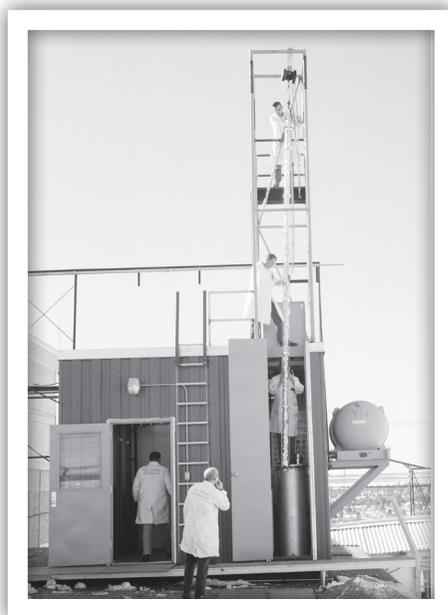
Photos from 1969 (above) and 1971 (below) show an ICONS distillation column at DP Site. The column went into a 100-foot-deep hole.

cylinder perhaps 20 feet high and several inches in diameter, which was cooled on the outside and heated on the central axis with a hot wire or rod.

Hydrogen containing some level of tritium was then fed to the thermal diffusion apparatus. The gases in the annular space circulate under natural convection, and then at the top and bottom you pull off streams—one of which would be tritium-rich. B. B. was very successful in developing working systems to produce large amounts of high-purity tritium.

The ICONS Program

I can talk with more authority about the early days of the stable isotope separation program, which developed into the ICONS program. (ICONS stands for Isotopes of Carbon, Oxygen, and Nitrogen.) Los Alamos operated various ICON columns from the late 1960s through 1989 when the technology was transferred to industry. The impetus for much of the early work of the stable isotope program, dating back to around 1960, was nuclear magnetic resonance research. In particular, there was great interest in getting quantities of oxygen-17 at a significant isotopic enrichment. The natural abundance of O-17 is about .04 percent, so anything would be a lot better than that. I believe that B. B. initially used gaseous thermal diffusion of O_2 to get fairly decent enrichments of O-17.

To improve upon the limited capacity of thermal diffusion and to get higher O-17 enrichments, B. B. tried cryogenic distillation of oxygen. While working with oxygen distillation, he learned that low-temperature distillation of nitric oxide had a much greater isotope effect in separating nitrogen and oxygen isotopes. And when I say low-temperature nitric oxide—its normal boiling point is about 120 Kelvin—we're down near to liquid nitrogen cryogenic temperature range. B. B., Joe Montoya, Bob Potter, and others designed, built, and operated a number of distillation columns containing nitric oxide. These were out at DP Site, and some of those original columns that were built there were about 20 to 30 feet long.

Expanding interest in carbon isotopes

Initially the incentive for distilling nitric oxide was to separate oxygen isotopes (O-17 and O-18) for research purposes. There was not much interest in nitrogen isotopes until it was learned that they were available in significant amounts at reasonable prices, and then a number of agricultural research programs began using enriched nitrogen-15. Eventually it came to pass that there was a great interest in carbon isotopes.

Nick Matwiyoff was one of the main leaders of the thrust in promoting the need for carbon isotopes for metabolic studies and labeling of many biochemicals. Thus in the late 1960s, while there were several columns being used to separate nitrogen and oxygen isotopes, B. B. and others started designing and building carbon monoxide distillation columns.

The isotope separation effect for carbon-13 versus carbon-12 in carbon monoxide in a single-equilibrium stage is about 1 percent. Compare this to the

effects for nitrogen and oxygen isotopes in nitric oxide (2.7 percent and 3.6 percent, respectively), and you need significantly longer columns for CO distillation. To house these columns, B. B. built a casing and vacuum jacket 145 feet long, which went through the alternate (deputy) group leader's office at TA-21. Eventually at least six distillation columns were operating inside this vacuum jacket. Many old-timers may recall seeing the small blue room that housed the control room on the roof of the single story CNC-4 labs at DP-West.

There were all kinds of comments suggesting that the alternate group leader move his desk a little bit away from the side of the room that the column was passing through, just in case something were to happen. Several years later, during the investigation of an explosion, we found that nitric oxide in a condensed state—liquid or solid—was a shock-sensitive high explosive. Not a real good explosive as far as weapons-type purposes, but a real bad one for research and operations. We changed our ways of living after that, and we shut down the columns through the deputy group leader's office.

Although our group was not particularly weapons-related, at least following the tritium days, the fact that we were part of a weapons laboratory, an explosives laboratory, allowed us to keep the operation going. When we found out that the nitric oxide was inherently explosive, we thought, "My gosh, how can we operate?" After consultation, some explosives people designed barricades for us to place around the columns at TA-46. The barricade tops were blast mats— temporary landing mats for airplanes in World War II—and the walls were four inches thick of steel and vermiculite. Our process could not have been allowed to continue without this protection.

Longest distillation columns in the world

B. B. was very active in promoting the isotope separation project and expanding the capabilities, increasing numbers of columns and larger production capacities. Under B. B.'s direction from the 1960s to the 1980s, the group built many new columns. Included were very large CO columns (up to 700 feet long) as well as NO columns at TA-46. We were proud of the extreme lengths (pun intended) that these columns went to, and we made the claim that we had built the longest distillation columns in the world. No one ever challenged our assertion on this point.

In the meantime, B. B. gave many talks on our work and promoted our processes for isotope separation. For us to be a production operation—which we were, regrettably, too much of the time—didn't really match well with the Laboratory's mission. Our stated goals certainly were to make research materials available to users and to transfer the technology to industry. We were sufficiently successful that we put ourselves out of business in that respect, because various private enterprises used our information (and assistance) to develop their own distillation processes. All the cryogenic distillation columns were shut down in 1989.

Nick Matwiyoff was a leader in promoting the need for carbon isotopes. In this photo from 1971, Matwiyoff inserts a chlorophyll sample into a holder for NMR studies.

Over a period of three years during the early 1970s, CNC-4's Isotopes Separation section transitioned from DP Site to TA-46. This photo from 1973 shows a large distillation column under construction at TA-46.

In this photo from 1971, Bob Potter (left), Isotopes Separation section leader; Eugene Robinson (center), CNC-4 group leader; and B. B. McInteer, CNC-4 associate group leader, inspect a 720-foot-deep exploratory hole drilled at TA-46.

An eye on mass spectrometry

B. B. always kept an interest in mass spectrometry. After the TA-46 isotope columns were operating fairly routinely, he turned his focus more to applications of our products and the research that was being done with the nitrogen isotopes. There was a lot of agricultural research being done at a Tennessee Valley Authority laboratory in Muscle Shoals, Ala., and at UC Davis on nitrogen applications, fertilizer studies, and the like, and they needed a means of analyzing large amounts of samples. Samples might contain milligram quantities of isotopic nitrogen, and thousands of samples would need analysis.

B. B., along with Joe Montoya, developed an automated mass spectrometry system that would not only do the mass spectrometry but also perform the necessary chemistry to convert the samples to gaseous nitrogen. The samples would be placed in little cupules in a plastic tray. Then the tray, moved by an early version of a Hewlett-Packard plotter, would center a sample under a moveable head that would come down, evacuate the air, squirt in reagents, condense water in the sample, and eventually run the gas into the spectrometer, which would automatically analyze the isotopic enrichment. The system had a capability of doing tens of thousands of sample analyses per year automatically. This was years before such automated analyses were as common as today.

After retiring from LANL, B. B. wanted to keep active technically. He bought his own mass spectrometer and, with Joe Montoya's help, set up a similar automated analysis system at his home. B. B. has run a business for a number of years, analyzing nitrogen isotope samples from all around the world.

TOM MILLS: I WAS B. B.'S GUINEA PIG

I was one of two guinea pigs who drank a carbon-13-enriched solution of labeled (sodium?) acetate; Nick Matwiyoff was the other. The acetate was about 60-percent enriched C^{13}, I believe. The potential tests were to see how people would metabolize samples as a possible replacement a glucose tolerance test, a standard diabetes test.

I had a high concentration of C^{13} in exhaled CO_2—about 3 percent C^{13}; natural is 1 percent. At the time Matwiyoff suggested it was because I had only recently been a "starving" graduate student and my metabolism was so high.

Actually, it may have shown something real along that line. I had difficulty with low blood sugars over the years and eventually developed diabetes.

I suppose the test was invalid because I did many of the analyses; it's not proper for the guinea pig to analyze himself.
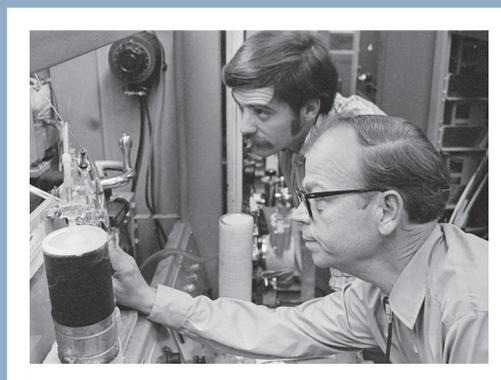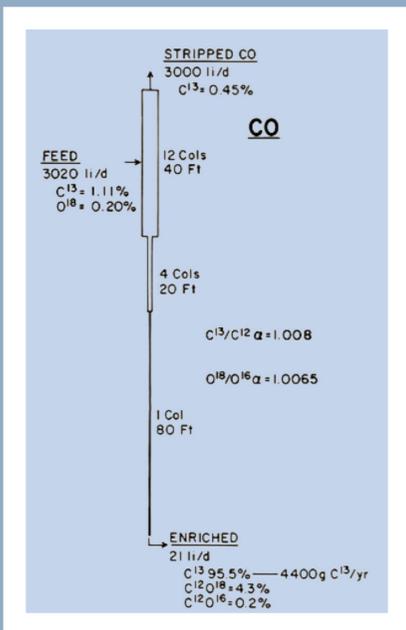

Tom Mills (left) and B. B. McInteer analyze breath samples using a mass spectrometer to determine carbon-13 content. This photo accompanied an article in the March 1973 The Atom *about a clinical trial of using breath, not blood, analysis for detecting diabetes.*
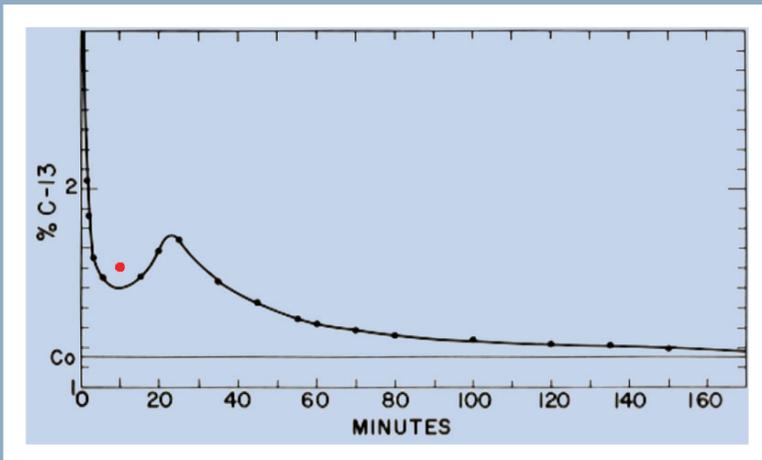
B. B. AND THE BURP

AS RECOUNTED BY CLIFF UNKEFER,
GROUP LEADER OF BIOENERGY AND ENVIRONMENTAL SCIENCE

Above: A typical cryogenic distillation system as developed by B. B. McInteer. Below: The data plot from the carbonated water experiment. The red dot is the burp.

Editor's note: Cliff Unkefer of Bioscience Division discussed a 1971 Atomic Energy Commission (AEC) seminar on the use of stable isotopes in clinical pharmacology held at the University of Chicago at which CNC-4 group leader Eugene Robinson and B. B. McInteer spoke.

The first paragraph of Gene Robinson's talk rings true to me because we still talk about it years later: "One thing that we at Los Alamos have discovered about isotopes is that if they are essentially free, or cheap, people will do experiments with them. If isotopes are kept at high prices, you may buy a gram at $1,000.00, but it sits on the shelf waiting for the definitive experiment, and no real use is made of it. Stable isotopes are now being produced at the Los Alamos Scientific Laboratory due to the efforts of Dr. B. B. McInteer and his associates. The techniques they use involve cryogenic distillation of liquid carbon monoxide and liquid nitric oxide."

Gene credited B. B. with the actual building of the columns at TA-21. They went from almost no carbon-13 produced per year to 4 kilograms per year.

B. B. didn't talk about isotope separation; instead he discussed an experiment he did on breath tests with mass spectrometers. He was never a man of many words; his paper is a page and a half describing his experiment, but real precision: "The drinking water was carbonated with 45 psi of carbon dioxide at 10 ºC. 100 mls contained 1.34 grams of CO_2 which corresponded to 0.35 grams of isotope ^{13}C."

McInteer's analysis reads in part: "Although the purpose of this experiment does not presume to include interpretation of the physiological process which are involved in the fate of CO_2 in seltzer water, several details seem obvious. The initial high value dropping rapidly is due to the enriched CO_2 entering the lungs directly during the time of drinking the sample. This highly carbonated solution is quite bubbly. The normal ventilation of the lungs dilutes this initial dose rapidly (about one minute time constant). The odd point at ten minutes is a burp. …"

LLEWELLYN JONES AND SPECTROSCOPY

BY ROBERT RYAN AND ROBIN McDOWELL

Authors' note: Because we both were drawn to Los Alamos by Llewellyn Jones' high visibility and excellent reputation outside of the Laboratory and spent a good portion of our careers working with him, we are pleased to have an opportunity to comment on his career. What follows is based loosely on the presentation given by Bob Ryan, which addressed the history of the group originally led by Eugene (Robbie) Robinson and later by Bob Penneman, who had served as the group's deputy for several years. This group will be referred to as INC-4, although it has had several other titles—CMF-4 and CNC-4—over the years.

We would like to acknowledge the input of Dale Breshears, who gave a detailed account of Rod's contributions to the MLIS program, and to the importance of the INC-4 effort in the early stages of that work; Ken Hedberg, who provided access to the literature at OSU; and Joe Nibler, a well-known spectroscopist at OSU who is well qualified to comment on Lew's career. Also of value were the comments of Bob [Penneman], Lew [Jones], and Greg Kubas as well as Dave Moody and Harvey Wasserman, former members and important contributors to the group.

Lew Jones received his Ph.D. from the California Institute of Technology in 1950, studying vibrational spectroscopy under Richard Badger, a towering figure in the field. His thesis was titled "Infrared Studies of Hydrogen Bonding of Methanol with Aromatic Hydrocarbons." The chemistry department at Caltech was a crucible for the development of structural techniques and for progress in new bonding concepts, bringing an enhanced understanding to molecular structure and its relationship to chemical reactivity. The department was chaired by Linus Pauling, who was awarded the 1954 Nobel Prize in chemistry for his work in the area of chemical structure and bonding.

In 1951 Lew came to Los Alamos and joined the group that was to become INC-4, which was then lead by Eugene Robinson; he remained there, was made a Laboratory Fellow in 1983, and retired in 1987.

During his career he used molecular spectroscopy techniques in pursuit of detailed determinations of force fields in small molecular species and their relationship to bonding principles much in the Caltech tradition. His work is described in more than 180 peer-reviewed papers published in the some of the most prestigious chemistry journals. His book, Inorganic Vibrational Spectroscopy, published in 1971, summarizes his earlier work and is a classic; it frequently provides the basis for lectures and has been required reading for university students studying structural chemistry as well as serving as a research resource.

Lew's research program was of the highest quality in terms of the care with which it was carried out and with respect to its implications for emerging concepts in chemical bonding, and it earned him an international reputation. He attracted the collaboration of many colleagues from throughout the chemical community. In addition his work drew several postdoctoral students, some of whom stayed in the group and were instrumental in defining the future of that section of the group, which continued research on structure, bonding, and reactivity. Clearly for the purpose of this conference, which celebrates the INC-4 group, Lew's presence has had a profound impact and this is the theme we will attempt to develop here.

Although much of his work was very much his own and was published without coauthors, the remainder can be roughly divided into five sections based on his coauthors and the role they played in defining the character of the vibrational spectroscopy effort or the future development of the group. These five coauthors are presented in the following table along with the span of their interaction with Lew and the number of publications coauthored:

	Period	Papers
Penneman	1953–1956	12
McDowell	1959–1978	14
Ryan	1967–1978	9
Swanson	1970–1991	44
Kubas	1974	2

Bob Penneman, who followed Eugene Robinson as group leader and whose leadership was key to the success of the group, was Lew's most frequent coauthor in his early years at Los Alamos. Rod McDowell developed an excellent vibrational spectroscopy program in the group, which was independent of Lew's effort, and later played a key role in major Los Alamos programmatic efforts. His efforts resulted in his appointment as a Laboratory Fellow. Bob Ryan developed a program in structural chemistry based primarily on diffraction techniques, which became a key part of the group's effort.

Basil Swanson also developed an independent and productive spectroscopy program, which led to his appointment as a Laboratory Fellow and to key leadership roles in the laboratory's chemistry programs. Basil was a coauthor on 44 of Lew's last 81 papers and their relationship spanned 21 years.

Greg Kubas came to Los Alamos to work with Lew, but his interest in preparative chemistry led him to develop an independent effort in that area, which has been recognized as one of the finest chemistry programs in the country. He also retired as a Laboratory Fellow. Kubas spoke at the seminar on "The Colors of Discovery." His article begins on page 30.

Lew Jones, 1962

Bob Penneman and Lew Jones

The first paper coauthored by Bob Penneman and Lew was published in the Journal of Chemical Physics in 1953 and addressed the infrared spectra of uranyl and the transuranium(V) and (VI) ions of neptunium, plutonium, and americium in aqueous solution. This study established that the U(VI), Np(VI), Pu(VI), and Am(VI) ions exist as symmetric and linear or nearly linear, XO_2^{++} moieties. For the series, the X–O force constant was expressed as a parabolic function of atomic number, exhibiting a maximum at NpO_2^{++}. This result is contrary to the behavior expected if there were a regular contraction in ionic radii for the series XO_2^{++}.

They revisited the subject in a 1955 Journal of the American Chemical Society article in which the infrared (IR) spectra of the series were observed in the solid phase. The U–O, Np–O, Pu–O, and Am–O force constants were determined to be 0.705, 0.698, 0.675, and 0.612 megadyne/centimeter, respectively. The cell constants showed that the bond distances decrease in the same order.

They concluded that a decrease in bond distance appears to be accompanied by a decrease in force constant, probably because the bond, though shortened by contraction of the electron shells of the metal, is weakened by interaction with
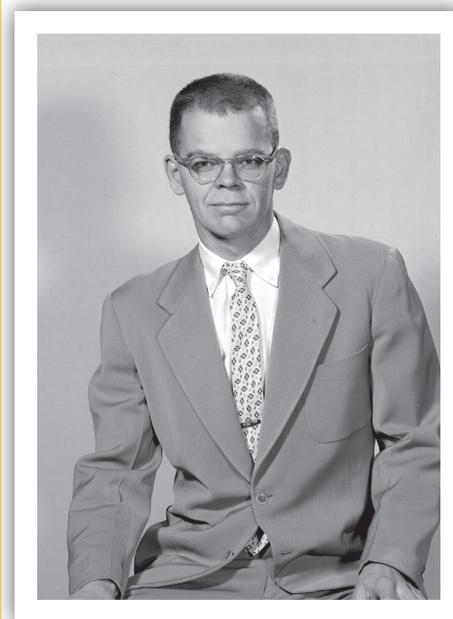
the extra-valence shell electrons. These two papers have been cited more than 200 times in the literature and are still cited today after more than 50 years.

A more extensive collaboration between Bob and Lew began in 1954 with the publication of a paper in the Journal of Chemical Physics on the cyanide complexes of silver and of gold in aqueous solution and absorbed on an anion resin. Their collaboration on cyanide complexes produced a total of eight publications and ended with a paper in Inorganic Chemistry, "Mixed-ligand complexes in mercury(II)-cyanide-iodide solutions: a Raman and ultraviolet study." Lew published more than 40 papers in the field of metal cyanide complexes during the early days of his career at Los Alamos, usually as the sole author.

Study of the metal complexes was an emerging field during the period of Lew's interest. The issue of whether the cyanide ion was bound to the metal through the carbon or nitrogen atom was not firmly established until 1959, when it was determined by neutron diffraction. The Los Alamos program provided major advances in the understanding of structure, bonding and reactivity issues in this area of research. As with the actinyl series mentioned above, this work has enjoyed an impressive citation rate over the years and remains of interest today.

We observe that Lew collaborated on research issues with other investigators who are considered to be giants in the field of chemistry; his publications include coauthors such as John C. Bailar, University of Illinois; Harry B. Gray, California Institute of Technology; and Ronald S. Nyholm, University College, London. Nyholm, properly addressed as Sir Ronald, was a famed inorganic chemist who was created Knight Bachelor for his services to science.

When asked how such an interaction came about, Bob Penneman, also a coauthor, provided an amusing anecdote. When presenting the results of an

The November 1969 issue of **The Atom** *magazine reported on a visit by British chemist Sir Ronald Nyholm to CMF-4. The caption read: Nick Matwiyoff, seated, discussed a nuclear magnetic resonance experiment with visitor Sir Ronald Nyholm, left, president, British Chemical Society, who recently toured CMF-4 laboratories with Group Leader Eugene Robinson, right, and Robert Penneman, center, alternate group leader. Professor Nyholm, who is also chairman of the chemistry department, University College, London, spoke at a CMF-4 Seminar on "Some Aspects of Modern Inorganic Chemistry."*
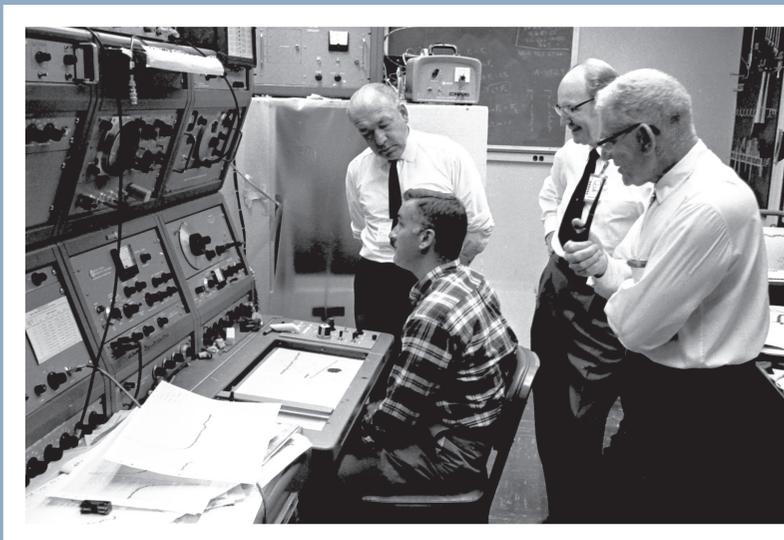
A Letter from Linus Pauling

It's worth noting that in the early years of his career, Lew maintained an active correspondence with Linus Pauling. Indeed, in a 1956 letter in support of Lew, Pauling stated in part:

"There's no doubt in my mind that Dr. Jones is a first-rate young scientist. The work he carried out here was of high quality. It was of my opinion that he was an excellent graduate student, included in the class of the best of our graduate students. Since he left Pasadena, he has published a number of papers. I've read many of these papers and have been impressed with the breadth of his interests and his effectiveness in solving the varied problems that he has attacked. Those of his papers that I have studied carefully have provided evidence of his unusual ability to carry out research."

Full copies of these documents are available at: http://pauling.library.orst.edu.

infrared study of pentacyano-, hexacyano-, and chloropentacyano-nickelate(II) in aqueous solution, at a meeting of the American Chemical Society, Bob was followed on the agenda by Nyholm, who rose, walked to the podium, simply stated that he could add nothing to the previous talk, and returned to his seat. They later decided that a joint publication was appropriate; it appeared in the Journal of the Chemical Society (1963). Shortly thereafter Nyholm visited our group in Los Alamos, presented a seminar, and spent the remainder of the day in discussions with individual investigators.

The role of Bob Penneman in determining the nature of the group during this period and later during his tenure as group leader can't be overemphasized. He had the ability to attract talented people to the group, he strongly supported them, and he fostered an outstanding esprit de corps. The result was a group of a dozen or so disparate (not desperate) individuals with a wide range of research interests who nevertheless worked as a cohesive whole and provided the Lab with broad capabilities in actinide chemistry and chemical structure and dynamics.

Rod McDowell's personal recollections

My thesis advisor at MIT was Richard C. Lord, in his day a prominent molecular spectroscopist and coauthor of "Practical Spectroscopy" (1948), the standard text. In the spring of 1957 I had just joined Lord's group, and when he heard that I was applying for a summer job at Los Alamos, he suggested that I should work with Lew Jones, for whom he had the greatest respect. Lord offered to write the Lab on my behalf; the employment office was accommodating and placed me in Bob Penneman's section of group CMF-4, at the old DP West site. This was to have a profound effect on my eventual career.
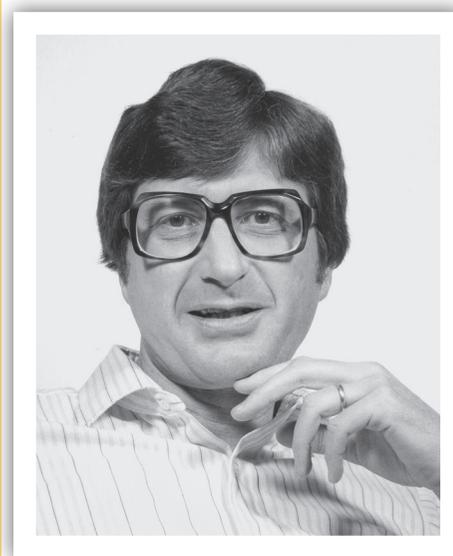
Rod McDowell, 1983
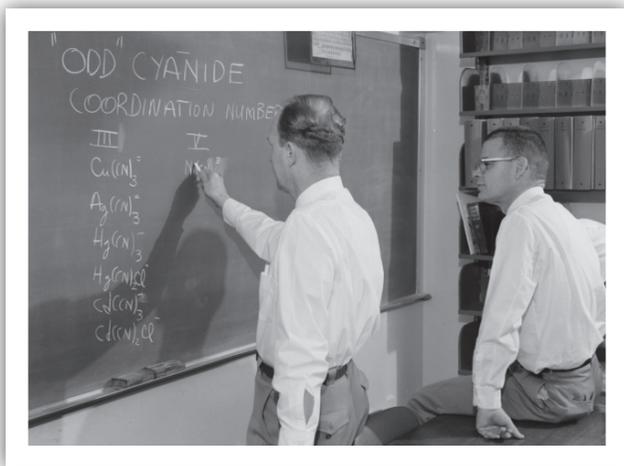
Bob Penneman (left) and Lew Jones discuss odd cyanide chemistry coordination numbers. Penneman says that at the time the photo was taken in 1962 "too many [people] believed strongly that only even coordination numbers were possible. We disabused them of that idea."

Lew was running an ambitious research program on the spectroscopy of complex ions in the solid phase, especially metal cyanides and uranyl complexes, low-temperature spectroscopy of condensed phases and matrix-isolated species, and infrared studies of equilibria in aqueous solutions. Much of this was in support of CMF-4's emphasis on actinide chemistry, but he was also interested in the high-resolution rovibrational spectroscopy of gaseous molecules, especially small tritium-substituted species such as TI, T_2O, and CT_4, in collaboration with the physics department at Ohio State University, which had several large vacuum grating spectrometers. (High resolution then meant, rather quaintly by modern standards, about 0.1 cm–1—that was about the best available anywhere in the world.)

Bob Penneman provided excellent support for Lew, whose lab included a Cary Model 14 ultraviolet-visible, near-infrared spectrophotometer and four prism and grating Perkin–Elmer instruments covering the infrared out to 200 microns and beyond, approaching the microwave region. In the 1960s he acquired a Cary Model 81 Raman instrument with, at first, a Toronto-arc source, soon upgraded to a He–Ne laser, and a Beckman IR-11 for the far infrared. This was a cutting-edge facility and the equipment surpassed that available almost anywhere in the country.

Lew always gave generously of his time, and if he was at first disappointed in my relative inexperience at molecular spectroscopy, he graciously concealed the fact. My education in the field owes almost as much to him as to my formal MIT courses and tutelage under Lord. In the summer of 1957 he, Hobie Kruse, and I gathered several times a week to discuss the Wilson–Decius–Cross F–G matrix method for force constant calculations. Lew provided the insight, Hobie wrote a program to do the calculations, and I learned a lot. I was obtaining spectra of deuterium- and tritium-substituted methanes, and that work eventually led to a long article by Lew and myself in the then-recently founded Journal of Molecular Spectroscopy on the force constants of methane, my first scientific paper (1959). This work benefited greatly from our access to tritium, not generally available, and that paper attracted some attention and was cited frequently for many years.

Finishing up at MIT, I jumped at the chance to join CMF-4 as a staff member in 1960. This decision was based partly on the scientific challenge; after two summers at Los Alamos I had developed great respect for Lew's scientific ability and integrity, and I'm sure picked up some of his work ethic. And part was the camaraderie and mutual support of the staff—it was a good group of people, and the interactions were rewarding quite apart from scientific collaborations. Even as a summer student, I had been made to feel part of the group, and those friendships influenced my decision. Friday evenings around 4:30 often found Larry Asprey, Jim Coleman, Tom Keenan, Hobie Kruse, Bob Penneman, Lew, and myself at the Legion or VFW, relaxing over beers and

discussing science, politics, and whatever else came to mind; there were often ad hoc parties during World Series games; there was the occasional hunting trip; and the annual CMF-4 Open at the golf course became legendary.

Lew's reputation was growing—I became aware of this at the first professional meetings I attended, when I realized that saying that I was at Los Alamos with Lew Jones immediately earned me some respect. The 1960s and '70s saw a series of summer students and postdocs, all of whom benefited from their interaction with him and many of whom went on to productive careers in spectroscopy. (The fact that one of these individuals soon abandoned science for Scientology was no doubt an aberration.)

Most importantly, some of these visitors decided, as had I, that this group was a great place to work. Bob Ryan arrived in 1966, bringing with him some computer programs that greatly facilitated our interpretation of the spectra; he became a major contributor to the group, and eventually group leader. Basil Swanson was a postdoc in 1970–71, and returned ten years later to collaborate extensively with Lew; he also became group leader. Greg Kubas arrived as a postdoc in 1972 and made his own mark at the Lab. By this time the spectroscopy program had so expanded that a larger facility was needed, and a new laboratory was built, replacing the rather cramped older quarters. In 1971 Lew published Inorganic Vibrational Spectroscopy, cementing his reputation as one of the authorities in the field.

After I joined CMF-4 I worked closely with Lew for a number of years. Of course, I began to develop my own research interests, as always happens, but our interaction was a fruitful one and resulted in some dozen papers from 1961 to 1976. Seven of these involved the spectroscopy, force constants, and bonding considerations for metal carbonyls, interesting compounds because they provide a way of getting recalcitrant metals into the vapor phase at room temperature. We studied $Ni(CO)_4$, $Fe(CO)_5$, the metal hexacarbonyls, and some mixed carbonyl–nitrosyl complexes, and these papers are still cited regularly.

The spectroscopy facility that Lew pioneered was a remarkable asset to the Lab. In addition to the instruments themselves, which represented top-of-the-line commercial instrumentation, there was our ability to work with highly reactive chemicals and radioactive materials from tritium to the actinides; the ready availability of nearly pure ^{13}C and ^{18}O provided by B. B. McInteer's isotope separation columns; and, perhaps most importantly, the combined experience developed from many man-years of dealing with the applications of spectroscopic techniques.

It was a rare month in which we didn't have a visitor from some other Lab group with a particular need for a spectrum or analysis, and in several cases we were deeply involved in large Laboratory programs. One of these was Operation Dominic in the summer of 1962, the last series of atmospheric nuclear tests.

Bob Penneman (left) and Lew Jones analyze data with what was a state-of-the art spectrometer at the time in 1962. Gary Eller remembers the drum when he came to Los Alamos in 1974 and thought: "What museum did that come from?"
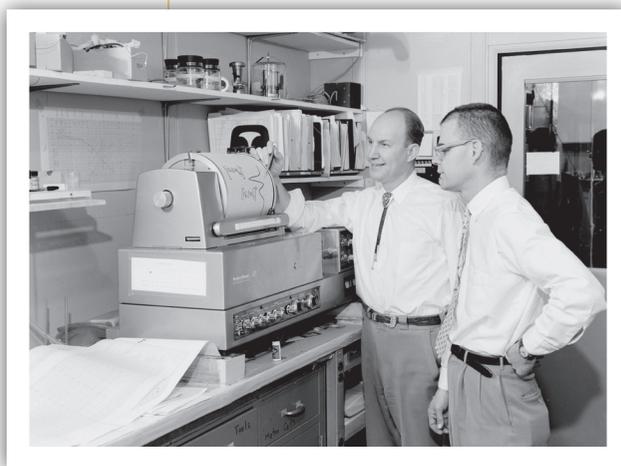
Starfish Prime as seen from Honolulu.
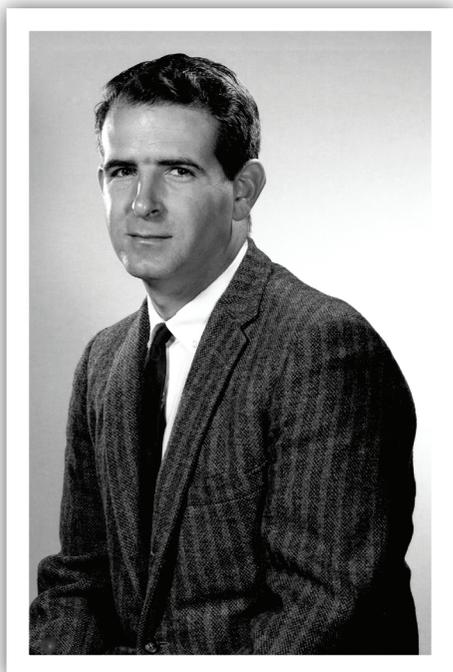
Temporarily assigned to Herman Hoerlin's high-altitude phenomenology group (J-10), I took a CMF-4 spectroscope to the Los Alamos station at the summit of Haleakala on Maui, where it recorded photographic spectra of the Starfish Prime shot, detonated 250 miles above Johnston Atoll with a yield of 1.45 megatons.

The molecular laser isotope separation (MLIS) program for uranium enrichment (Project Jumper), begun in 1972, also relied heavily at first on the facilities at DP West. Lew had equipment for and experience with matrix-isolation spectroscopy, and he, Larry Asprey, Sherm Rabideau, Bob Paine, and I collaborated on the vibrational and electronic spectra of matrix-isolated UF_6, though most of this work wasn't published for several years because of classification concerns. Meanwhile Larry, Bob, and I were recording the gas-phase spectra of UF_6. This early work established the ^{235}U–^{238}U isotope shift, which was of great interest for the isotope separation process. At about this time there was a reorganization, with Larry and I attached to a Laser Chemistry group (CNC-3) under the capable direction of Dale Breshears.

In 1976, attracted by the possibilities of the newly developed tunable-diode lasers (TDLs) that were being used in Paul Robinson's Applied Photochemistry Division, and which suddenly increased achievable resolution in the infrared by several orders of magnitude, I transferred to their facilities at TA-46 and rather reluctantly left DP West after sixteen years.

Most of my later work was with TDL spectroscopy of UF_6 and other hexafluoride molecules, but I sometimes needed broader spectral coverage than the lasers could provide, and I called on Lew well into the late 1980s, near the time of his retirement. By that time he was using the latest high-performance Bomem Fourier-transform infrared instrument, capable of 0.0025 cm–1 resolution, but he himself hadn't changed: cordial, cooperative, careful, thoroughly knowledgeable, and altogether a pleasure to work with.

Bob Ryan's personal recollections

I was finishing my graduate studies at Oregon State University (OSU) under the guidance of Ken Hedberg (also a Caltech graduate student during Lew's graduate days) when, as a result of a conversation with a recruiter from Los Alamos, I received a phone call from Lew inviting me on an interview trip to Los Alamos. Ken and his colleague Jack Decius, a very well known vibrational spectroscopist, both knew of Lew's outstanding reputation and strongly encouraged me to follow up on the opportunity.

I spent an exciting day with Lew and Bob Penneman and enjoyed conversations with Lew that lasted into the wee hours of the following morning, and I later accepted an offer to join the group as a post-doctoral appointee. I came to Los Alamos via a one-year detour to the Eidgenössische Technische Hochschule in Zurich, where I studied X-ray crystallography under Jack Dunitz.

When I arrived at Los Alamos I happily found myself immersed in a group of researchers whose capabilities exceeded the high expectations that I had developed on the basis of my interview trip. The group enjoyed a high level of

Bob Ryan, 1967

esprit de corps fueled by constant scientific exchanges as well as regular social interactions. Many of the group personnel shared my enthusiasm for outdoor activities and I count among my fondest memories several hiking experiences in the Pecos Wilderness, the San Juan Mountains, and elsewhere as well hunting, fishing, or rafting trips, etc. Many of these adventures were with Lew and/or Bob and indeed, interesting discussions of group research often took place around wilderness campfires.

My initial efforts were directed to the accurate determination of force fields in the series of molecules ONX where X is a fluorine, chlorine, or bromine atom. The spectroscopic data were measured using the isotopes of nitrogen and oxygen then available in the group. In the Jones tradition, the force fields determined from these studies were used to evaluate various then current bonding models and the resulting publications have been frequently cited.

Bob Penneman had a very active interest at that time in the chemistry and structural characteristics of the complexes formed between actinide and alkali metal fluorides. He had synthesized a large number of compounds and had made remarkably clever deductions concerning their structures based on powder diffraction results, optical properties and density measurements, etc., but he had done no single-crystal diffraction. Because that was a skill that I had learned in Zurich, Bob and I formed a productive collaborative relationship. After only a few months with Lew I was offered the position of staff crystallographer, which I accepted without hesitation.

As in Rod's case, although I was deeply engaged in developing an independent program, I remained interested in Lew's fascinating program and we did manage to maintain a scientific relationship long after that first year.

Looking back there is one collaboration that I find especially gratifying: Lew had developed a way of examining intramolecular interactions in terms of values that he called "interaction coordinates." These values were determined

Bob Ryan remembers interesting discussions around wilderness campfires. This photo from 1961 shows Larry Asprey (in red) and Lew Jones. The elk hunt was unsuccessful, according to Rod McDowell.

ANDY SHREVE: PATH-BREAKING SPECTROSCOPIC MEASUREMENTS

I came to the Lab as a spectroscopist and some of the people who are speaking at this conference are a large part of what attracted me. I had been reading their papers for years and had seen beautiful work coming from Los Alamos. Little did I know from the outside what kinds of facilities actually existed here for spectroscopy. One of the first discussions I had when looking at the large-frame argon ion lasers at TA-21 was one in which the word "hot" was used with "chilled water" in a way I had never encountered before. I relate this in part to give context to the truly beautiful and path-breaking spectroscopic measurements that have been made at Los Alamos. It's a great honor to follow in those footsteps.

Editor's note: Andrew Shreve came to Los Alamos in 1994 as a J. Robert Oppenheimer Fellow. He is currently a thrust leader for Soft Biological & Composite Nanomaterials in the Center for Integrated Nanotechnologies.

BOB LONDON: A MARVELOUS ENVIRONMENT

The people being honored during this conference created—as virtually everyone has said to this point—a marvelous environment at Los Alamos that favored all kinds of interactions. They saw themselves as facilitators and as creators of opportunities.

When I came to Los Alamos there was a Fourier transform nuclear magnetic resonance (FTNMR) spectrometer that was operating; this was at a time when there were not yet any commercially available FTNMRs, so we essentially cornered the isotope market—we had all the isotopes in the world. And there was also a group in H Division that was involved in synthesizing useful biological compounds from the labeled precursors.

So really, I couldn't imagine a more ideal situation in which to begin doing research.

Editor's note: Robert London served as principal investigator of the National Stable Isotope Resource at Los Alamos before joining the National Institute of Environmental Health Sciences—National Institutes of Health in 1983. He currently is the principal investigator with the Nuclear Magnetic Resonance Group.

by perturbing and constraining one coordinate while minimizing the overall potential energy of the molecule. The interaction coordinate, $(l)k$, is calculated by dividing the resulting increments in each molecular coordinate by the increment in the constrained coordinate. In the force constant language this is stated as $(l)k = \{Flk\}/\{Fkk\}$ where $\{Flk\}$ is a co-factor in the force constant matrix and is a long messy algebraic formula for even moderately sized molecules.

Jack Decius at OSU was an avid proponent of using compliance constants to describe the quadratic potential function of polyatomic molecules in place of the then common force constant language (the compliance matrix is merely the inverse of the force constant matrix). I brought to Los Alamos an elegant piece of software that had been developed at the Shell Development Co. and modified at OSU to use the compliance language. Lew quickly embraced the compliance approach and determined that his interaction coordinates could be expressed in terms of compliance constants as $(l)k = Clk/Ckk$ where Clk is now just a single element of the compliance matrix. This advance facilitates one's ability to understand intramolecular interactions and to develop related bonding concepts.

Indeed, in the publication reporting this result Lew pointed out that the calculation of interaction constants from molecular orbital calculations is straightforward and that his result would greatly simplify the determination of quadratic potential constants from these calculations. Clearly this is a suggestion that is followed frequently in the modern literature. Lew did a lot to help me develop my career and I'm happy to be able to point to something that I did of lasting value to him.

Those of us who had the good fortune to be drawn to Lew's excellent program will always remember him as an outstanding researcher and mentor and will harbor deep feelings of gratitude to him for the introduction we had on to how one meets the standards for doing quality research.

We note also that this gathering, in large part in his honor, makes it clear that Lew has had an enormous impact on the future of chemistry at Los Alamos. (The presentation concluded with a long thunderous standing ovation in recognition of Lew's accomplishments.)

LARRY ASPREY AND ACTINIDE FLUORINE CHEMISTRY

A RETROSPECTIVE BY P. GARY ELLER

There were many times in my 30 years at Los Alamos when I'd drive to work and think: What a great country, to come from where I was born and raised [rural West Virginia], and to work at this place with people like Bob Penneman, Larry Asprey, and Lew Jones. I was in the last generation that was able to work with the Manhattan pioneers on a mentoring basis. They taught me a lot, not just about chemistry, but also about life in general.

These were really exceptional people; they were quantitatively and qualitatively different. Marge Asprey, Larry's wife, fits that category, too. They are very modest about their accomplishments. What Marge didn't tell you was that in addition to supporting Larry and raising seven wonderful human beings, she got a degree in education and an advanced degree in nuclear engineering. And late in her career [in 2005], the American Nuclear Society recognized her accomplishments with the Walter H. Zinn Award, one of its most prestigious awards.

An anecdote: Larry worked for the Campbell Soup Co. from 1939 to 1942. Nobody seems to know exactly what he did in that period of time, but his family says that after that experience he was never able to eat soup again in his entire life.

The chemist's chemist

Larry was the chemist's chemist. He could do it all as a preparative chemist. When he worked in Glenn Seaborg's laboratory at the Chicago Met Lab, the purpose was to develop separations processes to recover plutonium-239 produced at the Hanford reactors. The chemistry of plutonium was unknown at the time, so they first had to establish that chemistry. He did a lot of wet chemistry and separations chemistry—pioneering work. Larry was a first-rate solid-state chemist, as well. Eventually he became a world-class authority in fluorine chemistry—self-taught, of course. He could do it all. My hat's off to him; few people can cover the waterfront like that in that way.

Larry, working with H. H. Anderson, was issued his first patent in 1947 based on work at the Met Lab on plutonium extraction with tributyl phosphate (TBP). This is an amazing piece of Larry's career; they basically developed the basis for the PUREX process. [PUREX = Plutonium Uranium Extraction. It is the standard aqueous reprocessing method used to recover plutonium and uranium from spent nuclear fuel.] TBP had been used for other separations before that and they adapted it to plutonium. The heart of the process is that TBP forms in high-acid concentrations—high-nitric acid, a neutral plutonium complex that's extractable into organics. Uranium(VI) also has that property. An
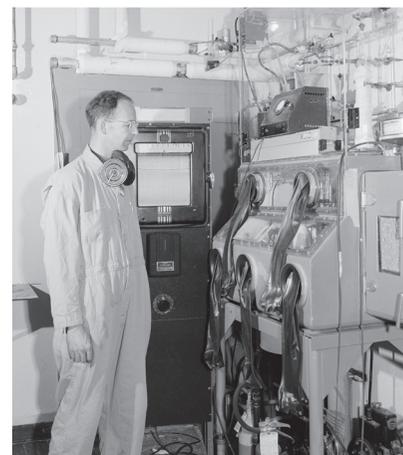
Larry Asprey at a glovebox at DP Site, 1953.
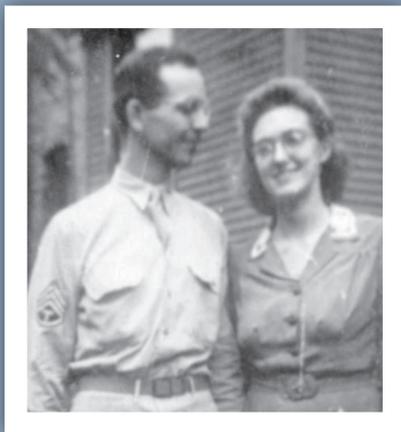
Larry and Marge Asprey, 1944.

Marge Asprey and Bob Penneman at the conference.

Marge Asprey: Larry's Early Years

When the war started he tried to volunteer for the Army as an officer because he had a degree, but his eyes weren't good enough; they wouldn't have him. So he was drafted. The Army sent Larry to Fort Warren, Wyo., where he was assigned to the office and told to set up the files for the fort. He told them he didn't know anything about filing, and asked if they have any books on the subject. "Nope," came the reply, "make it up." You can imagine what it was like for the people who came after him trying to find anything, where Larry made it up.

When the Army's Specialized Training Program (ASTP) was started he immediately signed up for it and got away; he didn't like office work. In the summer of 1943 he was sent to Ohio State at Columbus for the fall semester and he took some graduate classes in chemistry. In January 1944 he got new orders; he and some others were to go to Chicago. He was told he would be working on a highly secret project; it was not even supposed to be known that the Army was related to this.

Less than three weeks later, in February 1944, he and I met—I was also working on the project—and on May 3, 1944, we were married. Larry was released from Army in February 1946 and we went out to Berkeley, where he worked at Berkeley Lab. He received his Ph.D. in 1949 under Burris Cunningham. In 1949, once some houses were built, we came to Los Alamos.

Editor's note: Marge Asprey, the widow of honoree Larry Asprey, is a retired nuclear engineer who worked at Los Alamos for almost twenty years. She was the second woman ever awarded the American Nuclear Society's Walter Zinn Award.

adjustment of either valence or acidity allows the plutonium or uranium to be stripped out selectively.

Plutonium chemistry was basically developed at the Met Lab during World War II; americium came next. In his doctoral work at the University of California–Berkeley with B. B. Cunningham [a noted experimentalist], Larry separated the first pure americium compound, so it was natural for him to slide into the group that Bob Penneman was in at Los Alamos. They had an ample supply of americium coming from the Clementine reactor and from dregs that came from Hanford.

The group was involved in several firsts, including the first gram-scale separation of americium, in which Tom Keenan also was involved, at TA-21; the first americium(IV) compounds; the first observation of americium(V) disproportionation; measurement of the (III)/(IV) potential; identification of

americium(II); and the first recognition that americium metal has an unusual volatility, which has a tremendous practical implications for plutonium processing. They did the first distillation of americium metal and proved the linearity of $AmO_2{}^{2+}$. This basically constitutes the development of fundamental americium chemistry. That alone would have been an outstanding career, right? But there was much more to come.

An emphasis on publications

Another remarkable thing about that group—and Bob Penneman had a lot of responsibility for this—was the recognition of the need to get scientists out of their comfort zones and interacting with other scientists, not just in the United States, but globally. And so there was always an emphasis on publication.

One of the first publications that I could find from the TA-21 group was "Observation of Hexavalent Americium," by Larry [Asprey], S. E. Stephanou, and Bob [Penneman], published in the *Journal of the American Chemistry Society* in December 1951. This paper described the first oxidation of americium(III) directly to americyl—americium(VI)—by several means including use of peroxydisulfate. Larry and Bob each published about 150 peer-reviewed papers, and their names are so intermingled it's hard to separate one career at Los Alamos from the other.

In the 1960s the group's work included a lot of the fundamental chemistry of the actinide elements and a lot of really good structural and carbonate work.

WOODY WOODRUFF: A PAPER FROM 1969 STUCK WITH HIM

My indirect relationship with INC-4 goes back to when I was a graduate student at Purdue. One of the requirements of the candidacy exam was that people had to come up with an original research proposal that was actually different from what you were actually doing, and defend it. At that time I was interested in unusual oxidation states already and we had just had a lecture series from R. J. Gillespie about super-acid systems. And so my OP was to electrochemically generate high oxidation states of first-row transition metals and super-acid solvent systems.

To be able to defend that, I had to be able to come up with literature precedents for the idea that these very high oxidation states like copper(III) and (IV), nickel(IV), cobalt(IV) and (V) actually had some existence. I found maybe eight or ten papers on subjects like that, and I don't remember most of them, but for some reason the authorship of one of them has stuck with me through all these years. The paper is "The Absorption Spectrum of Potassium Hexafluoronickelate(IV)," which was published in the Journal of Molecular Spectroscopy in 1969—and the authors were Marty Reisfeld, Larry Asprey, and Bob Penneman.

This takes me back to mentoring that I had from Larry Asprey on lots of things, all of which were very interesting but some of which I really didn't want to know about. Like, I didn't know that Teflon would actually burn.

Editor's note: William "Woody" Woodruff is a Laboratory Fellow in the Inorganic, Isotope, and Actinide Chemistry group and is an external faculty member at the Santa Fe Institute.
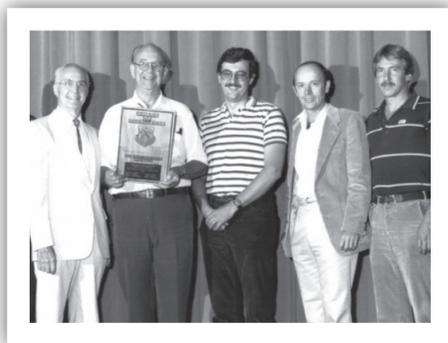
In 1986 an INC-4 team won a Weapons Recognition of Excellence Award for work on O_2F_2 (FOOF) use in PuF_6 production and recovery. From left to right are Bob Penneman, Larry Asprey, Scott Kinkead, Gary Eller, and Basil Swanson. John Malm was also on the team.

They studied tetravalent curium, berkelium, and californium compounds; transplutonium electronic spectra; protactinium fluoride compounds; transuranium carbonate chemistry; and proof of linearity of plutonyl(V).

In the 1970s the group researched actinide metal superconductivity, magnetism and structure, main-group fluorine chemistry, metal hexafluoride spectroscopy, and tetravalent and divalent lanthanide compounds. Larry became the go-to guy in the Laboratory when somebody wanted a pure actinide metal. He made them all, through berkelium. People like highly respected materials scientist Berndt Matthias associated with that group because that's where the materials could be obtained. There was a lot of work at the time on the unusual magnetic superconductivity, electronic properties, and structural properties of the actinides.

At the same time, the laser isotope programs were kicking up here, based on volatile fluorides, and so there was a tremendous amount of work published in more than 30 publications, many of which also bear Lew Jones' name with Larry Asprey's. Larry, again, was the guy who would prepare these difficult materials for the people who could characterize them.

The last part of Larry's career [Asprey retired in 1986] was focused on powerful oxidizers and dissolution agents and continuing his work with actinide metals. Larry received the Glenn T. Seaborg award the year he retired. It was long overdue, but he had this big detour from the early days of PUREX to many other accomplishments that were not directly separations oriented.

I was very privileged to learn at Larry and Bob's feet. I'm very pleased that Larry allowed me to coauthor two of his last publications. One paper has to do with neptunium chemistry ["Reactions of Dioxygen Difluroide with Neptunium Oxides and Fluorides," *Journal of Alloys and Compounds,* 1998], and the second has to do with superacid dissolutions ["Analytical Applications of Superacid Dissolution of Actinide and Lanthanide Substrates," *Journal of Radioanalytical and Nuclear Chemistry,* 1988]. And at retirement he was still finishing up work on actinide metals with people like Jean-Claude Spirlet and Joe Peterson ["Preparation and Purification of Actinide Metals," *Advances in Inorganic Chemistry,* 1987].

What inspiring legacies Larry Asprey and Bob Penneman left for those who followed!

GREG KUBAS' DISCOVERY LEADS TO A NEW FIELD OF RESEARCH

In 1984, Greg Kubas produced a seminal publication of a molecular hydrogen complex in which a sigma (σ) bonding electron pair in H_2 binds to a transition metal center in the molecule $W(CO)_3(PR_3)(H_2)$, thereby establishing a new form of chemical bonding. This unusual bonding is considered to be due to a combination of electron donation from the σ-bonding orbital of H_2 and backdonation from a suitable metal d-orbital to the H_2-antibonding orbital. The greater the contribution of either component, the more the H–H distance will increase relative to that of the H_2 molecule (0.75 angstrom). Beyond a certain point, we obtain what was once considered the "normal" extreme of a metal dihydride.

This new form of chemical bond became known as a σ-bond complex, and the molecule became widely known as the Kubas complex. Prior to this report, many in the field considered the hypothesis of M-H_2 coordination as totally absurd. Pursuit of such a theory might well have been career ending for a junior academic. At Los Alamos however, Kubas was able to forge key collaborations and make use of neutron and X-ray diffraction to provide key evidence for the side-on-bonded structure of molecular H_2 coordination, and to use nuclear magnetic resonance, vibrational spectroscopy, and electronic structure theory to characterize its unusual behavior—a combination of synthesis, spectroscopy, and theory that would later become the norm of the field.

I remember the Kubas paper well, as I was a graduate student at Indiana University at the time. Our research group discussed the paper in a group meeting, including recalculating the expected change in vibrational frequencies upon changing from H_2 to HD, performing Extended Hückel calculations, and debating why oxidative addition to form a metal dihydride (the norm at the time) did not occur in this unusual system. This same discussion and critique likely took place in academic labs across the country and around the world. This paper was certainly one of the most widely read and scrutinized research papers that year and would have a profound impact on the field.

Because of this discovery, Kubas is recognized as the founder of an entire field of research, a distinction that few others can claim. His discovery of metal complexes that bind dihydrogen molecules led to the 1993 American Chemical Society Award in Inorganic Chemistry and the 1994 E. O. Lawrence Award in Chemistry from the Department of Energy. His research on dihydrogen complexes led to new views of chemical bonding and hydrogen activation and opened new fields of chemical research on metal σ-bond complexes ranging from catalysis to metalloenzymes. In 2001, Kubas published a book entitled *Metal Dihydrogen and Sigma-Bond Complexes: Structure, Theory, and Reactivity* (Kluwer Academic/Plenum Publishers, August 1, 2001). The book quickly became the standard reference of the field.

The discovery of σ-bond complexes really established Los Alamos (and INC-4) as a marquee place to do world-class inorganic chemistry and preceded a long list of outstanding postdoctoral recruits and future leaders of the Laboratory.

—*David L. Clark, Plutonium Science Strategy Leader, Seaborg Institute*

About the author: Greg Kubas came to Los Alamos as a postdoc in 1972. He was named a Laboratory Fellow in 1987 and received the E.O. Lawrence Award in chemistry in 1994 for his discovery of molecular hydrogen complexes of transition metals and for his pioneering research on their chemical and physical properties. He is now an affiliate (retired Laboratory Fellow) in C-IIAC.

Some of these Werner complexes made by Greg Kubas are 45 years old. He was fascinated by the color change in just a slight ligand variation.

Transition-Metal Coordination and Activation of Sulfur Dioxide and Dihydrogen

The Colors of Discovery

As Recounted by Greg Kubas

INC-4 transformed me into a real professional scientist. I was what you'd call a synthesis junkie; it was almost an obsession. I'd seen pictures of the old alchemists with their retorts, so when I was in high school I got my father to get one at a local chemical supply house along with chemicals. I actually home-brewed some chromyl chloride—the volatile chromium(VI) complex is a red liquid—in my basement with no hood. It turns out it's a potent carcinogen, which I didn't realize at the time.

I loved growing crystals and all that kind of "hobby-chemistry." Werner complexes and crystals are very stable, and I still have samples that are 45 years old. I was fascinated by the color change in just a slight ligand variation; I was more interested in esthetics than real chemistry in some ways. It turned out that the often spectacularly bright colors of transition-metal complexes were a key factor in my synthetic chemistry research, particularly in the important discovery of dihydrogen complexes that I will talk about.

Lew Jones hired me in 1974 after my postdoctoral appointment to do vibrational spectroscopy and normal coordinate analysis. I worked with him for about eight months and realized that I wanted to do transition-metal chemistry, so I began doing iron–sulfur complex chemistry. Bob Penneman helped me write a proposal to the DOE (eventually the Office of Basic Energy Sciences) for sulfur dioxide (SO_2) chemistry, and I've had funding from the DOE for 35 years. The DOE funding was a real boon to my career.

Transition-metal SO₂ chemistry, 1974-1992

The idea was to scrub SO_2 from stack gases, but it evolved into more than that, including a lot of basic chemistry, and the program resulted in about 50 publications with coworkers like Dave Moody, Gary Eller, and Bob Ryan. We found that SO_2 binds to more substances and in more different ways (metal-coordination geometries) than any other molecule. It was both a strong Lewis acid and base; that was really interesting chemistry.

One of the first things we did—Gary Eller did a lot of this work—was to bind SO_2 to copper phosphine complexes containing sulfur ligands. The SO_2 stuck to the sulfur of these complexes reversibly. The complexes were white colored, and when you put SO_2 on them they changed to yellow, orange, and maybe all the way to red, depending on the SO_2 concentration and the groups on there. This was almost like a litmus paper. So for SO_2 detection you could actually detect SO_2 down to 100 parts per million or so, just using filter paper impregnated with this copper complex. We published the results in the *Journal of the American Chemical Society* in 1977, and we received a patent on it (Copper Mercaptides as Sulfur Dioxide Indicators) in 1979.

The main chemistry we did was on three modes of SO_2 bonding to mono-nuclear transition-metal complexes: SO_2 bound in η^1–planar or η^1-pyramidal geometries (where it's bonded via sulfur as either a Lewis acid or base), and also

Relevance to Energy of Dihydrogen Coordination

For hydrogen economy, H_2 production and storage are chemistry rather than materials challenges because the nature of bonding of hydrogen is crucial: molecular binding of H_2 molecules is much more favorable than atomic binding of hydrides. More hydrogen can be bound for hydrogen storage where weight is crucial; a material containing greater than 9 percent H_2 by weight is needed to be practical for vehicle use, which is a difficult challenge. Also, binding must be reversible with low energy (heat) changes when H_2 is added and removed from the solid storage material. Metal-organic frameworks (MOFs) are promising because they bind H_2 molecularly like a sponge.
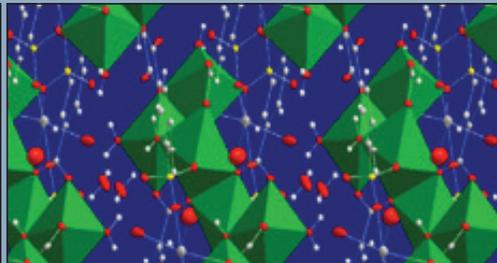
"Easy" in theory? Below, from left to right: a Buckyball metal complex, the tungsten-dihydrogen complex $WH_4(H_2)_4$ calculated by density functional theory, and H_2 binding on a nickel 5-sulfoisophthalate MOF material.
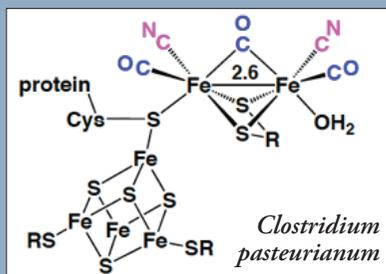

$MH_2(H_2)_4$

$C_{60}[ScH_2(H_2)_4]_{12}$
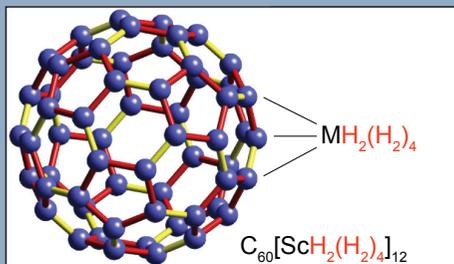
(Heben, Dillon)
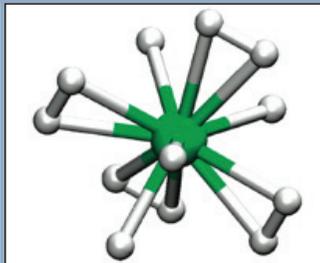
(Andrews, Gagliardi, et al.)

(Cheetham, et al.)

Clostridium pasteurianum

HYDROGENASE ENZYMES

Biological production of H_2 has been known for many decades but the mechanism was shrouded in mystery until relatively recently when the molecular structure of the hydrogenase enzyme's catalytic site was determined by John Peters in 1998 (shown in this illustration of *Clostridium pasteurianum*). These enzymes evolved billions of years ago in microorganisms and catalyze reversible interconversion of H_2 and protons/electrons to either utilize H_2 as an energy source or dispose of excess electrons as H_2 at very high rates (10,000 turnovers per second). Our own digestive tract contains hydrogen-producing organisms containing these types of structures (a sign of good health actually). The iron binds H_2 molecularly and either splits the H_2 or forms H_2 at the site where the H_2O ligand binds across from the biologically unprecedented CO ligand. Molecular rather than atomic binding of H_2 is crucial here, and the site is organo-metallic-like (almost like the complex we discovered), which is very rare in nature.

side bonded (η^2) via sulfur and one oxygen. (the Greek symbol "eta" with a superscripted number indicates the number of atoms of a ligand bound to a metal center in a coordination compound.) This was the first example of a side-bonded SO_2, and actually Dave Moody initially found it. Several other postdocs contributed to the work, including Gordon Jarvinen, Harvey Wasserman, Kim Martin, and even Carol Burns when she first was an undergraduate summer student with us.

It was spectacular work back then, and we basically wrote the book on transition-metal SO_2 chemistry. Bob Ryan did crucial analysis of the structure/bonding principles. We published a long review article in *Structure and Bonding* ("Structure and Bonding of Transition Metal-Sulfur Dioxide Complexes," 1981) and were able to define and correlate the characteristic infrared (IR) frequencies for all these different coordination modes with the reactivity of the complex with oxygen to give a sulfate complex via insertion of O_2. It was an impressive body of work.

One of the more interesting things we did was a catalytic reduction of sulfur dioxide with hydrogen on molybdenum and chromium sulfido complexes. We found that SO_2 underwent an unusual oxygen-transfer kind of reaction and effectively disproportionated into elemental sulfur and SO_3. The SO_2 initially stuck onto the sulfide ligand and a second SO_2 interacted to give a thiosulfate ligand (SSO_3) that was reduced with hydrogen, so the products in the end were sulfur and water. And it went really well—350 turnovers an hour at just a little over room temperature and pressure. It turns out this method works better than reducing it heterolytically on a ruthenium alumina catalyst. It was fascinating to see that we could do this chemistry in a homogeneous solution at that kind of rate; it was a very unusual catalytic system mechanistically.

SO_2 complexes lead to the discovery of dihydrogen complexes

We were making SO_2 complexes using very bulky phosphine ligands, like tricyclohexyl phosphine, on zerovalent group 6 centers, e.g. $Mo(CO)_3(PCy_3)_2(SO_2)$, and I got very poor yields: less than 20 percent. I thought we had to be able to do better than that, so I stubbornly kept pursuing trying to improve the yield by varying starting materials and reaction conditions. These reactions were carried out in organic solvents such as toluene, and I varied solvents as well. That poor yield led to the dihydrogen complex, because if it had not been for the poor yield, I probably would have gone on to something else.

So I switched to a cycloheptatriene precursor, $Mo(CO)_3(\eta^6–cyclohepta-triene)$, reacting it in solution first with phosphines under an "inert" nitrogen atmosphere and then SO_2. The orange SO_2 complex resulted, but it was a poor yield again. (Bob Penneman likes this story because I point out that color was very important in this discovery and in a lot of the work I've done.) It turns out that under nitrogen a yellow dinitrogen complex forms first before SO_2 addition, which we didn't know was an intermediate. But one day my nitrogen tank ran out so I substituted argon—and this led to the discovery.

By using argon instead of nitrogen, the nitrogen could not coordinate, and I noticed that in this case a purple complex initially formed before the SO_2 was added. This was later shown to be a 16-electron complex, $Mo(CO)_3(PCy_3)_2$, containing a so-called agostic C–H, where the C–H of the phosphine was coordinated. This 5-coordinate complex violated the 18-electron rule; I shouldn't be able to get a 5-coordinate system. Right away I knew I had something important in this finding, even without the hydrogen on it, in this purple complex. As I mentioned, color was important; the initial key observation telling me that stable intermediate complexes formed before the SO_2 addition.

So I took the cycloheptatriene complex under hydrogen and it made the dihydrogen (yellow) complex, and if you did it under argon you got the 16-electron system (purple complex). If you added hydrogen to this coordinatively unsaturated 16-electron complex you got the dihydrogen complex, accompanied by a purple-to-yellow solution color change. The reaction was totally reversible under vacuum or argon—even in the solid state—and it only worked with the bulky phosphines. I didn't realize the complex was coordinating *molecular* hydrogen (H_2), but I knew it was binding hydrogen reversibly, which was an important clue right there.

The first real clue as to whether H_2 was binding molecularly versus atomically as a dihydride involved an IR spectrum. I knew from my work as a grad student that if you substitute deuterium for hydrogen you see big spectral shifts. The first main clue here was a low-frequency deformational mode at 462 cm^{-1} for $W(CO)_3(PCy_3)_2(H_2)$ that shifted to 316 cm^{-1} for the deuterium complex, $W(CO)_3(PCy_3)_2(D_2)$. I was using a non-routine IR in Lew Jones' group—one

This photo from 1983 of Phil Vergamini (left) and Greg Kubas appeared in **Chemistry and Engineering News.** *Kubas is loading into a glove bag a crystal of the new metal complex that contains a bound molecule of hydrogen.*
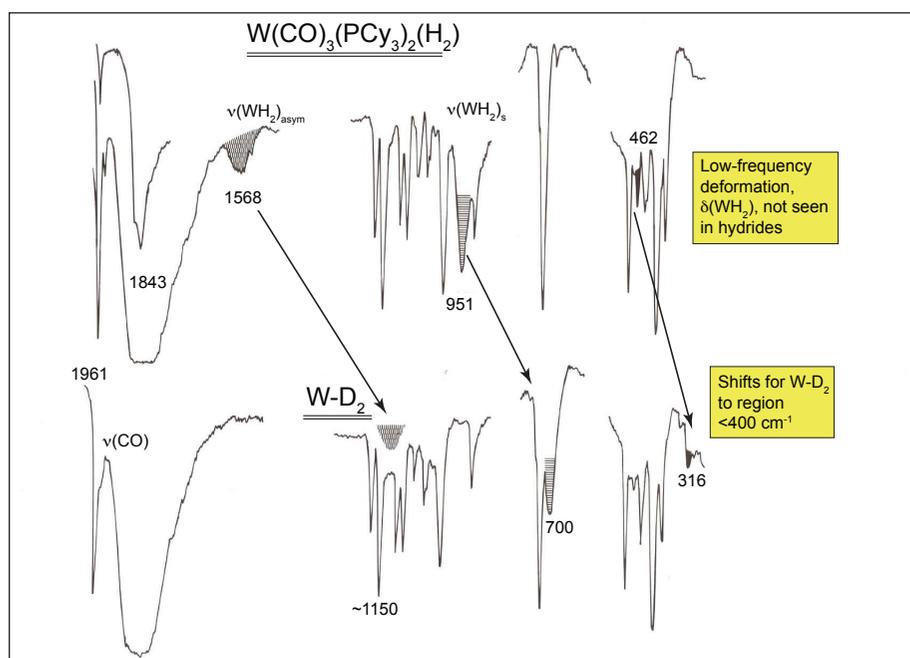
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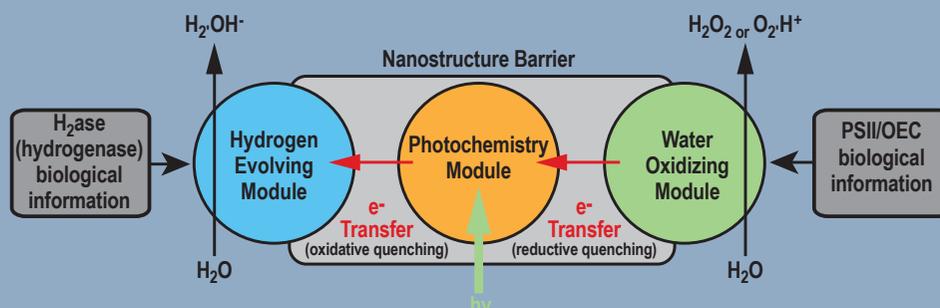
Biomimetic H_2 production, particularly solar driven (photocatalysis), is desirable and may take a cue from modeling of the active site of hydrogenase enzymes and photosystems and coupling these model systems. Formation of H–H bonds from protons and electrons will be crucial in the production of the vast quantities of H_2 needed and is extremely rapid at the iron sites in hydrogenase enzymes. Iron or other base metals rather than expensive platinum will be critical as catalysts. Several groups worldwide are investigating combining model catalysts with photo-chemical water splitting; one scheme is illustrated above. Water is ultimately the best source of hydrogen and would be oxidized in the right module in a molecular system mimicking biological photosystem II and electrons transferred to a hydrogen-evolving module mimicking hydrogenase.

that went below 400 cm^{-1} whereas most IRs didn't go below 400 cm^{-1}. So luckily I was able to see a peak appear in the spectrum of the D_2 complex that was shifted from that in the H_2 complex. This told me that it had to be due to something unusual but not a hydride because if this were a hydride you would not see this low-frequency peak.

It was almost exactly thirty years ago that I did the chemistry. I published a paper in 1980 in *Chemical Communications* saying that this bonding of hydrogen may be novel. That's probably the biggest understatement of all time— saying this is a "novel interaction." Six infrared spectral bands were found later for $W(CO)_3(PCy_3)_2(H_2)$, and Basil Swanson did the Raman and analyzed the data, but we still had not obtained the molecular structure.

The problem was getting a crystal structure because it's hard to locate hydrogens by X-ray diffraction. Initial studies by Bob Ryan did not show the H_2 molecule, just an empty site where it should be. Phil Vergamini kept after me to grow large single crystals of this complex for neutron diffraction studies. It took almost two years before I got crystals of an analogue, $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$, that Phil could use in a neutron diffraction study at LANSCE.

The initial findings indicated that the hydrogen was side-on bonded to tungsten. We eventually found that the H–H distance was about .82 angstrom (Å), so it's stretched a bit, about 10 percent longer than in free hydrogen. We also did get an X-ray structure (determined by Harvey Wasserman), but the problem

was there was disorder in the phosphine, so we never could formally publish the neutron structure. The whole process took several years (1979–1983), and Phil was the one who kept encouraging me to pursue this crystallographic work until we had the structural proof we needed.

Phil and I gave a talk in April 1983 at an American Chemical Society meeting in Seattle announcing that we had found a dihydrogen complex. Many people were skeptical because they did not believe dihydrogen could be coordinated as an H_2 ligand. Well-known researchers thought there was no way dihydrogen could coordinate to a metal complex in stable fashion, even from theoretical calculations, so everyone thought it was a hydride.

Additional and indisputable evidence that we had a stretched H–H bond coordinated to a metal was provided by nuclear magnetic resonance (NMR) spectroscopy. In an experiment suggested by Russ Drago (a consultant in INC-4 from the University of Florida), I made the hydrogen-deuterium (HD) complex. For the HD complex, you should get a splitting in the proton NMR signal for the metal-bound H because deuterium has a nuclear spin of one. The splitting should be triplet in a 1:1:1 intensity pattern if there is residual bonding between the H and D atoms but not if the H and D atoms are separated, i.e. H–M–D. This signal was found exactly as predicted and absolutely proved that we had HD coordinated to the metal as a molecular unit rather than as a hydride/ deuteride. The HD coupling was 34 hertz (Hz), and it's 43 Hz in HD gas.

Robert Crabtree at Yale University later found that the NMR relaxation time (T_1) was a lot shorter in H_2 complexes than that in metal hydrides, another valuable NMR criterion for H_2 coordination. He found that several known complexes thought to be classical hydrides were actually "nonclassical" dihydro- gen complexes. This really opened up the field, and dozens of new H_2 complexes were subsequently discovered by many researchers worldwide.

The discovery of the dihydrogen complex spanned five years. I first made the compound in 1979 and we (Bob Ryan, Basil Swanson, Phil Vergamini, Harvey Wasserman, and myself) published the results in January 1984 in the *Journal of the American Chemical Society.*

What's also interesting is that Nobel Laureate Roald Hoffmann of Cornell University did a theoretical calculation at almost the same time we published our paper. A few months later, in April 1984, he published that side-on bonding of dihydrogen in a chromium pentacarbonyl complex is favored over end-on. This was something that people hadn't thought about that much—that H_2 coordination could be stable. Both the experiment and theory came out at almost exactly the same time. It was noteworthy that Hoffmann performed his calculations without being aware of our work, while I was equally unaware of his calculations.

In a 1987 letter of recommendation Hoffmann wrote for my nomination as a Lab Fellow, he very graciously said that the H_2 complex and our SO_2 work "put Los Alamos on the map in inorganic chemistry, and in general I would
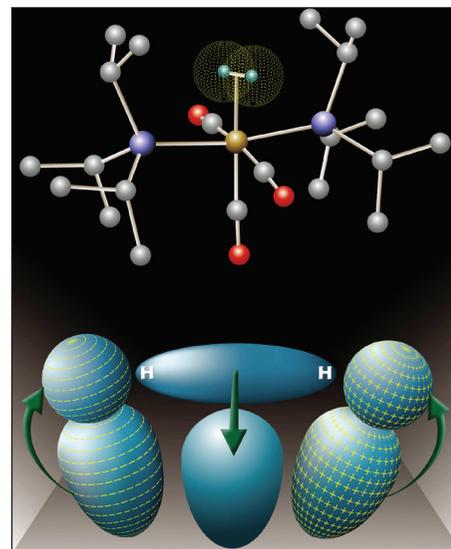
Backdonation is crucial in stabilizing M–H_2 bonding. This illustration shows the bonding in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$: donation of the bonding electrons in H_2 to a filled metal d-orbital and backdonation to the antibonding orbital of H_2.

say that this is long overdue and there is no way that Los Alamos can fulfill its mission in energy, laser, chemistry and materials areas without good inorganic chemistry. Materials must be made before the properties can be studied." I thought it was really nice that Roald acknowledged INC-4 in this way.

At the time it was well known that dihydrogen could be split on metal complexes to give dihydrides, a key step in industrial catalytic hydrogenation, but no one really knew how this took place. It was totally unknown whether the initial step in the H–H bond breaking process involved interaction of the H_2 bonding electron pair with a vacant metal orbital or whether a filled metal d-orbital interacted with the sigma star (σ^*) orbital of hydrogen (σ^* denotes an antibonding molecular orbital). We later established that both of these bonding components were critical in coordinating and eventually splitting the H–H bond.

It was interesting that the purple agostic complex was the precursor to the H_2 complex, yet we didn't realize it had this structure until its crystal structure was determined two years later by Harvey Wasserman. When we added hydrogen to it in solution, we found was that there actually was an equilibrium between the dihydrogen complex and a dihydride isomer. This clearly showed that the dihydrogen complex is the immediate in forming the dihydride. Cliff Unkefer did some nice NMR to show that we had an equilibrium of the dihydride and the dihydrogen complex in the same solution.

That was quite important in showing that activation of H_2 is very finely tuned in terms of the nature of ligands and metal. Replacing one phosphine by CO give an unstable H_2 complex, but replacing the CO ligands by phosphines gives a dihydride.

The hydrogen complex (M–H_2 bonding) was a new paradigm in chemistry. It's the coordination of a bonding electron pair, a 3-center 2-electron interaction of a bonding electron pair with a vacant metal orbital. Why would hydrogen want to do that? Jeff Hay in T-Division published in 1984 in *Chemical Physics Letters* the theoretical bonding analysis of this complex. And what stabilizes it is backbonding.

So you've got both sigma donation from H_2 to the metal, the 3-center interaction, plus backdonation from a filled d-orbital to the σ^* H_2 orbital. The calculations show that the energetics favor backdonation because there's a match of energies between the σ^* H_2 and the d-orbital. The latter interaction is very important; otherwise you would not be able to make a stable metal dihydrogen complex. H_2 does not bind to main group atoms stably because they are incapable of backdonation.

Juergen Eckert at LANSCE found crucial experimental evidence for backdonation by neutron scattering spectroscopy that showed that there was a barrier to rotation of H_2 about the $M–H_2$ axis. The hydrogen is not spinning freely, so there's got to be backdonation, otherwise this would be a free rotor. It was really neat to see all this coming together.

The field of $M-H_2$ σ complexes evolved tremendously. At this point more than 1200 papers have been published and 140 research groups worldwide got involved in dihydrogen chemistry, including six Nobel Laureates. And there are 600 or 700 complexes known now. Every metal, including technetium, is known to make a dihydrogen complex, even main-group systems, although these are not stable at room temperature because of the lack of backdonation.

What's interesting is the H–H distance varies from what it is in hydrogen gas all the way up to a dihydride, and the complex we made was a true dihydrogen complex, about .89 Å. But you can get elongated H_2 complexes where the H–H distance is stretched well over 1 Å. The H–H bond is stretched because of backdonation, so when you get too much backdonation you break the H–H bond because you're populating an antibonding orbital. And that's the mechanism of forming a dihydride. But you can actually get intermediate forms where you've got moderate backdonation that stretches the H–H bond but does not break it, so this was a very important finding.

Lew Jones, my original postdoctoral mentor, did a normal coordinate vibrational analysis of the $W-H_2$ complex. There are six normal modes: the H–H stretch, two $W–H_2$ stretches, two deformations, and a torsional (rotational) mode. Lew found that the force constant for the H–H stretch was much lower than that for free hydrogen: 5.7 in hydrogen gas versus 1.3 for the bound H–H. It's a lot lower obviously because it's bound, but there also is a very high interaction constant with the $W–H_2$ stretches that shows that these modes are highly coupled. Basically you can look at this as almost a 3-center "triangulo" interaction rather than a metal with an isolated H_2 stuck on it. Lew thus made a nice contribution to the research.

Kubas' oil painting talent has taken him full circle with his fascination of the colors of discovery.
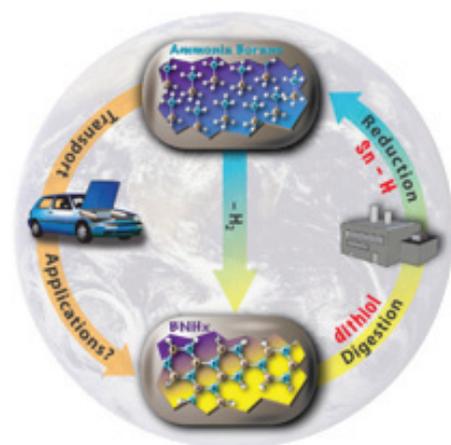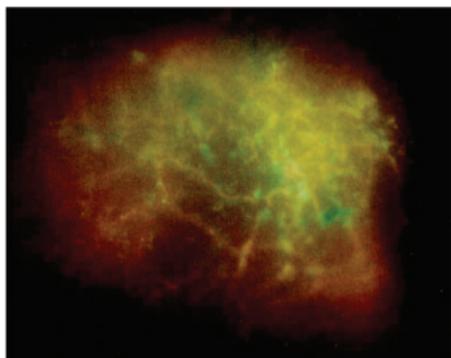
Talks Focused on Outgrowth of Science from the Early Days

"The four pioneers honored at this conference—Bob Penneman, Lew Jones, B. B. McInteer, and Larry Asprey—established capabilities in actinide, isotope and inorganic chemistry, and spectroscopy that attracted a wide range of very talented young chemists and scientists to Los Alamos," said Nan Sauer of the Institutes Office.

"These second-, third-, and even fourth-generation chemists continue to play critical roles in chemistry across the Laboratory. There are some amazing people here at Los Alamos who are the 'grandchildren' and 'great-grandchildren' of the four pioneers and are now technical leaders in their organizations," Sauer said.

Many of the people Sauer refers to were invited speakers at the conference. Their discussions focused on actinide transition-metal chemistry, theory and materials, environmental actinide chemistry, vibrational spectroscopy, and bioinorganic chemistry, as well as isotopes, nuclear magnetic resonance (NMR) spectroscopy, and biology.

Scott Kinkead of the High-Energy Focused Experiments Group talked about "From FOOF to Blowing Things Up"; **Eiichi Fukishima** of New Mexico Resonance discussed "From Solid-State NMR to Imaging"; and **Al Sattelberger** came from Argonne National Laboratory to speak on "Actinide and Technetium Chemistry: Déjà Vu."

Carol Burns, group leader of Nuclear and Radiochemistry, focused on "Metal-Ligand Multiple Bonding in Actinide Chemistry"; **Greg Kubas** of Inorganic, Isotope, and Actinide Chemistry discussed "The Colors of Discovery: Transition Metal Coordination and Activation of Sulfur Dioxide and Dihydrogen"; **John Bercaw** of the California Institute of Technology returned to talk about "Ethylene Oligomerization with Organochromium Catalysts"; and **Gordon Jarvinen** of the Seaborg Institute discussed "Separations Technology for Advanced Nuclear Fuel Cycles."

John **Gordon** of the Inorganic, Isotope, and Actinide Chemistry Group discussed "From f-Element Chemistry to Chemical Hydrogen Storage"; **Michael Hopkins** came from the University of Chicago to speak about "Properties and Reactions of New Transition Metal Photoreductants"; **P. Jeffrey Hay** of the Theoretical Division presented "Theoretical Adventures in Actinide and Transition Metal Chemistry"; and **Anthony Burrell** of Materials Chemistry discussed "Solution Routes to Oxides and Nitrides."

The Seaborg Institute's **David Clark** spoke on "Covalency Determination in Actinide Complexes through Synchrotron X-ray Spectroscopy"; **David Morris** of the Center for Integrated Nanotechnologies discussed "The Influence of INC-4 Science and Culture in Advancing Environmental Actinide Chemistry"; and **William "Woody" Woodruff** of Inorganic, Isotope, and Actinide Chemistry discussed "Isotopes in INC-4 (Infrared and Raman Version): From FOOF to Funky."

Mary Neu, associate director for Chemistry, Earth, and Life Sciences, presented a seminar on "Emerging New Roles for Chemistry at LANL: Continuing the Great Sciences Traditions"; **Pat Unkefer** of Bioscience Division discussed "From Discovery at TA-21 to a Million Acres of Wheat"; **Brian Dyer** of Physical Chemistry and Applied Spectroscopy discussed "From Protein Folding to Solar Water Splitting"; and **Olof Einarsdottir** of the University of California, Santa Cruz, presented "Ligand Dynamics and Radicals in Cytochrome *c* Oxidase."

Deputy Chemistry Division Leader **Basil Swanson** discussed "Early Science with Jones and Ryan to Biosensors"; **Robert London** came from the National Institutes of Health to talk about "NMR from INC-4 to NIEHS"; and Cliff Unkefer of Bioenergy and Environmental Science spoke about "Isotopes in INC-4." Director Emeritus **Sig Hecker,** now with Stanford University, discussed "Finding Actinides in North Korea" at the conference dinner.

Sessions were chaired by Swanson, Burns, Clark, Sauer, Chemistry Division Leader **Gene Peterson,** retiree **Ken Salazar, Andrew Shreve** of the Center for Integrated Nanotechnologies, and **James Brainard** of the Biosciences Center at the National Renewable Energy Laboratory.
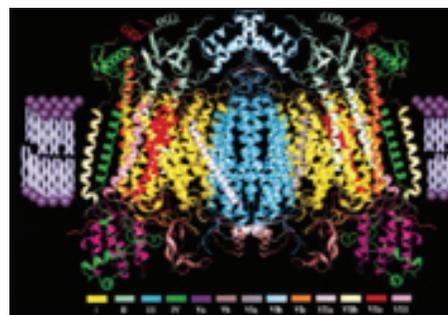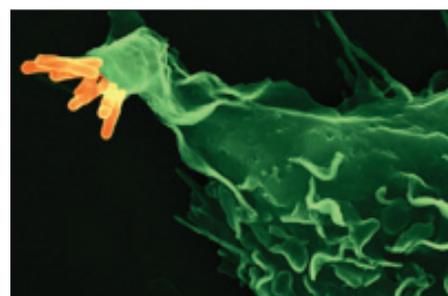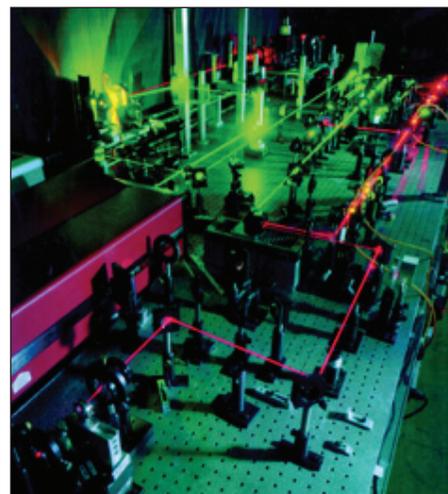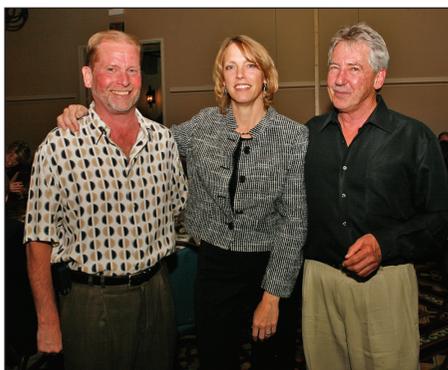
*Bob Penneman (center) with **Actinide Research Quarterly** scientific advisors Gordon Jarvinen (left) and Dave Clark.*

Los Alamos Director Emeritus Sig Hecker and Nan Sauer, Institutes Office director.

Gene Peterson (left), Chemistry Division leader; Mary Neu, associate director for Chemistry, Earth and Life Sciences; and Basil Swanson, deputy Chemistry Division leader.

DARLEANE HOFFMAN: SOME VIEWS FROM INC-DO

Darleane Hoffman (right) with Carol Burns (left), Nuclear and Radiochemistry group leader.

CNC (Chemistry and Nuclear Chemistry) was a new division formed in 1971 with George Cowan as division leader. I became CNC Division Leader in August 1979. Isotope and Nuclear Chemistry Division (INC) was established in 1981 after yearlong discussions, proposals, and hard work. They wanted to divide us into various parts, and we would just cease to exist; we prevailed. I was division leader and Nick Matwiyoff was deputy. And that recognized the stable isotopes and their applications—separations, biological, agricultural, all the other applications of stable isotopes. And I think they thrived.

The INC groups in 1981 included INC-3, Medical Radioisotope Research; INC-4, Isotope and Structural Chemistry (Bob Penneman was group leader, Larry Asprey and B. B. McInteer were associate group leaders); INC-5, Research Reactor; INC-7: Isotope Geochemistry; and INC-11, Nuclear and Radiochemistry. We kept having to divide INC-11 because it kept getting bigger and bigger. The minute you split it up it would regrow.

After a host of reorganizations, self-assessments, splits, raids, gifts, ups and downs, and so forth since INC was first established, it is somewhat rewarding to see most of Bob's old group and mine, as well as spectroscopy, in the current Chemistry organization chart. Inorganic, Isotope and Actinide Chemistry, parts of Analytical Chemistry, parts of Nuclear and Radiochemistry are here; and then Gene Robinson's group in Physical Chemistry and Applied Spectroscopy. Some of it, unfortunately, like biology, has split off, but the broad capability picture is different from the division structure.

At any rate, as Bob [Penneman] said, it was a great time, and I'll always look back on it with some pleasure—some ups, some downs, but mostly good.

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