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Chemistry-Nuclear Chemistry Division

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Compiled by
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FOREWARD

DIVISIONAL OVERVIEW

Darleane C. Hoffman
Nicholas A. Matwiyoff

The past year since our first annual report (LA-8717-PR, October 1979-September 1980) has been another productive one for the Chemistry-Nuclear Chemistry Division. On March 1, 1981, the Research Reactor Group transferred to CNC Division and became CNC-5. At the end of FY 1981, we had 175 people in the Division, including 102 professional scientists, 79 with the degree of Ph.D.

LOS ALAMOS NATIONAL LABORATORY CHEMISTRY-NUCLEAR CHEMISTRY (CNC) DIVISION

Under a new Laboratory program designed to recognize and reward scientific excellence within the Laboratory, 19 Laboratory scientists were named Laboratory Fellows. Three of these, Donald W. Barr, Jimmie D. Doll, and Jere D. Knight are in CNC Division. Donald W. Barr was also one of five scientists selected to receive a 1980 E. O. Lawrence Memorial Award for outstanding contributions in the field of atomic energy. He was cited "for his innovative and incisive diagnostic methods which assist weapons designers in understanding and interpreting different aspects of their work and lead to improved designs." Robert A. Penneman and Joseph Montoya were presented Distinguished Performance Awards by the Laboratory. During the year we hosted 14 postdoctoral appointees and one of the recipients of the prestigious J. Robert Oppenheimer Fellowship awarded by the Laboratory each year to one or two outstanding young scientists. Fourteen undergraduate and graduate students participated in our very successful summer program. Our interactions with scientists from numerous universities and research institutes in this country and abroad were facilitated both by visits from outside scientists to Los Alamos and by our scientists to other laboratories. Some 60 visiting staff members and consultants have worked with us here, 20 research visitors have participated in our LAMPF nuclear chemistry program, and more than 45 visiting scientists have given lectures and colloquia here. Many of our scientists have used facilities elsewhere including those at Lawrence Berkeley Laboratory, Lawrence Livermore National Laboratory, Sandia National Laboratory, Oak Ridge National Laboratory, the Gesellschaft für Schwerionenforschung (GSI) Darmstadt, West Germany, and the TRIUMF facility, Vancouver, B. C.

Visiting committees of eminent scientists reviewed our Medical Radioisotopes Research and Stable Isotopes Resource Programs. A new advisory committee, the Visiting Committee for Nuclear and Radiochemistry was constituted this year and met for the first time in May 1981. (See Appendix D.) They were most valuable in helping us set priorities for deployment of our resources in these areas of research.

The Third Annual Divisional Information meeting was held in September 1981. Division-wide Seminars of general scientific interest have been held on a regular monthly basis and have been well attended. (See Appendix E.)

For the first time, a long-range planning process was undertaken for the Division. In this process, we reviewed our current strategic areas of effort and our capabilities and facilities, tried to assess the potential for development in these areas, and attempted to project new areas to be emphasized or nurtured.

Our instrumentation and facilities for scientific research have been significantly improved (See Appendix B) and are state of the art in many areas. We continue to strive to maintain and upgrade our physical plant and to foster Division interaction among personnel at our many geographically separated sites. A significant addition of high quality laboratory space in refurbished Building 150 was occupied by part of Group CNC-4 this year. This building houses the new Nuclear Magnetic Resonance (NMR) Center and many of the research staff of the national stable isotopes resource. When the building is removed from the security area early this fiscal year, it should facilitate our interactions with the many uncleared visiting scientists we host. Additional clean

room space for a new two-stage mass spectrometer was installed in the Radiochemistry Building.

This report covers contributions during FY 1981 (October 1, 1980-September 30, 1981) to unclassified projects and to unclassified work related to the nuclear weapons program. Other Division quarterly and annual reports are also published for certain specific programs and should be referred to for more detailed information. Publications and presentations during FY 1981 are given in Appendix A for each group.

Some highlights from our accomplishments for FY 1981 are as follows.

- Very large abundances of iridium have been found for the first time in fresh-water-deposited sedimentary rocks where ratios of pollen species changed abruptly at the Cretaceous-Tertiary boundary. These findings are consistent with the theory that the great extinction at that time was caused by the impact of a large extraterrestrial object.
- Diffusion into the matrix has been found to be an important feature of retardation in the migration of radionuclides through tuff and other rocks. For tuff this means that the rock on both sides of a fracture acts like a sponge, soaking up radionuclides from water flowing through the fracture.
- Approximately one hundred gram quantities of the mass-21 methane ($^{13}\text{CD}_4$) and mass-20 methane ($^{12}\text{CD}_4$) tracers were used successfully to follow the path of an air mass from Norman, Oklahoma, through Missouri and then past Argonne National Laboratory, the National Bureau of Standards, and Savannah River Laboratory for a total distance of 3000 km.
- A technique has been developed to measure the internal energy distributions of products of photodissociation of molecules before the distribution is degraded by collisions. Pulsed laser photodissociation is coupled with pulsed Coherent Anti-Stokes Raman Spectroscopy to measure the collision-free photofragment electronic, vibrational, and rotational energy distributions within 6 ns.
- The first quantitative theoretical method for surface diffusion has been developed and used to calculate the self-diffusion coefficient for metallic rhodium on one of the faces of its crystals. The calculations are being extended to other faces, other systems, and to diffusion-controlled surface chemical reactions.
- General isotope exchange procedures have been developed for rapid labeling of radiopharmaceuticals with short-lived isotopes, e.g., bromine-77 labeled steroids for the early diagnosis of hormone associated tumors and for the *in vivo* determination of hormone receptor content.
- Bacteria that overproduce amino acids have been trained to selectively introduce carbon-13 labels from specifically carbon-13 labeled glucose or acetic acid. The amino acids are needed for human metabolic and nutritional studies; and the bacterial synthesis is more convenient and efficient than other methods previously in use.
- Over 58,000 stream sediment samples have been analyzed for uranium and 31 other elements with automated neutron activation analysis facilities in connection with a nationwide geochemical reconnaissance program.

- We have shown that soil samples can be nondestructively assayed for natural long-lived radionuclides (^{230}Th , ^{227}Ac , ^{210}Pb , etc.) at levels as low as 4×10^{-4} pCi/g.
- We have demonstrated that fission and spallation products produced with 800-MeV protons incident on thin metal targets can be transported via a He-jet system with an efficiency of 40-50% to a remote station as distant as 40 m.
- The inherent coordination and electronic unsaturation of $\text{Pt}(\text{PCy}_3)_2$ and $\text{Pt}[\text{P}(\text{t-Bu})_3]_2$ were utilized to promote reactions of bound SO_2 leading, in part, to an x-ray crystal structure analysis of $\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2$, the first reported three-coordinate platinum(0) sulfur dioxide complex.
- Synthetic and x-ray structural studies of a wide variety of d⁶ molybdenum- SO_2 complexes have led to stereochemical control over the metal- SO_2 bonding geometry as well as a comprehensive understanding of the bonding properties of side-on (η^2) bonded SO_2 . Selected complexes were found to be quite reactive towards strong Lewis acids, methylating agents, metal hydrides, and atmospheric oxygen.
- During our work towards synthesizing uranium(III) alkoxides, we prepared and determined the structure of a unique product, tetra- μ -phenoxy-di- μ_3 -oxo [bis(triphenoxytetrahydrofuranuranium(V) bis-tetrahydrofurandioxo-uranium(VI))]. This complex represents the first reported example of a mixed valent uranium alkoxide.
- The solid state structures of the organic explosives ammonium and potassium picrate have been accurately determined. Potassium picrate shows slightly elongated and presumably partially activated N-O bonds consistent with its enhanced sensitivity.
- Crystal chemical considerations have been applied to proposed nuclear waste forms and related materials to predict stability and actinide ion site preference.
- We have shown that the stability of Tc in geologic burial of nuclear wastes can be inferred from the containment of fission products by the Oklo natural reactor formation for over two billion years.
- We have found that osmium complexes should prove suitable for oxidation potential buffering of Pu(V) and (VI) systems and of Pu(III) and (IV) systems.
- Pressure cycling of water used for heat extraction from dry rock should reduce water loss from the extraction loop, but will also probably decrease the permeability of the rock.
- A new reaction vessel was developed for study of deep geothermal reservoirs, overcoming previous difficulties with temperature gradients.
- Experimental results with the Na-K-Ca geothermometer show agreement with the accepted empirical values.
- Solution models of Pitzer and Tamman-Tait-Gibson, and the Born equation, have been tested for their abilities to predict the properties of aqueous solutions at high pressures, temperatures, and concentrations.
- Comparison of Project Airstream aerosol filter samples with volcanic history between 1971 and 1981 indicates that half of the sulfate aerosol layer is of volcanic origin.

- Analysis of samples from heavy methane tracer experiments in the geothermal power area of Northern California is nearing completion with encouraging results.
- Heavy methane ($^{12}\text{CD}_4$) has been accelerated through the vertical Van de Graaff facility in our continuing development of an ultrasensitive technique for detecting this atmospheric tracer. Unexpected results have been obtained that indicate there is a high probability for large angle scattering of molecular fragments.
- The (n,2n) cross sections have been measured on the radioactive isotopes ^{88}Y , ^{88}Zr , ^{148}Gd , ^{150}Gd , and ^{173}Lu . The (n,p) cross sections for ^{148}Gd and the (n,np) cross section on ^{88}Zr were also determined.
- Experimental measurements have been performed on the radioactive targets ^{146}Sm and ^{148}Gd produced through the spallation reaction of 800-MeV protons on Ta in the LAMPF beam stop. With these targets we have been able, for the first time, to establish the theoretically important pairing vibrational states in the $N = 82$ isotopes produced with the (p,t) reaction.
- A unique time-of-flight magnetic spectrometer has been designed to perform direct mass measurements of a series of extremely neutron-rich and neutron-deficient nuclei with $A \leq 100$ to be produced by 800-MeV protons on ^{238}U targets. Construction of the spectrometer will begin in FY 1982.
- The similarity in measured yields of both neutron-deficient as well as neutron-rich fission product isotopes from 350-MeV positive pion-induced and 500-MeV proton-induced fission of ^{238}U indicates that absorption of the rest-mass energy of the pion (140 MeV) plays a prominent role in this nuclear excitation process.
- Our measurements of the theoretically important pion single-charge-exchange reaction $^{13}\text{C}(\pi^+, \pi^0)^{13}\text{N}$ as a function of pion energy show that the cross sections are substantially lower than previously reported values and are closer to theoretical predictions.
- From a study of the recoil properties of ^{11}C from the reactions $^{12}\text{C}(\pi^\pm, \pi\text{N})^{11}\text{C}$ it was learned that the energy dependence of the projected forward and backward ranges is markedly stronger for π^- than π^+ , suggesting important differences in the reaction mechanisms.
- The cross sections for the important primary pion beam monitor reactions $^{12}\text{C}(\pi^+, \pi\text{N})^{11}\text{C}$ at energies below 100 MeV were remeasured and were significantly lower and more precise than our previous ones.
- A dynamic coupling between the true pion absorption and charge-exchange channels and the use of the microscopic description of ^{18}O involving a core polarization were proposed to resolve a large discrepancy between observed and calculated angular distributions of the $^{18}\text{O}(\pi^+, \pi^-)^{18}\text{Ne}(\text{g.s.})$ reaction.
- Rates for the production of nuclides in meteorites by cosmic rays were calculated and used to study the exposure histories of meteoritic samples.
- An atlas of uranium emission intensities has been produced and distributed. It is becoming the accepted wavelength standard for calibration of lasers and spectrometers.

- The interaction of a pharmacologically important drug (methotrexate) with its target enzyme (dihydrofolate reductase) was studied using specific isotopic labeling [90%-2-¹³C] (methotrexate) in combination with NMR spectroscopy. The results provide quantitative information on the strength of the hydrogen bonding interaction between the methotrexate N-1 and a residue (presumably aspartate-27) on the enzyme.
- Research equipment and personnel involved in nuclear magnetic resonance have been combined into a single center. The NMR Center now includes two high resolution spectrometers for liquids (at 2.3 and 7.1 T), a variable wideline spectrometer for solids, and office space for 10 staff members and visiting staff members.
- During FY 1981 the isotope separation plant produced 8.5 kg ¹³C, 1.9 kg ¹⁵N, and 0.2 kg ¹⁷O having a combined value of \$66K.

CHEMISTRY-NUCLEAR CHEMISTRY DIVISION FUNDING PROFILE

FY-81 OPERATING: 15.2M\$
 FY-81 CAPITAL : 2.1M\$
 FY-81 TOTAL : 17.3M\$

WFO = WORK FOR OTHERS
 WSR = WEAPONS SUPPORTING RESEARCH
 ISR = INSTITUTIONAL SUPPORTING RESEARCH

MAJOR PROGRAMS:

	OPERATING
NUCLEAR WEAPONS DIAGNOSTICS	5.2M\$
CHEMICAL RESEARCH	2.3M\$
RADIOACTIVE WASTE ISOLATION	1.6M\$
STABLE ISOTOPES PRODUCTION AND DEVELOPMENT	1.4M\$
MEDICAL RADIOISOTOPES RESEARCH	1.1M\$
BASIC ENERGY SCIENCES	0.9M\$
GEOCHEMICAL & GEOTHERMAL STUDIES	0.6M\$

CNC
DIVISIONAL PERSONNEL AND FINANCIAL SUMMARY
FY-1981

	FUNDING ^A (\$ K)	FTE ^B AVERAGE LEVEL
DOE PROGRAMS		
DEFENSE	\$ 4 449	43
SUPPORTING RESEARCH	3 223	36
MEDICAL RADIOISOTOPES (ER)	1 078	13
CHEMISTRY-NUCLEAR CHEMISTRY RESEARCH (ER)	937	8
STABLE ISOTOPES INVENTORY	667	7
STABLE ISOTOPES DEVELOPMENT (ER)	410	4
GEOCHEMISTRY (ER) - GEOTHERMAL ENERGY (RA)	580	5
ATMOSPHERIC PROJECTS (ER)	424	4
URANIUM RESOURCE EVALUATION (RA)	392	5
MISCELLANEOUS DOE PROGRAMS	124	1
TOTAL DOE PROGRAMS	\$ 12 284	126
OTHER PROGRAMS		
NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS	1 465	16
NV: DEFENSE RADIONUCLIDE MIGRATIONS	250	3
OFFICE OF WASTE ISOLATION	230	3
NIH (STABLE ISOTOPES RESOURCE)	217	2
DoD	205	2
NASA	111	1
OTHER AGENCIES	540	9
TOTAL OTHER PROGRAMS	\$ 3 018	36
OVERALL TOTAL	\$ 15 302	162

^AEXCLUDING CAPITAL EQUIPMENT.

^BFTE = FULL TIME EQUIVALENT ROUNDED TO NEAREST WHOLE NUMBER.

NOT INCLUDED ARE 14 POSTDOCTORAL APPOINTEES, 1 POSTGRADUATE
RESIDENT IN NUCLEAR MEDICINE AND 1 J. ROBERT OPPENHEIMER FELLOW.

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CHEMISTRY-NUCLEAR CHEMISTRY DIVISION
OCTOBER 1980--SEPTEMBER 1981

Compiled by

R. R. Ryan

ABSTRACT

This report describes major progress in the research and development programs pursued by the Chemistry-Nuclear Chemistry Division of the Los Alamos National Laboratory during FY 1981. Topics covered include advanced analytical methods, atmospheric chemistry and transport, biochemistry, biomedical research, medical radioisotopes research, element migration and fixation, nuclear waste isolation research, inorganic and structural chemistry, isotope separation, analysis and applications, the newly established Nuclear Magnetic Resonance Center, atomic and molecular collisions, molecular spectroscopy, nuclear cosmochemistry, nuclear structure and reactions, pion charge exchange, radiochemical separations, theoretical chemistry, and unclassified weapons research.

I. ADVANCED ANALYTICAL METHODS

A. Automated Neutron Activation Analysis (M. M. Minor, S. R. Garcia, W. K. Hensley, M. M. Denton, and M. E. Bunker)

In 1975, the Laboratory was asked by DOE to design and manage a hydrogeochemical reconnaissance for uranium throughout the Rocky Mountain states of New Mexico, Colorado, Wyoming, and Montana, and the state of Alaska.¹ This effort was one facet of a more comprehensive program entitled the National Uranium Resource Evaluation (NURE), which is the most extensive geochemical and geophysical reconnaissance ever undertaken in the U.S. The goals of the program were to improve the estimates of the nation's long-range uranium resources and to iden-

tify promising areas for future private exploration. The program was terminated September 30, 1981.

CNC-5 has participated in this program by measuring the concentrations of U and other trace elements in stream sediment samples via neutron activation analysis (NAA), utilizing a computer-controlled irradiation and data-acquisition facility developed at the Omega West Reactor. Two analytical techniques are employed: delayed-neutron assay and gamma-ray analysis. The delayed-neutron technique, involving the detection of beta-delayed neutrons emitted by certain fission products, is used solely for uranium assay. The typical detection sensitivity for uranium in sediments or soil is 10 parts per billion (ppb). For liquids, the detection sensitivity for uranium is about 1 ppb.

The gamma-ray analysis method involves scanning the gamma spectrum of an irradiated sample with high-resolution Ge(Li) detectors at various times following a short neutron bombardment. Individual gamma-rays are identified with specific parent radioisotopes by means of a gamma-ray library stored in a computer, and from the gamma-ray intensities and weight of the sample, element concentrations can be calculated. The detection sensitivities range as low as a few ppb, and for 25 elements are ≤ 10 ppm. Spectra recorded at 20 min typically reveal Al, Cl, Dy, K, Mg, Mn, Sr, Ti, and V. A second count at 2 weeks yields concentrations of Au, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, Yb, and Zn. A few additional elements, including As, Br, Ga, and W can be detected after a delay of 4 days.

Four-hundred samples per day can be analyzed by the CNC-5 NAA facility if spectra are recorded at 20 min and 2 weeks only, which yields concentrations for 32 elements. During FY 1981, over 58,000 NURE samples were analyzed in this way, bringing the grand total for that program up to 180,000 samples. The utility of the enormous amount of geochemical data contained in these multielement analyses is just now beginning to be appreciated.

In addition to the NURE samples, over 7,600 samples were analyzed for other programs during FY 1981. The sample types were quite varied, including oil shale, coal residues, vegetation, uranium mill tailings, honey bees, hamster lungs, and human urine. The urine samples (3,900 in FY 1981) are analyzed for fissile material as part of the Laboratory's health monitoring program.

REFERENCE

1. P. L. Aamodt, "Hydrogeochemical and Stream Sediment Reconnaissance for Uranium," Los Alamos National Laboratory report LASL-77-34 (December 1977).

B. Radiometric Analysis of Uranium Mill Tailings (J. W. Starner and M. E. Bunker)

Uranium mill tailings piles pose major health and environmental hazards from (1) the emanation of ^{222}Rn gas, and (2) the leaching of α -active radio-nuclides and toxic stable elements by surface and/or groundwater. In connection with DOE's Uranium Mill Tailings Remedial Action (UMTRA) project, we have developed an analytical capability, based on gamma-ray spectroscopy, for assaying field tailings and laboratory-conditioned tailings for small quantities of long-lived radioactive contaminants.

The long-lived radionuclides of greatest concern are ^{226}Ra (1600y), ^{230}Th (7.7×10^4 y), and ^{210}Pb (22y). The latter two emit only low energy gamma-rays (67.8 keV from ^{230}Th ; 46.5 keV from ^{210}Pb), which are rather strongly absorbed by the sample itself because the sample must be massive (15 to 80 g) to get sufficient counting rate. We have essentially bypassed all geometrical problems by comparing the intensities of the gamma-rays emitted by a Canadian certified radiometric reference material (U = 0.177%, Th = 0.104%) and the sample material in question, with both samples canned in identical containers that have been sealed for at least 2 weeks in order for radioactive equilibrium to take place. The gamma-ray spectra are observed with high-resolution Ge(Li) detectors shielded with 4 in. of Bi. One of the detectors has a Be window that is essentially transparent to 50-keV quanta. By counting individual samples for at least 16 hours, we have been able to observe gamma rays from the following radionuclides (or their short-lived daughters): ^{235}U , ^{238}U , ^{231}Pa , ^{230}Th , ^{228}Th , ^{228}Ra , ^{227}Ac , ^{226}Ra , ^{210}Pb , and ^{40}K . In favorable cases, we can detect individual radionuclides at levels as low as 0.01 d/s/g, corresponding to 4×10^{-4} pCi/g, far below the levels of environmental concern. The low-energy portion of a typical gamma-ray spectrum is shown in Fig. 1. The recorded spectra are analyzed by means of a computer program that calculates, for each line observed, the number of disintegrations/s/g of the parent nuclide.

Fig. 1.
Low-energy portion of a uranium mill-tailings gamma-ray spectrum.

Sample analyses obtained by the above technique have been used in helping perfect UMTRA field-test methods and in assessing the effectiveness of mill tailings conditioning concepts being studied by the Laboratory's Environmental Science Group (LS-6).

C. Thermo-Optic-Based Differential Measurements of Weak Solute Absorptions with an Interferometer¹
(D. A. Cremers and R. A. Kelier)

There are many areas in which it is important to measure optical absorptions of a solute that are significantly less than background absorptions due to the solvent or solute. For example, the ability to detect trace amounts of actinide compounds having low solubility in ground water is important for nuclear waste management. The high optical absorptivity of water makes this problem particularly difficult. Techniques with the sensitivity to detect weak solute absorptions have to contend with noise on the larger background signal. In these cases, the minimum detection limit of these techniques may not be realized

because of the background noise. To regain the maximum detection capabilities of these methods, it is advantageous to have a differential method of measuring weak absorptions in which the large background absorptions are nulled out.

We have developed a thermo-optic, interferometric method of measuring small differences between weak optical absorptions of solutions. A signal that would be produced by the interferometer in a nondifferential configuration was suppressed by a factor greater than 400 by using the interferometer in a differential mode. With the background signal suppressed, differences in absorptivity between the cells $\sim 1/100$ th of the background were measured. The smallest absorption measured with the interferometer was $\sim 5 \times 10^{-6} \text{ cm}^{-1}$, which is comparable to or below that actually measured using other thermooptic techniques.

In Fig. 2, a comparison is made between results obtained with the apparatus in a differential and nondifferential configuration. The advantages of the differential technique are already evident.

An analytical curve for I_2 in CCl_4 is shown in Fig. 3. The detection limit (signal $\geq 2\sigma$) is

Fig. 2.

Comparison of results obtained with the apparatus in a differential (O) and nondifferential (□) configuration. In both cases, the background absorption was $2.3 \times 10^{-3} \text{ cm}^{-1}$. The solute absorptivity (α_s) added to one cell to increase the absorption above the background level is plotted on the abscissa.

Fig. 3.

Demonstration that the smallest absorptivity measurable with the interferometer is $\sim 5 \times 10^{-6} \text{ cm}^{-1}$. The solution was I_2/CCl_4 and the laser power was 100 mW.

$\sim 5 \times 10^{-6} \text{ cm}^{-1}$ in the presence of background absorption by CCl_4 of 1.2×10^{-5} .

With CH_3OH as solvent, an increase in absorptivity of one cell $\sim 2 \times 10^{-5}$ could be detected in the presence of a background absorption of $2.3 \times 10^{-3} \text{ cm}^{-1}$. In water, the smallest absorptivity measurable was $3 \times 10^{-4} \text{ cm}^{-1}$. The poor performance in water reflects the fact that water is not a good solvent for thermo-optical measurements.

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1. D. A. Cremers and R. A. Keller, "Thermo-optic-Based Differential Measurements of Weak Solute Absorptions with an Interferometer," LA-UR-2807, submitted to Appl. Opt.

D. The Use of the Optogalvanic Effect and the Uranium Atlas for Wavelength Calibration of Pulsed Lasers¹ (N. J. Dovichi, D. S. Moore, and R. A. Keller)

We have demonstrated that the optogalvanic effect in a commercial hollow cathode discharge can be used to calibrate the wavelength scale of a cw dye laser to an accuracy of $\pm 0.002 \text{ cm}^{-1}$.²

A similar technique for the wavelength calibration of pulsed lasers in the visible spectral region, or any laser in the ultraviolet spectral region, is complicated by wavelength independent photoelectron emission that results when high intensity laser light strikes the cathode surface. Photoelectron emission is especially troublesome in the ultraviolet spectral region where the photon energy exceeds the work function of uranium metal (3.63 eV). In the presence of this background signal, wavelength dependent signals associated with uranium transitions can be difficult or impossible to observe.

We have constructed a tubular hollow cathode discharge tube such that the laser light can pass through the center of the discharge without striking the cathode surface. Using this tube, we have shown that optogalvanic signals (OGS) associated with uranium transitions can be observed with excellent signal to noise when the discharge

is irradiated with the output of a pulsed, tunable laser. With this tube, the nonresonance background signal is minimal even in the ultraviolet spectral region (Fig. 4). We have demonstrated that this system can be used to calibrate the wavelength of pulsed lasers, and we have compared the magnitude of the OGS to the uranium emission spectrum intensity in several wavelength regions. The results for the ultraviolet spectral region are shown in Fig. 4.

We have also shown that a commercial hollow cathode discharge tube can be used as a wavelength standard for pulsed lasers at wavelengths $>3500\text{\AA}$, if the laser power is kept low enough to minimize nonresonance background contributions.

Fig. 4.

Comparison of the ultraviolet OGS from the tubular discharge tube (top) with the ultraviolet emission from a commercial hollow cathode lamp (bottom).

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- E. Accurate Wave-Number Measurements of Uranium Spectral Lines¹ (B. A. Palmer, R. A. Keller, F. V. Kowalski, and J. L. Hall)

The uranium emission spectrum is useful as a wave-number standard for calibrating spectrographs, monochromators, and tunable lasers. The spectrum has many sharp lines widely distributed throughout the IR, visible, and UV spectral regions, which provide a selection of strong lines in any region of the spectrum. Other advantages of the spectrum include small Doppler width, absence of hyperfine structure, and availability of commercial emission sources.

An atlas of graphs showing the emission spectrum of uranium in the region of $11,000\text{--}26,000\text{ cm}^{-1}$, along with tables of wave numbers, relative intensities, and assignments has been issued.² Data for the atlas were obtained by recording the emission spectrum from a uranium hollow-cathode discharge on the Fourier-transform spectrometer (FTS) at Kitt Peak National Observatory. The wavenumber accuracy was estimated as $\pm 0.003\text{ cm}^{-1}$. Possible systematic errors in the wave numbers listed in the atlas were due to (1) uncertainties in the absolute wave number of the He-Ne laser used as a reference in the FTS, (2) small angular misalignment between the source and the He-Ne reference, (3) improper correction for wave-number-dependent phase shifts on reflection at the mirrors, and (4) inaccuracies in the location of the zero path difference. The wave numbers reported in the atlas are absolute in the sense that all corrections were made to the best of our ability and no arbitrary

adjustments were made to bring the results into agreement with previous measurements of uranium emission spectra. The agreement among the FTS results and previous measurements at Los Alamos and at the Laboratoire Aimé Cotton supports the accuracy of all three sets of measurements.

To check the accuracy of the wave numbers reported in the atlas and to provide benchmarks of higher accuracy, we measured the wave numbers of 10 uranium lines. The optogalvanic effect (OGE) was used to position a tunable dye laser at the center of the optical transition. An evacuated scanning interferometer (lambda meter) was used to compare the wave number of the laser with the wave number of an iodine-stabilized He-Ne laser. The absolute wave numbers of the uranium lines were measured with an accuracy of $\pm 0.0006 \text{ cm}^{-1}$. For the 10 lines, the average difference between the atlas measurements and the work reported here is

$+0.0007 \text{ cm}^{-1}$ (atlas-present), which is well within the estimated accuracy of the atlas. We also measured the wave numbers of two thorium lines with an accuracy of $\pm 0.0006 \text{ cm}^{-1}$, and we found that our results agreed with previous measurements. Our results are summarized in Tables I and II.

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TABLE I
COMPARISON OF WAVE-NUMBER MEASUREMENTS ON URANIUM WITH PREVIOUS VALUES

JILA ($\pm 0.0006 \text{ cm}^{-1}$)	Los Alamos FTS ^a ($\pm 0.002 \text{ cm}^{-1}$)	Los Alamos ^{b,c} ($\pm 0.01 \text{ cm}^{-1}$)	LAC ^d ($\pm 0.003 \text{ cm}^{-1}$)	Tube	Gas	Current (mA)	Power (mW)
16900.3852				B	Ne	25	2.2
16900.3853				B	Ne	25	2.4
16900.3859				B	Ne	11	2.4
16900.3860				B	Ne	35	2.6
16900.3850				B	Ne	25	92
16900.3855	16900.3866	16900.3806	16900.3875				
15501.6084				B	Ne	25	20
15501.6087				C	Ar	25	20
15501.6086	15501.6094	15501.6179	-				
15631.8548	15631.8548	15631.8560	-	A	Ne	25	-
15638.3657	15638.3668	15638.3587	-	A	Ne	25	18
15688.2119	15688.2116	15688.2000	-	A	Ne	25	24
16309.4344	16309.4360	16309.4332	16309.4370	B	Ne	25	20
16450.1442	16450.1454	16450.1446	16450.1465	B	Ne	25	9.2
16505.7725	16505.7721	16505.7694	16505.7731	B	Ne	25	12.4
16929.7582	16929.7590	16929.7579	-	B	Ne	25	80
17070.4676	17070.4685	17070.4670	17070.4692	B	Ne	25	10

^aB. A. Palmer, R. A. Keller, and R. Engleman, Jr., Los Alamos Scientific Laboratory report LA-8251-MS, July 1980.

^bD. W. Steinhaus et al., Los Alamos Scientific Laboratory report LA-4501, October 1971.

^cThe wave numbers listed in this column are from measurements made on strong lines and exhibit larger-than-average errors because of some self-reversal.

^dS. Gerstenkorn et al., Astron. Astrophys. **58**, 255 (1977).

TABLE II
COMPARISON OF WAVE-NUMBER MEASUREMENTS
ON THORIUM WITH PREVIOUS VALUES^a

JILA ($\pm 0.0006 \text{ cm}^{-1}$)	Los Alamos FTS ^b ($\pm 0.003 \text{ cm}^{-1}$)	NBS ($\pm 0.0014 \text{ cm}^{-1}$)
16250.3971	16250.3980	16250.3976
16558.0209	16558.0201	16558.0193

^aNeon-filled hollow cathode operated at 25 mA. Laser power 30 mW.

^bUnpublished values from a thorium atlas in preparation.

^cA. Giachetti², R. W. Stanley, and R. Zalubu, J. Opt. Soc. A. 60, 474 (1970).

F. Laser Photoionization Mass Spectroscopy¹ (C. M. Miller and N. S. Nogar)

The mass spectral analysis of atomic mixtures can be extremely difficult in cases where the element(s) of interest is multiisotopic, and there exist isobaric interferences in the samples of interest. This problem is particularly common in analysis in weapons radiochemical diagnostics. A potential method for overcoming this difficulty is the use of narrow-band lasers to selectively photoionize only the element of interest, thus eliminating the production of isobaric ions.

We are currently using excimer lasers, and excimer-pumped dye and photodissociation lasers as the light sources for photoionization-time of flight mass spectrometry (see Fig. 5). Initial experiments on ArF-laser single photo photoionization of Yb have produced detection limits $\leq 10 \text{ ng}$ (Fig. 6) and ionization selectivity with respect to Lu ≥ 5 . Furthermore, we have demonstrated the ability to ionize $\geq 90\%$ of the atoms passing through the laser focal volume during the laser pulse. This suggests that much lower detection limits can be expected, probably $< 1 \text{ pg}$. Further, the technique used appears to have widespread applicability (Table III).

To improve selectivity, we are exploring the use of multiphoton photoionization processes that utilize optical resonances with real

Fig. 5.

Schematic of experimental apparatus. Abbreviations: M=Mirror, I=Iris, L=Lens, PM=Power Meter, BS=Beam Stop, CP=Cryopump, EM=Electron Multiplier, DISC=discriminator, MCS=multichannel Scaler, DDG=Digital Delay Generator, MINI=Minicomputer (11/34), HC=Hard Copy. In this view, the sample filament is 2 cm behind the laser beam as it passes through the source region.

Fig. 6.

Sample-size dependence of the ion signal for pulse energies of 10 mJ. Samples were $\text{Yb}(\text{NO}_3)_3$ evaporated from a 1700°C Re filament and interrotated for 1 min. Error bars represent standard deviation for three (Δ) or more than three ($\cdot$) analyses of the same sample.

TABLE III
AUTOIONIZING STATES OF THE LANTHANIDES
ACCESSIBLE WITH PRIMARY OR RAMAN-SHIFTED
EXCIMER LASER WAVELENGTHS

Element	Energy Level (eV)	Primary Laser medium	Shifting Medium	Shift ^a
La	5.961	ArF	HD	S ₁
Ce				
Pr	5.900	ArF	H ₂	S ₁
Nd	5.547	ArF	L-N ₂	S ₅
Pm				
Sm	6.039	ArF	D ₂	S ₁
Eu	5.672	ArF	D ₂	S ₁
Gd	6.126	ArF	L-N ₂	S ₁
Tb				
Dy	6.019	KrF	H ₂	AS ₂
Ho	6.101	KrF	D ₂	AS ₃
Er	6.153	ArF	CD ₄	S ₁
Tm	6.789	ArF	CH ₄	AS ₁
Yb	6.419	ArF	--	--

^aS = Stokes Shift, AS = Anti-Stokes, numerical indicates order of shift.

intermediate states. Using 452 nm radiation from a tunable dye laser to ionize Lu via a resonance enhanced two-step process, we have observed ionization selectivity $\geq 50:1$, compared to Yb or Cs at the same wavelength. We are currently exploring the analytical potential of this ionization scheme. Multiple photon ionization schemes based on the use of photodissociation lasers are also being pursued. Photolysis of TII with the 193nm output of an ArF laser produces lasing on a Tl excited-to-ground state transition at 376 nm. This laser output can, in turn, be used to photoionize Tl via a resonance enhanced two-photon process. We anticipate this ionization process to be both highly selective, because the laser light is necessarily resonant with a Tl transition, and very sensitive, because all hyperfine states can be addressed simultaneously.

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II. ATMOSPHERIC CHEMISTRY AND TRANSPORT

A. Ten Years of Stratospheric Sulfate Measurements Compared with Volcanic Activity (W. A. Sedlacek and E. J. Mroz, A. L. Lazrus* and B. W. Gandrud*)

The existence of a layer of sulfate aerosols in the lower stratosphere was discovered by Junge and Manson¹ in 1960. Since that time, a few measurements have confirmed its presence and given rise to various thoughts about the extent and source of the layer. There is still some difference of opinion as to the proportions of the sulfate that come from biogenic, anthropogenic and volcanic sources. The aerosols in the lower stratosphere have been shown by numerical models to have considerable impact on the surface temperature of the earth and, hence, climate. Measurements following a few of the very large volcanic eruptions in the past 100 years confirm the general conclusions of these models.

Project Airstream² aerosol filter samples have been analyzed for sulfate during about the last ten years. This past year we have retrieved data from files here and at the National Center for Atmospheric Research (NCAR), retrieved and analyzed filters that had been in storage at NCAR and the USDOE Environmental Measurements Lab. (EML), and developed computer codes to examine the data as a complete set. Each sampling cycle yielded about 100 data points with each sample spanning approximately three degrees of latitude at a particular altitude. Four altitudes are covered at each latitude. The latitude range was 75°N to 51°S in the early 1970's but has been reduced to 75°N to the equator in recent years. Examination of the data points revealed great variations in local sulfate concentrations, that ranged from 0.1 parts per billion by

* National Center for Atmospheric Research.

mass (ppbm) to over 10.0 ppbm. Often locales having significantly high sulfate concentrations could be associated with explosive volcanic eruptions that had been observed to inject material to stratospheric altitudes. However, there were also similar regions of enhanced sulfate for which no documented volcanic injection could be found. In three of these cases, subsequent investigation into meteorological and satellite image data revealed volcanic sources that had previously gone unobserved.³⁻⁵ We now believe that there are potentially as many as eight additional such poorly documented volcanic injections into the stratosphere during 1971 to 1981. The number of these episodes, eleven, is not greatly different from the number of documented stratospheric volcanic injections, nineteen, during the same time period (three of these would not have been documented in the stratosphere except for fortuitous examination of GOES satellite photos).

We have attempted to determine what fraction of the stratospheric sulfate aerosol came from volcanic origins. By averaging the data from each sampling cycle and plotting vs time (Fig. 7) we are presented with a picture of the variations in

Fig. 7.

Average stratospheric sulfate concentrations for each sampling cycle as a function of collection time. Total data and only northern hemisphere data are plotted separately. After April 1974 sampling did not extend very far into the southern hemisphere except for October 1980. Documented stratospheric injections of volcanic debris and undocumented but "sulfate-suggested" injections are indicated by time dependent arrows along the top.

sulfate aerosol concentrations. Large values are clearly associated with the major volcanic eruptions of Fuego volcano in 1974, the series of eruptions of Mt. St. Helens in 1980 and the recent eruptions of Alaid and Pagan. Based on the presumption that stratospheric sulfate that originated from biogenic and anthropogenic sources at the earth's surface should be in a state of near chemical equilibrium because of its nearly constant production rate and the time delay in diffusion from the surface to the stratosphere, we concluded that sulfate concentrations from these sources could not exceed the lowest values observed. Two time periods of relatively constant low sulfate concentrations occurred during the decade, mid 1973 to early 1974 and late 1978 through 1979. Using the data from these two periods to establish an ambient sulfate concentration that might come only from nonvolcanic sources and comparing that with the average for the entire decade revealed that at least 55% of the stratospheric sulfate present during the decade of the 70's was clearly of volcanic origin. As a check of this conclusion, we tried weighting the data by the number of samples in each cycle and also by partitioning into northern and southern hemispheres. The results varied from 53% to 57%. This result is only a lower limit for the fraction of the stratospheric sulfate resulting from volcanoes, because we can not exclude noneruptive volcanic sources that release sulfur gas species into the boundary layer with subsequent diffusion to the stratosphere, or slower chemical conversion of more stable sulfur gases injected into the stratosphere, from contributing to the ambient stratospheric sulfate.

A third conclusion from the decade of stratospheric sulfate data is the rate at which volcanic debris injected into the stratosphere is removed from the stratosphere. The sulfate aerosol injected by Fuego volcano in October 1974 had an e-fold removal rate of 11.5 months. Calculation of a removal rate for debris from the 1980 eruption of Mt. St. Helens is precluded by interference from following eruptions of Mt. St. Helens itself, Gareloi, Alaid, and Pagan. These rates are dependent, of course, on the altitudes at which the volcanic debris is put into the stratosphere, the nature of the material (distribution of particle sizes

and fraction that is ash vs sulfur species), the latitude of the injection, etc.

Hofmann and Rosen⁶ have contended, by comparing ambient periods in their balloon-borne dustsonde data to the data of Junge from 1960, that there is a 9% per year rise in stratospheric sulfate that they attribute to anthropogenic sources. Our work may suggest a 7% per year increase, but the data on which this conclusion would be based are those which have the smallest signal to noise ratio and, consequently, the least precision. If indeed fossil fuel combustion is contributing to the ambient stratospheric sulfate aerosol (which produces a cooling effect at the earth's surface) and also contributing to the increasing atmospheric CO₂ concentration (which produces a warming effect at the earth's surface), this is an instance of natural buffering of man's influence.

There are obviously several more things to be learned from this data set about rates of dispersion, stratospheric transport, turbulence, and climatic effects that we have not yet begun to examine.

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B. Atmospheric Tritium and ¹⁴CO₂ (A. S. Mason)

The airborne atmospheric tritium program and its support of the USDOE Environmental Measurements Laboratory's ¹⁴CO₂ activities became part of Project Airstream at the beginning of FY 1981. CNC-7 assumed scientific direction of the program in addition to continuing the field support it had provided since 1975.

The October 1980 deployment marked the first substantial stratospheric tritium sampling in the Southern Hemisphere and established an excellent baseline for future studies in that region. There had been no significant tritiated water vapor (HTO) inputs into either hemisphere since 1976. This 4-year time span is a factor of 3 to 4 longer than the characteristic times for interhemispheric and stratosphere-troposphere exchange, thus the profiles and inventory obtained reflect a quasi-equilibrium condition. Figure 8 shows the HTO profiles obtained. The April and July 1981 deployments were conducted in the Northern Hemisphere, extending the unique long term data base for study of water and hydrogen transport and chemistry by tracer applications.

Interpretive efforts with the HTO data have resulted in improved estimates of the removal time of water from the lower stratosphere. This has considerable significance in the modeling of atmospheric chemistry in the altitudes significantly impacted by air transport exhaust products.

Operational utilization of the tritium sampling equipment for collection of CO₂ was first performed last October with good success. This accomplishment permitted the replacement of an obsolete whole air sampling system by an improved and cleaner system in July. Although the new system is unable to collect a sufficient sample for ¹⁴CO₂ determination, it is highly superior in all other respects. The EML is procuring additional sampler components for further expansion of the ¹⁴CO₂ collection program.

Fig. 8.

Atmospheric HTO concentration isopleths in pCi/SCM from Airstream 20 deployment in October 1980. The dotted line represents the average tropopause height along the flight path. Isopleths were generated by weighted interpolation of adjacent data points.

Atmospheric $^{14}\text{CO}_2$ data are important in the study of the global climatic impact of fossil fuel burning because they are a measure of the dilution of contemporary CO_2 , which has a modern ^{14}C content, with fossil CO_2 from which the ^{14}C has decayed.

A cooperative effort is underway in Los Alamos to design a local system for extraction of atmospheric tritium and CO_2 samples from collection traps. The equipment will support both H-Division's new ground level HT/HTO sampler and the CNC-Division Project Airstream sampler. Both samplers are based on technology developed at the University of Miami. The available tritium counting equipment is adequate for the health-related project, but does not at present offer the sensitivity required for the meteorology and atmospheric chemistry applications.

C. Ultrasensitive Analysis of Heavy Methanes (M. Fowler, J. Wilhelmy, J. Tesmer (P-9))

Progress toward the FY 1981 goal of demonstrating that the vertical Van de Graaff accelerator could be used to measure very low abundance ratios of $^{13}\text{CD}_4$ in CH_4 has been limited by the available accelerator time. Additionally, an accident involving the accelerator's elevator has further limited available time.

We considered several detection methods and chose an electrostatic analyzer as part of the detection scheme. During June we had the first opportunity to accelerate CD_4^+ in the Van de Graaff. $^{12}\text{CD}_4$ was chosen for this trial rather than $^{13}\text{CD}_4$ to prevent possible contamination problems. During this run, $^{12}\text{CD}_4^+$ was accelerated to 3 MeV and

yielded several unanticipated beams ranging from mass = 1 to mass = 32. The gas consumption of the ion source was estimated to be a few cc/h, an encouraging result.

Subsequent to this first run, the detection scattering chamber was finished and installed on one of the 4 in. beam lines. A second test with $^{12}\text{CD}_4$ was made using the new scattering chamber and a 0.1 mg/cm^2 gold scattering foil. In this experiment we again observed several unexplained peaks in the scattered ion spectrum. Another experiment using O^- and OH^- gave scattered O^- ions of the predicted energies. These data are shown in Fig. 9.

We plan to repeat the CD_4^+ experiments and to characterize the scattered molecular fragments. Installation of a generating voltmeter (GVM) should allow much more precise measurement and control of the accelerator voltage. We will then try to implement the full detection scheme as outlined in last year's annual report. We hope that we can then address the problems of tuning and operation of the accelerator with essentially zero extracted beam.

Fig. 9.

Oxygen ions scattered at 48.9° by a 0.10 mg/cm^2 gold foil.

Finally, we will try to actually make some quantitative measurements and decide if we must resort to a different type of ion source (electron bombardment vs duoplasmatron).

D. Atmospheric Studies in Complex Terrain (ASCOT)

(M. Alei, J. P. Balagna, J. C. Banar, C. J. Duffy, D. W. Efurd, M. M. Fowler, D. J. Frank, P. R. Guthals, J. D. Knight, A. E. Norris, G. E. Oakley, A. E. Ogard, and D. J. Rokop)

A series of five meteorological tracer experiments was performed to study nocturnal airflows in the geothermal power production area in Northern California. The objective of these experiments was to generate a set of data to provide inputs to subsequent modeling efforts. Of particular importance in this case is the need to assess the impact of the developing power industry in this area. Although a large number of participants from many laboratories were involved in various aspects of these experiments, the main contribution by the division to the project was providing tracer experiments using two tracers, $^{12}\text{CD}_4$ and $^{13}\text{CD}_4$, developed at Los Alamos.

In each experiment the two tracers were released simultaneously but at different elevations to elucidate the relative vertical mixing of the air along the transport path. It was hoped to be able to learn about the interaction of the shallow drainage winds flowing down the valleys with the warmer air aloft. The tracers were contained in small pressurized bottles and flowed to the release points via plastic tubing. For the elevated releases, the tracer delivery tube was held aloft with a 5-m^3 tethered helium-filled balloon. Sampling was made by collecting whole air samples of 5 to 30 l in volume.

Figure 10 shows the area studied along with the location of the release and the samplers. The heavy methane tracer release location is designated by H.M. Integrated 8-h samples were collected at the numbered locations using Los Alamos-developed samplers. Half-hour sequential samples were also collected over an 8-h period at positions S-1 and S-4. In addition, vertical profiles were determined at position S-4 and the Sandia National Laboratory site.

Fig. 10.

General Area Map of ASCOT Experiments in Northern California. Coordinates are UTM coordinates in miles.

Samples collected from four of the five experiments have been analyzed and modeling of the data has begun. Some of the results from experiment 4 are shown in the accompanying figures. The results from the two sequential samplers are shown in Figs. 11 and 12. Only the data for $^{13}\text{CD}_4$ are shown here since the $^{12}\text{CD}_4$ tracer exhibited similar behavior. The leading edge of the $^{13}\text{CD}_4$ tracer plume arrived at position S-1 about 30 min. after the start of the release, indicating a mean transport speed of about 1.0 m/s. The arrival of the plume at position S-4 was delayed by about 1.5 h corresponding to a plume speed of about 1.1 m/s between S-1 and S-4. At both S-1 and S-4 the bulk of the plume had passed in a period of about 1 h after the onset.

Vertical profiles of the tracers measured at position S-4 as a function of time are shown in Fig. 13. Here it is interesting to note that the highest concentrations of the tracers were measured in the 0 to 400-ft elevation range even though the $^{12}\text{CD}_4$ was released at 300 ft above ground level and that very little of either tracer was observed at the highest sampling altitude. The passage of the plume as inferred from the time sequence of the

Fig. 11.

$^{13}\text{CD}_4$ concentration as a function of time at position S1 during ASCOT experiment 4.

Fig. 12.

$^{13}\text{CD}_4$ concentrations as a function of time at position S4 during ASCOT experiment 4.

Fig. 13

Heavy methane tracer concentrations measured as a function of time and altitude at position S4 during ASCOT experiment 4.

vertical profiles is in good agreement with that measured by the sequential sampler at the same location (S-4).

Another set of vertical profiles was measured at a site (SNL) about 2.3 km from S-4. The results of these measurements are shown in Fig. 14. The data are presented in a different format than that in Fig. 13 because the samples were essentially instantaneous measurements. The points of interest are that the plumes at the SNL site are elongated relative to that at S-4 and that the plumes of both tracers arrived at the same times and peaked at about 2.5 h after the start of the release. It is also noteworthy that the plumes arrived at the SNL station about 1/2 to 1 h later than at S-4 even though the SNL station was 2.3 km farther from the release point. Essentially no $^{13}\text{CD}_4$ was observed at the highest altitude (1000 to 1500 ft) as in the case for S-4 but $^{12}\text{CD}_4$ was observed

at the highest altitudes sampled. Finally, the concentrations of tracers measured at the SNL station are about a factor of 10 lower than at S-4, and the highest concentrations of tracers are still observed near the ground. No results from the integrated samples are presented here because of the difficulty in relating the various sites without including the topography and winds.

Estimates have been made of the total amount of tracer passing the sequential samplers, and it is possible to account for all of the $^{13}\text{CD}_4$ released, but there must have been a substantial amount of $^{12}\text{CD}_4$ in locations where no sampling took place. The most likely explanation at this time is that the $^{12}\text{CD}_4$ was mixed into winds above the ground boundary layer and was transferred out of the experimental area. A detailed analysis of the winds present during the experiment is underway to verify this hypothesis.

Fig. 14.

Heavy methane tracer concentrations measured as a function of time and altitude at the SNL Balloon Sampling Site during ASCOT experiment 4.

The data from these tracer experiments will be combined along with tracer results from the other ASCOT participants to form a data set describing the general nocturnal air shed in the experimental area.

To facilitate analysis of the large number of samples from these experiments, a second system for separation of methane from air samples was constructed, tested and put into operation. Over a period of several months more than 300 samples returned from the ASCOT experiments were successfully processed on this apparatus.

The apparatus used for transferring air samples from plastic bags (up to 20 l volumes) into metal cylinders has been converted from manual to pneumatic valve operation. The piston transfer pump has been replaced by a bellows model that may be evacuated and will compress air from an inlet pressure of 1 atm to a maximum outlet pressure of 115 psi. The entire apparatus has been assembled in a cabinet mounted on wheels for easy mobility.

III. BIOCHEMISTRY

A. Nuclear Magnetic Resonance Studies of the Interaction of Bacterial Dihydrofolate Reductase with Specifically Labeled Inhibitors (R. E. London, R. L. Blakley,* L. Cocco,* J. P. Groff,* C. Temple, Jr.,** and J. A. Montgomery,**)

Nuclear magnetic resonance (NMR) is the only spectroscopic technique capable of probing individual nuclei of complex molecules or mixtures of molecules in solution. We have previously carried out NMR studies of dihydrofolate reductase in which a strain of *S. faecium* auxotrophic for the amino acids was utilized to obtain the specifically labeled enzyme. Labeling experiments utilizing [methyl- ^{13}C] methionine, [guanido- ^{13}C] arginine, and [γ - ^{13}C] tryptophan have been carried out, allowing studies of the dynamic characteristics of the enzyme, as well as a characterization of the interactions with substrate, cofactors, and inhibitors. Dihydrofolate reductase is of particular interest because it is a target for chemotherapeutic agents such as methotrexate, used in the treatment of various types of cancer, and trimethoprim, an inhibitor of bacterial reductase, which is now used extensively in combination with sulfa drugs for treating a variety of infectious diseases.

To obtain information of value in understanding the molecular basis for the inhibitory action of these drugs, an alternative labeling approach was followed in which the drug, rather than the enzyme, was isotopically labeled. The C-2 position of the pteridine ring of the inhibitors was selected as the optimal site for carbon-13 enrichment for several reasons: (1) quaternary carbons such as C-2 show minimal broadening in biological macromolecules, and thus give resonances that are relatively sharp and readily resolved; and (2) this position is adjacent to the protonation site at N-1 of the pteridines and hence its NMR parameters, particularly the chemical shift, would be sensitive to protonation believed to be important in determining the affinity of these drugs for the following enzyme.

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¹³C NMR studies carried out with the labeled methotrexate in solution indicated a high sensitivity of the chemical shift of the C-2 resonance to protonation of N-1, with a total shift of about 6.0 ppm.¹ The pK for the drug was determined to be 5.73. In contrast, studies with the enzyme complexed methotrexate indicate that it is protonated beyond pH 10.0.^{1,2} This dramatic increase in pK reflects the strong hydrogen bonding interaction between the protonated drug and the enzyme. Although such an interaction is known to occur from the crystal structure determined for the corresponding enzyme from *L. casei*,³ a determination of the change in pK is critical to an understanding of the inhibition mechanism of this class of drugs. Thus, previous determinations of the pK of the bound drug utilizing uv difference spectroscopy indicated a value of 8.55 for the pK of bound methotrexate.⁴ As a result of the relatively smaller change in pK in the enzyme-drug complex, factors other than the hydrogen bonding interaction to N-1 were implicated in the inhibition mechanism. In contrast, our results indicate that this single interaction is sufficient to produce the high inhibitory potency observed for methotrexate. This labeling approach is optimal for probing specific drug-enzyme interactions.

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B. Conformational and Dynamic NMR Studies of Biologically Active Peptides (R. E. London, C. J. Unkefer,* J. M. Stewart,** and J. R. Cann**)

During the past decade there has been an increasing awareness of the physiological importance of biologically active peptides. Recently developed solid phase peptide synthesis techniques provide an ideal methodology for the incorporation of stable isotopes into various systems of interest. In collaboration with Profs. John M. Stewart and John R. Cann at the University of Colorado Medical School, we have utilized these labeling techniques in studies of the biologically active nona-peptide, bradykinin, sequence: Arg-Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg. The kinins exhibit a broad range of pharmacological actions that include contraction of the uterus, ileum, and venules; bronchoconstriction; relaxation of the duodenum and arterioles (leading to lowered blood pressure); increased capillary permeability; leucochemotaxis; and causation of pain.¹

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Carbon-13 chemical shift analysis as a function of pH and spin lattice relaxation measurements indicate that the peptide is conformationally mobile in solution.² Alternatively, circular dichroism (CD) measurements have suggested that the Ser⁶-Pro⁷-Phe⁸ residues of the peptide adopt an intramolecularly hydrogen bonded γ -turn structure, the probability of which is temperature dependent. The NMR measurements have shown that this is at most a minor conformer of the peptide, the probability of which does not appear to be temperature dependent.^{3,4}

Our more recent studies of the peptide have focused on the three proline residues that play a significant role in determining peptide conformation. In contrast to the conformational homogeneity of peptide bonds formed with amino acids that are trans planar, peptide bonds formed to imino acids such as proline tend to adopt either the cis or trans geometries, with the cis and trans structures defined in terms of the orientation of successive α -carbons. All of the peptide bonds involving Pro residues of bradykinin were found to be predominantly trans, however, an unexpected conformational heterogeneity was found in the bradykinin analog in which Gly replaced Ser at position 6: ([Gly⁶]-bradykinin). NMR studies utilizing an isotopically enriched peptide, [90%-1,2-¹³C₂Gly⁶]-bradykinin, indicate that this heterogeneity reflects the presence of both cis and trans isomers of the Gly⁶-Pro⁷ peptide bond.⁵

More recently, each of the Pro residues in the peptide has been replaced with AIB (α -aminoisobutyric acid) residues. The latter represent a more conformationally constrained amino acid that is analogous to one of the possible conformational forms of proline. Bioassay results indicate that only the AIB⁷ substituted analog is relatively active.⁶ Recent NMR studies carried out in DMSO solvent indicate that the AIB² and AIB³ analogs have a much higher probability for adopting a β -turn conformation involving the four N-terminal residues. It therefore appears that this conformation is inactive. Further studies of the peptide analogs in water, as well as parallel CD studies, are currently in progress.

The cis/trans conformational heterogeneity noted above for the Gly⁶-bradykinin has also been

observed in other biologically active peptides. For example, a pH dependent cis/trans ratio has been observed in angiotensin, presumably corresponding to the His⁶-Pro⁷ bond.⁷ In this case, it was proposed that this ratio might be an important determinant of biological potency. To understand this phenomenon better, we have recently carried out studies of the dipeptide, His-Pro, as well as the tri-peptide, Acetyl-His-Pro. In addition to our carbon-13 NMR studies, ¹H NMR spectra were obtained at 400 MHz in Trondheim, Norway. Analogous to the observations in angiotensin, increase in pH leads to a dramatic increase in the cis/trans ratio, with the deprotonation of the imidazole side chain clearly the significant factor. The ¹H NMR analysis indicates that at lower pH, the protonated imidazole forms an ionic bond with the terminal carboxyl group, stabilizing the trans conformation. This stabilization is lost as the imidazole is deprotonated, increasing the cis/trans ratio.

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C. In situ Metabolic Studies of Microorganisms and Perfused Organs Using Isotopic Labeling and Nuclear Magnetic Resonance (T. E. Walker, C. H. Han, J. Y. Hutson, R. E. London, W. E. Wageman, C. B. Storm,* C. J. Unkefer,** and N. A. Matwiyoff)

We have extended our studies with *Microbacterium ammoniaphilum* to include several *in vivo* ¹³C NMR experiments using [1-¹³C]glucose as a substrate.¹ From these results we have been able to observe the effects of oxygen on the levels of various metabolites as shown in Fig. 15. The level of succinate is low with sufficient aeration but increases significantly following a cut off of oxygen. The effect on L-lactate is even more dramatic, increasing from undetectable levels and then decreasing upon resumption of the oxygen flow. Two interesting metabolites were also observed, α , α -trehalose and α - and β -glucosylamine. Although the trehalose is a naturally occurring disaccharide² (particularly in yeasts), the glucosylamine appears to be an artifact derived from the reaction of glucose and ammonium ion present at relatively high concentrations.³

We have been able to quantitate several biochemical pathways important for the synthesis of L-glutamate by carefully evaluating the label

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Fig. 15.

Time dependence of the metabolite intensities from a series of proton decoupled Fourier transform ¹³C NMR spectra (25.2 MHz) of an oxygenated suspension of *Microbacterium ammoniaphilum* initially containing [1-¹³C (90 atom %)] glucose. The time given for each point is the interval for accumulation of the spectra after transfer of the cells to fresh medium containing [1-¹³C]glucose. Oxygen supply was cut off and restarted at the times indicated.

distribution in L-[¹³C]glutamate derived from [1-¹³C]glucose. The enrichment at C-4 in the product is equal to half the enrichment in the starting glucose provided that the only direct pathway to glucose is the Embden Meyerhoff pathway and the first third of the Krebs cycle. The percent participation of the phosphogluconate pathway can be calculated from Eq. 1 because the ¹³C-1 label is lost in the first step of the pathway.

$$f \cdot (\alpha_i/2) + (1-f) \cdot 0 = \alpha_o \quad (1)$$

In this equation, f is the fraction of molecules that are metabolized via the Embden Meyerhoff pathway, α_i the initial enrichment of the [1-¹³C] glucose and α_o the observed enrichment of C-4 in the product glutamate. By this technique, we calculate that only 13% of the glucose is processed by the phosphogluconate pathway.

Quantitation of the glyoxylate and Krebs cycle activities can be approached using the observed

glutamate enrichments and a mixture analysis of the different isotope isomers. It is important in this type of study to obtain accurate carbon enrichment values by ^1H NMR rather than by ^{13}C NMR because of the correlated nature of the carbon labeling that complicates the ^{13}C - ^{13}C coupling analysis in the ^{13}C NMR spectra. Table IV summarizes the important labeling pathways, the labeling patterns that result, and the percent participation of the different pathways. Clearly the most significant pathway (58%) is through phosphoenolpyruvate and the first third of the Krebs cycle. The observed Krebs cycle activity (6%) was initially unexpected because this cycle is presumably shut down because of the reduction of α -ketoglutarate dehydrogenase activity.⁴ Evidence for the activity of this cycle comes primarily from the observed negative correlation in the labeling of C-1 and C-2 of glutamate.

TABLE IV
POSSIBLE LABELING PATTERNS FOR C-2, C-3, AND C-4 OF
[^{13}C]GLUTAMATE DERIVED FROM [$1\text{-}^{13}\text{C}$]GLUCOSE

Pathway Designation	Labeling Pattern	Source of Label	Pathway %
X	$\overset{\circ}{\text{C}}_1\text{-}\overset{*}{\text{C}}_2\text{-}\overset{*}{\text{C}}_3\text{-}\overset{*}{\text{C}}_4$	Phosphoenolpyruvate carboxylase + 1/3 Krebs cycle	58
Y	$\left\{ \begin{array}{l} \overset{*}{\text{C}}_1\text{-}\overset{*}{\text{C}}_2\text{-}\overset{*}{\text{C}}_3\text{-}\overset{*}{\text{C}}_4 \\ \text{C}_1\text{-}\overset{*}{\text{C}}_2\text{-}\overset{*}{\text{C}}_3\text{-}\overset{*}{\text{C}}_4 \end{array} \right.$	Fumarase activity + single turn of glyoxylate cycle	26
Z	$\overset{*}{\text{C}}_1\text{-}\overset{*}{\text{C}}_2\text{-}\overset{*}{\text{C}}_3\text{-}\overset{*}{\text{C}}_4$	Multiple turns of Krebs or glyoxylate cycles	10
W	$\left\{ \begin{array}{l} \overset{*}{\text{C}}_1\text{-}\overset{*}{\text{C}}_2\text{-}\overset{*}{\text{C}}_3\text{-}\overset{*}{\text{C}}_4 \\ \text{C}_1\text{-}\overset{*}{\text{C}}_2\text{-}\overset{*}{\text{C}}_3\text{-}\overset{*}{\text{C}}_4 \end{array} \right.$	Single turn Krebs cycle	6

* Indicates a labeling probability α derived from the enrichment of the acetyl CoA.

$\circ$ Indicates a labeling probability β derived from the enrichment of the bicarbonate pool.

By following the enrichment at C-3 and C-4 in the experiment depicted in Fig. 15, we have further deduced that during the course of the reaction, the relative importance of the pathways changes such that only later does the glyoxylate pathway become important. If this pathway can be blocked by an appropriate inhibitor, we should be able to decrease the label at C-3 and thus produce [2,4- ^{13}C] glutamate that is more selectively enriched.

The yield of L-glutamate from acetate was poor from *M. ammoniaphilum*, therefore, we began working with *Brevibacterium flavum*,⁵ which produces L-glutamate in a yield of ca. 20% from acetate. The labeling pattern is the same as that derived from *M. ammoniaphilum*, namely [$1\text{-}^{13}\text{C}$]acetate produces [$1,5\text{-}^{13}\text{C}$]glutamate and [$2\text{-}^{13}\text{C}$]acetate produces [$2,3,4\text{-}^{13}\text{C}$]glutamate. The label at C-1 of glutamate, however, is actually observed in glutamate from both substrates, which suggests that when producing glutamate from acetate, the Krebs cycle must be very active in contrast to the results obtained from glucose grown cells.

An isoleucine requiring mutant of *B. flavum*⁶ is being used for the biosynthesis of ^{13}C and ^{15}N enriched L-proline from ammonium sulfate and glucose. The labeled L-proline will be used in a variety of NMR studies on the structure of proteins and peptides. Proline is a particularly interesting amino acid because of the possible cis-trans isomers and its importance in determining tertiary protein structure. The labeling pattern of ^{13}C enriched proline should be identical to that of L-glutamate produced from the same substrate by the parent organism. The mutant, however, produces only poor yields of L-proline from acetate and thus if one desires L-[$1,5\text{-}^{13}\text{C}$]proline, it must be made by a different route. Two possibilities are being pursued. In the first, the organism is grown on glucose, the cells harvested and transferred to a medium containing [$1,5\text{-}^{13}\text{C}$]glutamate. This technique presumably would require a second carbon source for energy production that could exchange with the labeled glutamate unless glutamate dehydrogenase activity is blocked. The second technique involves making a cell-free extract that is used

to catalyze production of L-proline from labeled L-glutamate. This method requires the addition of catalytic amounts of ATP and NADPH plus a system for regenerating them as they are used. The mutant B. flavum also produces varying amounts of alanine, valine and glutamate dependent on growth conditions and may prove to be a good source of these amino acids as well.

Our studies of ^{13}C -enriched amino acids have also been extended to the aromatic amino acids L-tyrosine and L-phenylalanine. These ring-labeled aromatic amino acids will be used in a variety of investigations aimed at understanding the metabolism of phenylalanine in the genetic disease phenylketonuria, in determining enzyme-substrate interactions, in making biophysical measurements on phenylalanine and tyrosine containing peptides, and on oxygen incorporation into neurochemical metabolic pathways. The best synthetic route to these amino acids is the synthesis of ^{13}C enriched phenol from [^{13}C]acetone, the biosynthesis of tyrosine from phenol using Erwinia herbicola and conversion of tyrosine to phenylalanine. The biosynthesis of tyrosine by E. herbicola⁷ proceeds by the enzyme β -tyrosinase operating in the reverse (anabolic) direction and is induced by growing the bacteria in the presence of L-tyrosine. This enzyme is very versatile and will utilize a variety of compounds as substrates, e.g. D- or L-serine, pyruvic acid, pyrocatechol, m- and o-cresols and m- and o-chlorophenols.

In addition to ^{13}C NMR studies on the metabolism and biosynthesis of labeled amino acids, we have begun a program of study of whole organs perfused with ^{13}C enriched substrates. Although the technique of organ perfusion is well documented,⁸ the application to the study of metabolism by ^{13}C NMR is relatively new.⁹ We are focusing initially on the mouse liver, which provides us with a wide range of experimental options including the uptake of glucose, the synthesis of glycogen, the metabolism of drugs, and gluconeogenesis. The microsurgical techniques necessary for perfusing an intact mouse liver are tedious; however, as we are able to use larger organs (such as rat liver) in larger NMR tubes, the procedures will become easier. We expect eventually to report on a variety of metabolic experiments involving not only liver but

other organs and tissues as well. Mammalian cells grown in tissue culture and labeled with ^{13}C enriched substrates will also be studied.

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The amino acid histidine is of particular interest in biological systems because it is known to be part of the active site of many enzymes. This activity is directly related to histidine's propensity for complexation of metal ions by way of the basic nitrogen of its imidazole ring. Figure 16 shows the structure of histidine and the various forms in which it exists in aqueous solution as a function of pH.

For the past several years we have been using ¹⁵N NMR to study the interaction in aqueous solution of Zn²⁺ and Cd²⁺ with imidazole, 1 methyl-imidazole and, most recently, histidine. We have found that the association of the metal ion with the basic nitrogen of the imidazole ring produces measurable shifts in the NMR signal for both nitrogens. From a study of the magnitudes and directions of these shifts as a function of solution composition and pH, we get information about the specific site of metal-ion attachment and the maximum number of imidazole rings associated with a single metal ion.

In the most recent study with histidine, we have shown that Zn²⁺ or Cd²⁺ can complex histidine in its amphionic form (Fig. 16) with complexation constants and ¹⁵N NMR shifts comparable in magnitude with those for complexation between the same metal ion and imidazole. In addition, the two tautomers ("βN₃" or "βN₁," Fig. 16) of the histidine amphion complex the metal ion with approximately equal facility. These results indicate that ¹⁵N NMR may prove to be a useful tool for studying the active sites in the more complex enzyme systems. Besides providing a possible means for distinguishing those histidine residues involved in the active site (associated with metal ion) from those which are not, the technique might also yield information about the geometry and kinetics of the metal-ion association.

IV. BIOMEDICAL RESEARCH

A. The National Stable Isotopes Resource

(N. A. Matwiyoff and R. E. London)

The national stable isotopes resource (SIR) is operated as part of the ICONs program, named for the isotopes of carbon (¹²C, ¹³C), oxygen (¹⁶O, ¹⁷O, ¹⁸O), and nitrogen (¹⁴N, ¹⁵N). The program encompasses the production of large quantities of the separated isotopes by the low-temperature distillation of CO and NO; the development of efficient synthetic methods for the incorporation of the isotopes into complex molecules; the improvement of techniques, especially nuclear magnetic resonance (NMR) and mass spectroscopy, for the analysis of isotopically labeled compounds; and participation with extramural investigators in cooperative research and development programs to develop the utility of stable isotopes in the biosciences and in environmental studies. The focus of the SIR, a joint effort of Groups CNC-4 and LS-5, is on developing uses of stable isotopes in the biosciences by

- Producing and providing enough separated ¹³C, ¹⁵N, and oxygen to support the program;
- Synthesizing labeled compounds for accredited investigators when those compounds are not readily available from commercial or other sources at acceptable costs;
- Developing an active program of research collaboration with investigators in the biosciences community, providing as necessary, isotope labeled compounds and analysis and data interpretation with NMR and mass spectrometry;
- Advising and assisting investigators using isotopes of carbon, oxygen, and nitrogen;

Fig. 16.

The amino acid histidine is shown in the various forms in which it can exist in aqueous solution depending upon pH. As pH is increased (from left to right in the above figure) the dominant species goes from the positively charged cation to the electrically neutral amphion to the negatively charged anion. In addition, the amphion and anion can each exist in two tautomeric forms distinguished by whether N₁ or N₃ of the imidazole ring is protonated.

- Hosting visiting scientists for training in use of stable isotopes and encouraging exchanges of talks, short courses, and extended research opportunities;
- Collaborating with other resources in synthesis and mass spectrometric and NMR analyses to speed development of isotope methodology; and
- Performing core research designed to keep the resource at a state-of-the-art level.

Highlights of several projects supported by the SIR during the past year are described below.

1. Total Body Water Measurement in Humans with ¹⁸O and ²H Labeled Water. Accurate and rapid determinations of total body water (TBW) would be valuable in many clinical situations. These include assessment of fluid status in patients with heart failure, renal failure, or severe burns. In addition to these clinical uses, TBW measurements were needed for the determination of body composition in nutritional studies. During the past four

decades, numerous indirect methods for the determination of total body water have been used. Each of these has been based on the dilution principle. Water-soluble tracers such as antipyrine or urea have been tried, but give rise to errors because the tracers are either bound to proteins, rapidly metabolized and excreted, or are slowly and incompletely distributed to all the body components. The best and most frequently used tracers have been water labeled with either tritium or deuterium. Deuterium or tritium labeled water traditionally has been used for the measurement of total body water by application of the dilution principles. However, these methods have not enjoyed wide clinical use. The use of deuterium is hampered by the tedious and time consuming nature of the analysis, whereas the use of tritium involves a radiation hazard. In addition, exchange of the label with nonaqueous hydrogen in the body raises questions about the accuracy of total body water values. Using isotopically labeled compounds obtained from the stable isotopes resource, Dr. P. D. Klein and

co-workers at the Baylor College of Medicine, Children's Nutrition Center and the MIT Clinical Research Center have shown that water labeled with ^{18}O can yield faster and more accurate results. Total body water was measured simultaneously using water labeled with both ^{18}O and ^2H . The ^{18}O and ^2H dilutions were measured by mass spectrometry. The relative precision of the body water value using the ^{18}O method was 2% for both serum and breath analysis. The ^{18}O was fully equilibrated within 2 to 3 hr after administration, and results from the analysis of breath CO_2 could be readily obtained within 1 hr after sampling. The H_2^{18}O dilution space averaged 3% less than the ^2HHO dilution space, because the latter exchanges with nonaqueous hydrogen. For this reason, the H_2^{18}O dilution should be a more accurate measure of total body water than the ^2HHO dilution.

2. Biosynthesis of L-Amino Acids Selectively Enriched with Carbon-13. The staff of the stable isotopes resource has developed many of the synthetic methods for the incorporation of stable isotopes into natural products, drugs, and other compounds of interest in tracer and structural studies. Current work is focused on the biosynthesis of those L-amino acids for which efficient organic synthesis methods are not now available and for which there is a need either in human metabolic and nutritional studies or in the investigation of the structure and dynamics of proteins enriched with labeled amino acids. In the use of biological systems for the selective enrichment of natural products there are two prime practical considerations: (1) the optimization of the incorporation of the ^{13}C label from the precursor into the product; and (2) the minimization of the degree to which the label becomes randomized in the product because of the flux of the precursor and its metabolites through various pools. This year, the staff of the resource has developed methods for the manipulation of mutant bacteria that overproduce amino acids so that they selectively introduce ^{13}C labels from specifically ^{13}C -labeled glucose and acetate. The bacterial synthesis is convenient and efficient and should result in substantially reduced costs for these materials when the technology is transferred to private industry.

3. Synthesis and Solution Structure of the Type 2 Blood Group Oligosaccharide. The oligosaccharide components of glycoproteins and glycolipids are of interest because of their demonstrated roles in several recognition events. Knowledge of the solution conformations (structures) of these oligosaccharides is limited, yet is essential for the complete understanding of their specificities. The most promising approach to establishing solution conformations of such complex oligosaccharides is nuclear magnetic resonance (NMR) spectroscopy which, in certain systems, can give data interpretable in terms of conformations of component monosaccharide rings and conformations about the glycosidic bonds. Application of NMR spectroscopy requires the isolation or synthesis of substantial amounts of oligosaccharides (>20 μmoles). Data acquisition is facilitated by larger amounts of material, and certain interactions can be assessed only if compounds enriched with ^{13}C at specific sites are prepared. Professor R. Barker and his coworkers at Cornell University, using precursors supplied by the stable isotopes resource, have accomplished the enzymatic synthesis of 20 - 50 mg amounts of the immunologically active core trisaccharide of the ABO Type 2 blood group antigens specifically enriched with ^{13}C . The solution conformation of the monosaccharide components of the core trisaccharide was shown by ^{13}C NMR spectroscopy to be similar to those of the unsubstituted monosaccharides or their simple glycosides.

B. Development of a Data Base for Carbon-13 Enriched Molecules (R. E. London and M. A. Phillippi)

The design of sophisticated biological nuclear magnetic resonance (NMR) experiments involving isotopic labeling requires a data base that includes such parameters as relaxation behavior, coupling constants, ^{13}C assignments, etc. We have collected and published these data for a variety of biologically interesting systems. During the past year, we extended our studies on the effects of multiple isotopic enrichment on the relaxation behavior of enriched systems.

Multiple ^{13}C enrichment in a molecule introduces the possibility of ^{13}C - ^{13}C dipolar interactions that can contribute significantly to the

relaxation behavior of the labeled spins. Generally, the $^{13}\text{C} - ^{13}\text{C}$ dipolar interaction is considerably smaller than the $^{13}\text{C} - ^1\text{H}$ dipolar interaction for directly bonded spins. As a result, the former effect is readily observable only for nonprotonated carbons. Enrichment below the 100% level allows simultaneous observation of the ^{13}C resonance corresponding to the singly labeled species, and the ^{13}C multiplets corresponding to the multiply labeled molecules. Because the only difference in the relaxation behavior of these two sets of signals is the $^{13}\text{C} - ^{13}\text{C}$ dipolar interaction, subtraction of the results obtained for the singly and multiply labeled species allows quantitation of the $^{13}\text{C} - ^{13}\text{C}$ dipolar term. This result can in turn be related to the molecular dynamics of the corresponding carbon - carbon bond. In contrast, the typical ^{13}C relaxation measurements on unlabeled systems are sensitive to the molecular dynamics of the carbon - hydrogen bonds in the molecule. Thus, this approach provides data more directly related to the motion of the molecular skeletal framework of carbon bonds.

We have extended these results to include the effects of long rotational correlation times that frequently characterize macromolecules of biological interest. In general, the recovery of the total magnetization after an initial inverting pulse is bi-exponential:

$$A(t) = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t}$$

Results for a nonprotonated carbon (spin A) bonded to a protonated carbon (spin M) are illustrated in Fig. 17. From this figure, it can be seen that for most values of the rotational correlation time, the recovery curves for both spins are approximately exponential, i.e., coefficients C_1 and C_2 are close to 1 or 0. This generalization breaks down near correlation times of 10^{-7} s, at which both recovery curves become significantly nonexponential. For slower motions than this, a "spin diffusion" process becomes dominant, causing both the nonprotonated and protonated carbons to exhibit identical relaxation behavior, which is dominated by the contributions of the protons directly bonded to spin M.

Fig. 17.

Spin lattice relaxation behavior for an $AM\{X\}$ system where A corresponds to a nonprotonated carbon for which $r_{CH} = 2.16 \text{ \AA}$, M corresponds to a protonated carbon with $r_{CH} = 1.09 \text{ \AA}$, and the proton(s) X is decoupled. (a) illustrates the T_1 behavior for A(Δ) and M($\square$) carbons in the absence of dipolar carbon-carbon interaction, the T_1 contribution corresponding to the carbon-carbon dipolar interaction with $r_{CC} = 1.53 \text{ \AA}$ and the two reciprocal eigenvalues λ_1^{-1} and λ_2^{-2} describing the relaxation of the A and M spins in the cross-relaxing system. Isotropic motion with rotational correlation time indicated on the abscissa is assumed. For long correlation times the carbon - carbon relaxation times become equal in magnitude. (b) corresponds to the same calculation but assuming $N_H = 2$ (i.e., two protons directly bonded to M), hence corresponding to the theoretical behavior of labeled glycine. (c) Coefficients C_1 and C_2 corresponding to the eigenvalues λ_1 and λ_2 plotted in (a) as a function of the rotational correlation time. As can be seen from the curve, the spin lattice relaxation behavior is effectively exponential over most of the range of correlation times considered and corresponds to the eigenvalue λ_2 . (d) Coefficients corresponding to the eigenvalues λ_1 and λ_2 for the M relaxation. As a result of the crossover near $\tau = 10^{-7}$ s, the relaxation behavior is transferred from the λ_1 to the λ_2 curve for very slow motion.

In addition to these results, we have noticed an unexpected phenomenon in some of the multiply labeled systems examined during the past year. In particular, unprotonated ^{13}C nuclei bonded to protonated ^{13}C nuclei exhibit unexpectedly broad resonances. This result does not reflect the $^{13}\text{C} - ^{13}\text{C}$ dipolar interaction, but instead can be ascribed to the effect of the rapidly relaxing,

protonated carbon. It has long been known that $1/2$ nuclei bonded to quadrupolar nuclei can show line width effects from the rapid relaxation of the quadrupolar spins. In the present case, the rapid relaxation of the protonated carbon in a biological macromolecule leads to a similar effect. Calculations of the expected lineshape can be used to deduce the spin lattice relaxation time of the directly bonded, protonated carbon, and the result compared with a direct measurement.

We believe that these measurements and theoretical studies are of importance for the eventual application of ^{13}C labeling in studies involving biological macromolecules.

C. Radiobromination of Bromosulphophthalein, (P. Wanek and Z. Svitra)

Bromosulphophthalein (BSP) has been used extensively for the detection and measurement of human liver dysfunction. The test is based on the ability of the hepatic parenchyma to rapidly remove the dye from the blood and more slowly excrete it into the bile ductules and bile duct. This mechanism may be either delayed or accelerated depending on the condition of the liver and its drainage structures.

Radiolabeling BSP would broaden its utility, in that liver abscesses, ascites tumors and the state of the gall bladder could be assessed. Also, the amount of the dye needed for diagnostics can be reduced substantially.

We have chosen to radiobrominate BSP (^{77}Br -BSP) using a process that involves the electrophilic addition of *in-situ*-produced $^{77}\text{Br}_2$ to the organic dye. Five mg of BSP and 0.3 mg of KBrO_3 powders are placed in a sterile 1 ml serum vial. A Teflon-backed rubber stopper is crimp-sealed over the vial. To dissolve the powders and to adjust the pH to 1.0, 0.2 ml of an equal mixture of sterile water and 1 M HCl is added through the rubber septum using a disposable syringe. One to three mCi of aqueous $^{77}\text{Br}^-$ is then added. The vial is rotated to insure mixing and allowed to stand at room temperature for 30 min. Sulfur dioxide gas is bubbled through the solution to insure

reduction of oxidized Br species to Br^- . The pH and isotonicity are adjusted using NaOH and sterile phosphate filtration. This method is adaptable to a "cold kit" preparation.

Quality control is easily performed using ascending paper radiochromatography. Whatman #1 chromatography paper is spotted with 1 to 3 μl of labeled dye solution. A separation of $^{77}\text{Br}^-$ from BSP and ^{77}Br -BSP is accomplished within 75 min using an acetate buffer, pH 4.5. In this system, Br^- migrates to an average R_f of 0.87, BSP and ^{77}Br -BSP to R_f 0.67. Any radiopharmaceutical contaminants resulting from the reaction are found at a distance of less than R_f 0.56. Other chromatographic systems described in the literature^{1,2} do not separate these labeled contaminants, nor are these contaminants described in similar iodination work^{2,3}.

Using this labeling method, we have found that 3.1 mCi of ^{77}Br can be added to 5 mg BSP with a minimum labeling yield of 97-98%. However, varying percentages of radiopharmaceutical contaminants continue to be a problem. As many as five labeled impurities have been found chromatographically. These radioactive species may enter the liver and be metabolized at considerably different rates, thus altering the function test. Efforts are continuing to identify and remove these contaminants.

Biological studies using ^{77}Br -BSP are encouraging. A preliminary biodistribution study in the rat model using a $^{77}\text{Br}^-$ BSP containing less than 10% radiocontamination (including 2% free $^{77}\text{Br}^-$) was found to be completely cleared from the blood within 10 min and 90% cleared from the liver within 45 min. These results compare favorably with human clearance of BSP.

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D. New Radiobromination Methods. Radiobromination Via Aryltrimethylsilyl Intermediates (D. S. Wilbur and K. W. Anderson)

Radiobromine-labeled compounds are of interest in radiopharmaceutical development. It is therefore of primary importance that methods be available for introducing radiobromine into a variety of types of compounds in various positions. For compounds containing aromatic rings it is generally accepted that the best position to radiohalogenate is on the aromatic ring. This preference arises from the fact that aryl-halogen bonds are usually more stable than other carbon-halogen bonds. Thus, the radiobromine will probably be less labile *in-vivo*.

At present there are several methods of introducing radiohalogens into highly activated rings (e.g. phenols and anilines); however, only a few methods have appeared in the literature for introducing radiobromine into less active aromatic rings. Particularly noteworthy is the *in-situ* generation of a radiobrominating agent produced by the oxidation of bromide-77 with tetrafluoro-N-chlorosuccinimide (TFNCS).¹ Radiobromination of toluene in trifluoroacetic anhydride with this method yielded a mixture of ortho- and para- ⁷⁷Br-bromotoluene in 52% radiochemical yield. Unfortunately, for practical laboratory radiobromination of compounds this method has two drawbacks: all experiments must be conducted in a dry box and a mixture of radiobrominated compounds arises. The only other methods reported for radiobrominating aromatic rings that are not highly activated involve the decomposition of diazonium salts² or triazine analogs³ of compounds in the presence of salts of bromide. Although these methods are regiospecific, yielding only one aryl position radiobrominated, the yields for the reactions are consistently very low.

It has been known for nearly three decades that aryltrimethylsilyl compounds will react with electrophilic bromine to yield arylbromides;⁴ however, this method has not been utilized to introduce radiobromine into aryl compounds. Because the

aryltrimethylsilyl intermediates are often easily synthesized,⁵ an investigation to determine if they could be used to introduce radiobromine (regio-specifically) into aromatic rings was carried out. To simplify the evaluation of the reaction parameters, a model compound study was begun by synthesizing the three regioisomers of toluene,⁶ i.e., ortho-trimethylsilyltoluene (o-TMST) 1, meta-trimethylsilyltoluene (m-TMST) 2, and para-trimethylsilyltoluene (p-TMST) 3.

Aryltrimethylsilyl Toluenes

Cleavage of Aryltrimethylsilyl Toluenes

Reactions of aryltrimethylsilyl compounds had previously been reported in carbon tetrachloride^{4,7} and methanol⁸ solvents using bromine (Br₂), but none have appeared where the brominating agent was generated *in-situ*.⁹ As methanol and ethanol have been shown to be good solvents for the *in-situ* generation of brominating agents,¹⁰ our initial studies dealt with the cleavage of aryltrimethylsilyl tolunes with brominating agents (non-radioactive) generated *in-situ*. A variety of brominating species were investigated as potential radiobrominating agents (Table V). Of those looked at, N-bromosuccinimide(NBS) and NBS/chloride appeared to be inferior to N-chlorosuccinimide(NCS)/bromide and tert-butylhypochlorite(TBHC)/bromide. The reaction of NCS/bromide was chosen for radiobromination studies because NCS reacts with aryltrimethylsilyl tolunes(TMST) very slowly, whereas TBHC reacts rapidly with TMST's. Although the reactions of the oxidizing agents with bromide are much faster than with TMST, radiobrominations on a "no-carrier-added" (nca) level¹¹ employ a large excess.

TABLE V
STABLE BROMINATIONS^a

	Rxn Time	NBS	NBS/Cl ⁻	NBS/Br ⁻	TBHC/Br ⁻
p-TMST	5 min ^c	14	11	86	100
	1 hr	72	88	91	b
m-TMST	5 min	2	1	37	13
	1 hr	4	17	75	99
o-TMST	5 min	9	11	86	100
	1 hr	55	82	85	--

^aValues were obtained by GLC and represent percentages of observed peaks in the brominated product.
^b(-) values were not taken.
^cTime was measured from addition of oxidizing agent.

of oxidizing agent. Therefore, the chlorination reactions are important, as the chlorinated products must ultimately be separated from the radiobrominated products.

Preliminary radiobrominations were conducted with bromine-82 ($T_{1/2} = 35.3$ hr, $\gamma = 776$ keV), which has a low specific activity and is not suitable for *in-vivo* imaging, but can be used for some initial biodistribution studies. The reaction of NCS/bromine-82 did give good radiochemical yields (Table VI), as might be expected because the chemistry should be the same as for stable brominations. Comparison of the radiochemical yields (10 to 12%) recently reported¹² for preparation of bromine-82 labeled haloperidol exemplifies how much better this method is.

Attempts to utilize NCS as the oxidant in nca radiobrominations with bromine-77 ($T_{1/2} = 57$ hr, $\gamma = 239$ & 521 keV) did not give the desired radiobrominated products. However, use of the more reactive TBHC for the oxidizing agent gave reasonable radiochemical yields (Table VI). Unfortunately this method does introduce considerable amounts of the chlorinated products, which frequently may be separated from the radiobrominated products by high performance liquid chromatography. Comparison of the yields obtained with this method versus those obtained when oxidizing with TFNCS¹ demon-

strates that this method is superior. Indeed their method also yields chlorinated products.

Studies with varying the pH of the reaction solution for the *in-situ* radiobrominations with TBHC/BR-77 indicated that much poorer yields would be obtained at decreased pH, but somewhat better yields might be obtained at increased pH. Because highly nucleophilic bases such as hydroxide ion are undesirable because of potential side reactions with other functional groups, the nonnucleophilic base potassium tert-butoxide (TBO-) was studied. Interestingly, somewhat different results were obtained for the nca radiobrominations (Table VI). More work must be done with these reactions before the observed differences can be explained.

Studies are continuing with radiobrominations via aryltrimethylsilyl derivatives. Further studies will be conducted involving the introduction of radioiodine (I-131: $T_{1/2} = 8.08$ days, $\gamma = 364$ keV and I-123: $T_{1/2} = 13.3$ hr., $\gamma = 159$ keV) aryltrimethylsilyl intermediates.

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TABLE VI
RADIOBROMINATIONS^a

	Rxn Time	NCS/ ⁸² Br ⁻	TBHC/ ⁷⁷ Br ⁻	TBHC/ ⁷⁷ Br ⁻ TBO ⁻
p-TMST	5 min	93	46	16
	1 hr	94	52	74
m-TMST	5 min	62	40	<1
	1 hr	80	67	46
o-TMST	5 min	92	58	95
	1 hr	93	63	--

^aValues were obtained by HPLC and represent percentages of radioactivity that eluted at same retention time as brominated products.

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- V. ELEMENT MIGRATION AND FIXATION: GEOCHEMICAL STUDIES
- A. Rock-Water Interactions (R. Charles, R. Vidale, G. Bayhurst)
1. Introduction. Experimental and theoretical work is continuing on the chemical reactions expected in deep geothermal reservoirs, particularly the hot dry rock reservoir at Fenton Hill. A new reaction vessel (Sec. 2.) as well as a new analytical procedure (Sec. 3.) have been developed. Previously, one rock type was reacted with recycled aqueous fluid in the experimental circulation systems. The systems have now been modified and recalibrated with respect to temperature to allow pre-equilibration of fluid with one rock type and flow of the fluid over another rock type (Sec. 4.). Beside imitating analogues in natural systems, this experiment has application to the Fenton Hill project. Observed reactions can be related using multisystems (Sec. 5.).
2. Temperature Calibration of a New Rapid Quench Vessel. Temperature gradients within cold seal pressure vessels are of constant concern to experimental petrologists. The rapid quench pressure vessel suggested by Greenwood (verbal communication) and developed by Wellman¹ is very sensitive to orientation and pressure media. The vessel consists of two 3.2-cm-diam rod vessels 30.5 cm long attached in series by high pressure cone seals. One vessel is heated and the other water cooled. The sample temperature is dropped quickly at the end of an experiment by tipping the vessel so that the sample capsule slides down the open bore from

the heated vessel into the water cooled vessel. Bert, et al.² and Ludington³ pointed out deficiencies in this design because of unacceptable temperature gradients across the sample capsule if the vessel was horizontal, using water as the pressure medium.

A different vessel designed by Vidale consisting of one piece of Rene 41 61 cm in length and 3.2 cm in diameter that was calibrated and found to have acceptable gradients. Calibrations were done over 6.8 cm of the hot end of the vessel at angles of inclination (measured from the horizontal) of

-10°, -5°, -2.5°, 0°, 2.5°, 5°, and 10° at temperatures of 300, 450, 600, and 750°C and 2 kbar = P_{tot} . Results show a water pressure medium is satisfactory at all temperatures if the hot end is raised +5° (see Fig. 18).

A similar set of measurements were performed on a standard 30.5-cm vessel with a filler rod. The results show the temperature gradient to be essentially inclination-independent from -10° to +10° although the temperature correction is inclination-dependent.

Fig. 18.

temperature gradients (°C) for the 61-cm rapid quench vessel at the angles of inclination indicated. At +10°, the hot end of the vessel is raised 10° from the horizontal.

3. The Effect of HF on the Analysis of Al, Ba, Ca, Mg, and Sr in the Presence of Si. The development of geothermal energy production and geologic storage of nuclear waste has resulted in a need to characterize, in terms of major and trace constituents, waters introduced into geologic systems, natural groundwaters and waters resulting from rock-water interaction laboratory experiments. Frequently, only limited quantities (10 ml or less) of sample from laboratory experiments are available, thus necessitating the use of a multi-element analysis technique. The Spectrometrics Inc. Model III-A direct reading D. C. argon plasma emission spectrometer system has been found suitable for these analyses.

To maximize the parallel data acquisition capability of the spectrometer system, a multielement standard representative of the samples being analyzed is necessary. Many of the water samples resulting from high pressure, high temperature rock-water interaction studies have silicon to sodium ratios of 7.3 or more. Commercially available silicon standards for plasma emission and atomic absorption spectrophotometry are prepared from Na_2SiO_3 dissolved in water, giving a silicon to sodium ratio of 0.59. Thus, sodium silicate is not suitable for preparing a multielement standard that will be used to analyze samples having much more silicon than sodium.

Silicic acid was dissolved in a dilute HF (approximately 2 to 3M) solution to prepare a low sodium silicon standard. This solution was standardized versus a commercial Na_2SiO_3 silicon standard. After standardization, the silicic acid solution was used as a stock solution of Si to prepare multielement standards suitable for use in the analysis of our water samples.

As a check on the accuracy of the D.C. plasma determinations, a variety of groundwaters were analyzed by conventional flame atomic absorption (AAS) and by D.C. plasma emission spectroscopy (DCPES). Results for Al, Ca, Mg, and Si showed large discrepancies between the two methods, with the emission results being consistently low.

The samples were made 0.1M in HF and reanalyzed by emission. The reanalysis indicated a significant increase in apparent concentration of these elements, approaching those obtained by AAS.

This observation led to a series of experiments designed to evaluate the effects of varying concentrations of both Si and HF on the DCPES analysis of Al, Ba, Ca, Mg, and Sr.

A series of solutions containing 1 $\mu\text{g}/\text{ml}$ of each of the above elements (analytes) plus Si at 10 $\mu\text{g}/\text{ml}$ were prepared containing added HF concentrations ranging from none to 0.025M. At 0.003M HF the Al emission signal showed a 30% increase in intensity relative to the solution with no added HF, and Ba, Ca, Mg, and Sr showed a 15% increase. Solutions containing 1 $\mu\text{g}/\text{ml}$ analytes plus 50 $\mu\text{g}/\text{ml}$ Si showed the same results as the previous experiment. When the concentration of analytes were raised to 10 $\mu\text{g}/\text{ml}$ and the concentration of Si raised to 300 $\mu\text{g}/\text{ml}$, relative enhancements ranged from 120% for Al to 20% for Mg, plateauing at 0.005M added HF. No increase of emission intensities were observed for any of the analytes as a function of added HF without the presence of Si.

To successfully analyze samples having high silicon to sodium ratios, it is necessary either to standardize the silicon channel on a single element basis, i.e., with a separate standard, or to add HF to the samples to match the level of HF in the multi-element standard prepared using the HF silicic acid stock solution.

4. Granite - Amphibolite Interaction. Hot dry rock geothermal reservoirs may contain rocks of differing bulk composition as does the Fenton Hill system (see Laughlin and Eddy⁴). The modified circulation system, designed to examine reaction between aqueous fluid and different rock types is shown schematically in Fig. 19. In the current experiment, fluid pre-equilibrates with Tijeras Canyon granite in the ballast vessel and then passes over prisms of Soudan amphibolite in the temperature gradient vessel at the temperatures indicated. Both rock types are similar in composition to the less plentiful cores of granodiorite (9519 ft depth) and amphibolite (5983 ft depth) found in the hot dry rock reservoir.

The reservoir fluid was sampled before circulation was initiated using sampler I and is monitored throughout the experiment. Fluid exiting the rod vessel was sampled (sampler II) at 2, 7, 16 days, and 5 wk and will be sampled at 8 wk. The first

Fig. 19.

Schematic diagram of the temperature gradient system. Rock prisms are located at the temperature indicated ($\pm 5^\circ\text{C}$). The ballast vessel and the tubing connecting it with the temperature gradient vessel are held at run temperature. The system from fluid sampler II to the ballast vessel is at room temperature. Total pressure is 1/3 kbar.

analyses indicate transport of Na, K, Fe, F, and Cl to the amphibolite and Ca away from the amphibolite. Na-K-Ca chemical geothermometer temperatures from the ballast reservoir have remained constant at about 300°C . Fluid from the temperature gradient vessel yields temperatures of about 275°C . Transport of K (K metasomatism) is expected to reveal growth of K-bearing micas, clays, and possibly zeolites on the amphibolite.

5. Multisystems. Modeling of rock-water interactions may be done by calculating all possible reactions between the phases observed, both original and secondary (experimentally grown), after the method of Schreinemaker⁵ as modified by Korzhinskii⁶, and Zen^{7,8}. The purpose of this development is to relate divariant phase assemblages, found either in the field or experiment, to one another by sets of intensive variables. Examples of such variables are pressure, temperature, and chemical potentials (μ_i) of water, carbon dioxide, oxygen, and sulfur.

According to the phase rule:

$$f = c - p + 2$$

(degrees of freedom) (components) (phases)

For the divariant assemblages mentioned above, $f = +2$. If one wants to relate a number of diva-

riant assemblages, f will, in general, be less than 2 and can be negative. Systems with $f < 0$ are called multisystems. These contain a number of invariant, univariant, and divariant assemblages. Table VII lists some examples.

A computer plotting routine was developed to generate multisystem nets in chemical potential space for $f = -1$ and $f = -2$. This year it has been expanded to handle systems where $f = -3$.

The nets have direct application in the experimental systems. Charles and Bayhurst⁹ developed a net explaining the alteration grown on grandiorite when reacted with distilled water and detecting other assemblages not directly observed. An $f = -3$ system consisting of two components and seven phases is being used to relate the phase assemblages found at Sulphur Springs (Jemez Mountains) in $\mu_{\text{O}_2} - \mu_{\text{H}_2\text{O}}$ space. This net is partially completed and is described in the work on Sulfur Springs.

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TABLE VII
NUMBER OF ELEMENTS IN MULTISYSTEM NETS (c = components)

Degrees of Freedom	Phases	Invariant Assemblages	Univariant Assemblages
0	c + 2	1	c + 2
-1	c + 3	c + 3	$\frac{(c + 2)(c + 3)}{2}$
-2	c + 4	$\frac{(c + 3)(c + 4)}{2}$	$\frac{(c + 2)(c + 3)(c + 4)}{2 \cdot 3}$
-3	c + 5	$\frac{(c + 3)(c + 4)(c + 5)}{2 \cdot 3}$	$\frac{(c + 2)(c + 3)(c + 4)(c + 5)}{2 \cdot 3 \cdot 4}$

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- B. Geothermometer (R. Charles, T. Benjamin, R. Vidale, and P. Rogers)
- The Na-K-Ca geothermometer, which is used in geothermal systems to determine the maximum temperature in the geothermal reservoir from the concentrations of Na⁺, K⁺, and Ca²⁺ in the emergent aqueous solution, is assumed to operate by equilibration of the aqueous solution with a mineral phase assemblage at depth. The constants of the empirical expression derived by Fournier and Truesdell¹ should be a function of the thermodynamic parameters of the controlling mineral reaction.
- Experimental results show the fluid equilibrates with the rock over a period of 1 to 4 months depending upon the temperature of the experiment. Figure 20 displays the results for two experiments. Data are taken from Charles² and Charles and Bayhurst³. Grandiorite reacted both at 200°C and 300°C yields Na-K-Ca geothermometer temperatures in agreement with the empirical thermometer (±15°C). In general, experiments show that rocks containing the

Fig. 20.

Temperatures calculated from the solution chemistry using the empirical Na-K-Ca geothermometer of Fournier and Truesdell¹ for granodiorite reacted at known temperatures of 200°C and 300°C. Horizontal lines centered at 200°C and 300°C represent the estimated $\pm 15^\circ\text{C}$ error in the empirical geothermometer. Equilibration takes about 1 wk at 300°C and about 4 months at 200°C.

three feldspar endmembers plus quartz reacting with water yield Na, K, and Ca concentrations that fit the geothermometer. Alterations found on the rock after reaction with water include clays and zeolites.

The standard literature values for the thermodynamic parameters of a quartz-feldspar plus water reaction are not consistent with the constants of Fournier and Truesdell¹. The constants in the geothermometer expression have been re-evaluated by a method of least squares using both the data used by Fournier and Truesdell¹ and the experimental data of Charles⁴ and Charles and Bayhurst³. The resultant thermodynamic parameters also eliminate feldspar-quartz as the controlling phase assemblage and, in conjunction with the experimental observations mentioned above, suggested that many different alteration phase reactions involving thermodynamically similar clays and zeolites may buffer the solution to the observed compositions. A single formulation of the Na-K-Ca geothermometer may, therefore, be appropriate over a given temperature range for dilute aqueous systems in a number of different altered rocks.

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C. Sulphur Springs (R. Charles, R. Vidale, G. Bayhurst, and C. Duffy)

D. Ruthenium and Technetium Geochemistry at the Oklo Natural Reactors (D. B. Curtis, T. Benjamin, and A. J. Gancarz)

Sulphur Springs in the Jemez Mountains in Northern New Mexico is possibly the only vapor-dominated geothermal reservoir in the Jemez. In cooperation with ESS Division, we have been mapping and gathering samples in order to describe the development of this hydrothermal system through time.

Principal alteration phases observed at Sulphur Springs are alunite ($\text{KFeAl}_2(\text{SO}_4)_2(\text{OH})_6$), alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$), halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), szymolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$), pyrite (FeS_2), adularia (KAlSi_3O_8), and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). In addition, there is almost ubiquitous quartz and sulphur. Occurrence of the two-phase assemblages alunogen + adularia, szymolnokite + pyrite, szymolnokite + alunogen, halotrichite + alunogen, and alunite + kaolinite suggest at least part of the Sulphur Springs system may be treated as an assemblage with two inert components.

Table VIII expresses the system as a multi-system with $f = -3$, which consists of 32 invariant assemblages and 17 univariant assemblages resulting from compositional degeneracies. Currently, this net is being oriented in $\mu_{\text{O}_2} - \mu_{\text{H}_2\text{O}}$ space to determine the relative positions of the divariant (2 phase) assemblages mentioned above. The relatively older alterations (alunite bearing) are related to the younger (alunogen, halotrichite, and szymolnokite bearing) through this net.

1. Introduction. Geologic burial is the favored method being considered for the disposal of commercially generated radioactive wastes. Appropriately chosen sites are thought to be relatively inert environments with respect to the stability of engineered waste containers. In addition, the geologic media itself will provide the ultimate containment, assuring that the wastes will remain isolated from the biosphere for adequate periods of time. However, efforts to evaluate the effectiveness of this geologic environment in this regard are limited by our understanding of the effects of natural, physical, and chemical processes acting over periods of time much longer than that recorded by any human experiences. The Natural Repository Analogue program is a research effort to study the chemical processes and conditions that affect the retention and transport of elements in the earth's crust. The work examines the stability of elements in the geologic record and their response to natural conditions over appropriately long periods of time.

Thick lenses of uraninite at the Oklo uranium mines in the Republic of Gabon in equatorial Africa sustained nuclear fission for a period of a few hundred thousand years at a time two billion years before the present. The mere existence of these

TABLE VIII
THE SULPHUR SPRINGS SYSTEM

Phases	Inert Components	Mobile Components	Mobile Phases
alunite	Fe	O	quartz
alunogen	Al	S	sulphur
halotrichite		K	
szymolnokite		Si	
adularia		H ₂ O	
kaolinite			
pyrite			

ants of naturally occurring fission reactors attest to their remarkable stability for about half the age of the earth. They are a direct demonstration of the ability of the earth's crust to contain waste from nuclear reactors for geologic periods of time. As such, they validate, in principle, the concept of geologic disposal of such wastes. However, more significantly the reactors provide the opportunity to characterize quantitatively the stability of the rocks which contain them with respect to more than 30 elements, the products of neutron capture, nuclear fission and radioactive decay and the transport of these elements into the geologic surroundings. For these purposes stability refers to the loss or gain of specific chemical elements within a defined period of time and transport refers to the movement of element from sites where they are deficient to sites where they are enriched relative to some time in the past. This examination can be done on a system that has many physical and chemical properties similar to proposed repositories, has existed in a crustal environment for geologic periods of time, and has been subjected to many of the conditions that must be considered in evaluating the stability of man-made facilities.

Technetium-99 is a radionuclide of particular concern in the storage of radioactive wastes. It has a half life of 2.13×10^5 years, necessitating storage times on the order of a million years. After such an interval, 96% of the ^{99}Tc will have decayed to the stable nuclide ^{99}Ru . Technetium is an element that does not occur naturally, in significant quantities on the earth, so that its geochemical properties must be inferred from experimental and theoretical considerations. At the Oklo reactors approximately 700 kg of ^{99}Tc were produced. The isolation and transport of this extinct radionuclide can be studied today by the relative abundances of its stable daughter ^{99}Ru .

2. Characterization of the Stability and Transport of Ruthenium and Technetium. Chemical elements were produced and destroyed in the natural reactors. With the exception of the decay of naturally occurring radioactive elements, such processes are not known to have naturally occurred at any other place in the earth. A list of these

nuclear products includes a third of the naturally occurring elements and several that are principally man-made. They were the result of the three important nuclear processes; fission, neutron capture and radioactive decay. The composition of this nuclear material basically depends upon three reactor operating parameters: 1) The elapsed time since the reactors were critical defines the initial abundances of the naturally occurring isotopes of uranium, the primary fuel for the reactors. 2) The duration of nuclear criticality determines the relative contributions of time-dependent nuclear processes. 3) The neutron fluence and neutron energy distribution control the number and proportion of the energy-dependent neutron induced processes. These parameters are determined by measuring absolute or relative abundances of nuclides that are particularly sensitive to at least one of the operating parameters and assumed to be unaltered during or since the nuclear processes occurred. Differential equations are formulated describing the variation of these parameter-sensitive abundances due to production and destruction by time-dependent processes. Finally, appropriate values are calculated by iterating operating parameters until solutions to the differential equations match the isotopic ratios or nuclide abundances of the parameter sensitive species. These parameters are used to calculate quantities of elements produced in the sample. Quantities produced compared with those presently in the rock characterize the gain or loss of nuclear products.

Four isotopes of ruthenium are produced by fission: ^{99}Ru , ^{101}Ru , ^{102}Ru and ^{104}Ru . The latter three are produced instantaneously, that is the isobaric precursors are short-lived relative to the time scale of relevant geologic processes. However, the formation of fissiogenic ^{99}Ru is delayed by the long-lived precursor ^{99}Tc . If, at some time within one million years after the time of production, conditions were such that ruthenium and technetium were chemically fractionated, it would be manifested today by depletions or enrichments of ^{99}Ru relative to the other fissiogenic isotopes of Ru. Such fractionation is quantified by the ratio

$$\Delta^* = \frac{(^{99}\text{Ru})/(^{101}\text{Ru} + ^{102}\text{Ru})_{\text{measured}}}{(^{99}\text{Ru})/(^{101}\text{Ru} + ^{102}\text{Ru})_{\text{produced}}}$$

If Δ^* is less than unity, technetium was preferentially depleted relative to ruthenium. Values greater than unity indicate fractionation of the two elements in the opposite sense.

Because ^{99}Tc and ^{99}Ru are related by time dependent radioactive decay, the degree of Ru/Tc fractionation places limits upon the time when fractionation occurred and the extent to which the two elements were fractionated. If a Tc/Ru fractionation factor is defined as follows,

$$f = (\text{Tc/Ru})_A / (\text{Tc/Ru})_B,$$

where A is the ratio immediately after fractionation and B the ratio immediately before, the relationship between f , Δ^* and T_f , the time of fractionation is

$$f = 1 - \frac{1 - \Delta^*}{e^{-\lambda T_f}}.$$

An upper limit is established on this time when $f=0$, i.e. all ^{99}Tc is removed from ruthenium. Considerations of all available ruthenium isotopic data from Oklo places limits on the time of fractionation between 4 and 16×10^5 years after the end of production. This length of time during criticality and a few hundred thousand years thereafter has been defined as the thermal period. The thermal period in the rocks that comprised the reactors was characterized by large radiation doses from a variety of radioactive emanations. Neutron fluences were as high as 10^{21} n/cm^2 and decaying fission products produced $\sim 10^{10}$ curies of beta-gamma emitting radioactivity. Total energy production was $\sim 10^4$ MW-years, which resulted in increased temperature, perhaps as high as 600°C in some rocks. Hot aqueous solutions were circulating through the rocks within the reactor zone during this time.

There are abundant ruthenium isotope data on samples from two regions of nuclear reaction, zone 2 and zone 3-4. These data show that the degree of element loss was different in each of the two zones. In zone 2, 26% of the fissiogenic $^{101,102,104}\text{Ru}$ and 34% of the mass 99 element (Ru and/or Tc) are missing. The missing proportions in zone 3-4 are 8% of $^{101,102,104}\text{Ru}$ and 15% of mass 99.

These represent deficiencies of ~ 100 kg of ruthenium and ~ 70 kg of mass 99 from zone 2 and ~ 6 kg ruthenium and ~ 4 kg of mass 99 from zone 3-4. The variable quantities not only reflect differences in the proportions lost but also differing quantities produced in each of the two zones.

The degree of chemical instability with respect to these elements correlates with the intensity of the nuclear reactions in each of the two zones. Thermal plus resonance neutron fluences in zone 2 were $\sim 10^{21} \text{ n/cm}^2$, whereas in zone 3-4 they were $\sim 10^{20} \text{ n/cm}^2$. Corresponding beta-gamma activity levels were $\sim 10^{27}$ and $\sim 10^{28}$ disintegrations. Estimated power outputs were 1.9×10^4 MW-years for zone 2 and 1.5×10^3 MW-years for zone 3-4, corresponding to thermal loadings of 140 W/m^2 and 5 W/m^2 , respectively. These values bracket predicted thermal loadings of proposed repositories during the thermal period. In this respect the Oklo reactors represent an excellent natural analogy to proposed geologic-repositories. The differing element retention properties in the two zones must be in response to these differing conditions and, thus, constrains the period of element redistribution to the thermal period.

Distances over which the deficient elements have been transported can be determined from their excesses in rocks peripheral to the zones of criticality. There are very little data on such rocks, however three peripheral samples contain quantities of excess ruthenium and excesses of ^{99}Tc relative to Ru. Each of these samples was taken at locations between 10 and 15 m from the edge of the nearest reactor zone. The samples all lie updip from the reactor zones in the same stratigraphic plane at positions that are consistent with mobilization by thermal convection of hydrothermal fluids. However, samples from beneath the reactor zones must be analyzed before such an interpretation can be verified. Concentrations of excess fissiogenic ruthenium and technetium in peripheral rocks are consistent with containment within a few tens of meters of the reactor zones. These represent distances of transport for these elements.

Redistribution of ruthenium and technetium must be considered with respect to two processes. First, the nuclear products escape from their uraninite host. Solid state diffusion seems to be the

Most plausible process to account for the initial product release. Once the nuclear products are outside the host grain, a second set of processes control their migration. These involve hydrology and the chemistry controlling the distribution of the elements between mobile and immobile phases. Although the two processes are interdependent, we have evaluated the data in the extreme as though each in turn were rate controlling. In this way, conservative limits can be established for each.

The critical value in examining diffusive loss is the effective diffusion coefficient, D/a^2 , where D is the Fickian diffusion coefficient and a is the effective radius of the host grain. A model of $^{101,102}\text{Ru}$ loss by diffusion during the thermal period was used to calculate an average value for D/a^2 of $7.8 \times 10^{-8} \text{ year}^{-1}$ in zone 2 and $2.5 \times 10^{-8} \text{ year}^{-1}$ in zone 3-4. Similar model considerations yield similar estimates for the value of the effective diffusion coefficients of ^{99}Tc . These considerations also suggest that 60-70% of the mass ^{99}Tc deficiency can be attributed to the loss of ^{99}Tc .

Once the elements were released from their uraninite hosts, they were removed from the rock and transported over distances of 10 to 15 m. They could have been transported over those distances very quickly and remained immobilized since or transported continuously for some extended period of time. We have argued that the loss of elements from the reactor zone must have coincided with the thermal period. Consideration of continuous transport by fluid flow through the reactor zones for the duration of the thermal period suggests that the rate of movement of ruthenium and technetium was $10 \text{ } \mu\text{m}/\text{yr}$.

An aspect of the waste management program that has received considerable effort is the measurement of sorption ratios. This ratio is defined as the concentration of an element on a solid phase relative to its concentration in a coexisting aqueous phase. Many values have been measured in the laboratory and used in models of hydrologic flow to infer the retardation of element migration by sorption (or other reversible processes) on immobile phases of the rock. If the processes controlling the distribution are in equilibrium, this quantity is the equilibrium distribution coefficient (K_d). We have evaluated an "apparent distribution

coefficient" of 10^4 mL/g for ruthenium and ^{99}Tc . This value is no more accurate than several orders of magnitude, but it is, nevertheless, a large value and points out the remarkable ability of the Francevillian sandstones to contain these nuclear products even after they were released from containment in uraninite.

Limits on the quantity of uranium removed from the reactors by dissolution of uraninite were used to calculate the volume of water that flowed through them. This calculated value was 10^{12} L flowing at a rate of about $5 \text{ m}/\text{yr}$. Dividing the quantities lost from the reactor zones by this volume provides estimated molar concentrations of 10^{-10} of ruthenium and ^{99}Tc in the aqueous phase. Again, the values represent rather broad assumptions, but they are likely to be accurate within two or three orders of magnitude. Certainly they represent the most meaningful observation available regarding the concentration of these rare elements in aqueous solutions in deep crustal rocks.

To examine possible controls on the aqueous concentrations of these elements, the thermodynamic stability of their oxides with respect to aqueous species was considered. Solubilities are influenced by the formation of complexes, the ionic strength of the aqueous phase, the formation of solid solutions, multiple host phases etc. However, because virtually nothing is known about such complexities with respect to these trace elements nor the conditions at Oklo during the thermal period, only the simplest cases have been considered. Both ruthenium and technetium have multiple valence states. The tetravalent oxide of both elements is very insoluble while the oxidized oxyanion is soluble. Thermodynamic data were used to calculate the concentration of the oxidized species in equilibrium with the reduced oxide as a function of temperature. The oxygen fugacity was that in equilibrium with the hematite-magnetite buffer at $\text{pH} = 7.5$. These are conditions that lie in the middle of the uranium ore stability field on an Eh vs pH diagram. Table IX shows the remarkable temperature dependence of the concentration of the oxidized species.

Data were not available to calculate the change of the free energy of the ruthenium reactions as a function of temperature. Values in the table were

TABLE IX
CALCULATED CONCENTRATION OF AQUEOUS SPECIES IN
EQUILIBRIUM WITH THE TETRAVALENT OXIDE (MOLES/LITER)

T(°C)	[TcO ₄ ⁻]	[RuO ₄ ⁻²]	[Ru(OH) ₂ ⁺²]
25	4.6 x 10 ⁻²²	1 x 10 ⁻⁵²	1 x 10 ⁻²²
50	1.9 x 10 ⁻¹⁹	7 x 10 ⁻⁴⁷	5 x 10 ⁻²²
100	9.0 x 10 ⁻¹⁵	9 x 10 ⁻³⁸	3 x 10 ⁻²¹
200	1.2 x 10 ⁻⁸	3 x 10 ⁻²⁵	5 x 10 ⁻²⁰
300	1.2 x 10 ⁻⁴	4 x 10 ⁻¹⁷	3 x 10 ⁻¹⁹
400	8.0 x 10 ⁻²	2 x 10 ⁻¹¹	9 x 10 ⁻¹⁹

determined assuming this quantity was constant throughout the temperature range. In general ΔG_R decreases with increasing temperature and the concentration of ruthenium species are likely to be increasingly greater with increasing temperature than those given in the table. Note that the concentration of aqueous tetravalent ruthenium (Ru(OH)₂⁺²) is significantly less than the estimated concentration at Oklo. Simple dissolution of this oxide does not appear to have been a significant factor in the mobility of ruthenium. The concentration of the oxidized species of ruthenium and technetium at 25°C are also far below the concentration determined at Oklo. However, the temperature dependence of these reactions is so strong that at temperatures likely to have been attained by the reactors, the calculated concentrations are well within those determined in the fluids at Oklo. This observation further substantiates our premise that these two elements were redistributed during the thermal period. In addition, the strong temperature dependence suggests that the distances of transport were controlled by the temperature gradient around the reactor zones.

E. Development of Eh Buffers (B. P. Bayhurst,
T. Newton, A. E. Ogard, and G. Rundberg)

The behavior of an element that can exist in more than one oxidation state will depend on the oxidation potential, or Eh, of the solution in which it is found, as well as on the pH, and the

concentrations of complexing anions. For this reason it is important to control the Eh in laboratory experiments designed to determine solubility, distribution ratios, etc. One way of controlling Eh in laboratory experiments involves the use of Eh buffers. These are analogous to pH buffers but consist of equilibrium mixtures of the oxidized and reduced forms of a particular substance.

Our investigation of possible redox buffers has focussed on redox indicators because a large number of these systems have been studied and a wide range of potentials is available.¹ However, in addition to having an appropriate potential, a satisfactory Eh buffer system must be relatively stable in both the oxidized and reduced forms, show relatively rapid redox reaction rates with the actinide species of interest, but not react in other ways.

Our work has involved the organic indicators indigo carmine and thionine, and various complexes of osmium in the +2 and +3 oxidation states. It appears that the organic systems will be most useful at Eh values near or below 0 V., for use with uranium species, and the inorganic systems will be useful at Eh values between 0.1 and 0.9 V, for use with plutonium.

Work at Eh values below that of the H₂O₂-O₂ couple, (0.68-0.059-pH) V., is difficult because of oxidation by O₂ in the air. We find it necessary to work in an inert-atmosphere glove box when studying systems with Eh values less than about 0.1 V.

The formal potential (that given by equimolar concentrations of oxidized and reduced forms) for indigo carmine is reported to be (0.291-0.059-pH) V.¹ Using this dye we have maintained stable Eh values of -0.19 ± (0.02) V at pH 7 for several days. However, indigo carmine is not without difficulty: unstable Eh values are observed if attempts are made to reduce the last 0.01% using a potentiostat. Also, we have been unable to reproduce the reported Eh-pH function. Our values at pH = 1.1 and 7.6 are 0.10 V lower and 0.04 V higher, respectively, than the published values.¹

Our preliminary experiments with thionine show that it may be useful at Eh values somewhat higher than those provided by indigo carmine. The formal

potentials are reported to be 0.563 V and 0.064 V at pH = 0 and pH = 7, respectively. Reasonably satisfactory behavior was observed at pH 5.6 after stirring the solution and sparging it with argon for several days, then reducing the solution with a potentiostat. After this treatment, the measured formal potential came to within 0.003 V of the theoretical value in 3 days. This length of time may indicate slow attainment of equilibrium at the electrodes.

Our work with osmium complexes has proven less difficult than that described above, primarily because higher formal potentials have been involved. With the help of Prof. D. M. Klassen, Visiting Staff Member from McMurry College, we have prepared seven osmium complexes with formal potentials ranging from about 0.42 to 1.05 V. The preparative methods used were based on those described in the literature.^{2,3} In addition, Prof. Klassen has provided a sample of a complex with a formal potential of 0.15 V., $\text{Os}(\text{acac})(\text{bipy})_2\text{Cl}_2$.*

The stabilities of the complexes in solution were determined by observing changes in spectra as a function of time. These experiments were run in cells sealed after sweeping out the air with argon. The tris-complexes, $\text{Os}(\text{bipy})_3^{2+}$ and $\text{Os}(\text{dimebipy})_3^{2+}$, with formal potentials of 0.88⁴ and 0.69 V, respectively, were found to be the most stable. The complexes $\text{Os}(\text{acac})(\text{bipy})_2^{2+}$ and $\text{OsCl}(\text{py})(\text{dimebipy})_2^{2+}$ were found to be least stable, showing spectral changes at room temperature as large as 4%/day at certain wave lengths.

The rates of reduction of Pu(VI) to Pu(V) and of Pu(IV) to Pu(III) by the osmium buffers were found to be quite rapid. This is expected on the basis of the minimal structure changes associated with the reduction. The apparent second order rate constants for four such reactions are summarized in Table X.

The reduction of Pu(V) to Pu(IV), or the reverse, involves a drastic change in structure ($\text{Pu}^{4+} \rightleftharpoons \text{PuO}_2^{2+}$, in acid). Reactions involving this change were found to be very much slower than those summarized in Table X. The rate constant for the

TABLE X
REDUCTION OF PU(VI) AND PU(IV)^a

Reductant	Potential (V)	Rate Constant ($\text{M}^{-1}\text{sec}^{-1}$)	
		Pu(VI)	Pu(IV)
$\text{Os}(\text{bipy})_3^{2+}$	0.885	4.4×10^4 ^b	6.8×10^2 ^b
$\text{Os}(\text{dimebipy})_3^{2+}$	0.694	3.7×10^5 ^c	1.9×10^4 ^b 1.5×10^4 ^c

^a $24 \pm 2^\circ\text{C}$, $\sim 2 \times 10^{-6}$ M Pu, $(2-6) \times 10^{-6}$ M reductant.

^b 0.01 M HClO_4 .

^c 0.001 M HClO_4 .

oxidation of Pu(IV) by $\text{Os}(\text{bipy})_3^{3+}$ was found to be $\sim 4 \text{ M}^{-1} \text{ s}^{-1}$ in 0.001 M HClO_4 . Similarly, the reduction of Pu(V) by $\text{Os}(\text{dimebipy})_3^{3+}$ in 0.006 M HClO_4 was found to have a rate constant $< 3.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. This corresponds to a half-time for reaction in 10^{-4} M $\text{Os}(\text{II})$ of > 25 day.

The conclusions we have reached from this work are: a) further development will be required before satisfactory buffer systems are available for potentials below ~ 0.2 V., b) certain of the osmium complexes will almost certainly be useful where Pu(V) and Pu(VI) are predominant and where Pu(III) and Pu(IV) are predominant, and c) osmium complexes may react too slowly for use where Pu(IV), or Pu(III), and Pu(V) are predominant.

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* Abbreviations for the ligands are bipy = 2,2'-bipyridine, dimebipy = 4,4'-dimethyl, 2,2'-bipyridine, py = pyridine, acac = acetylacetonate.

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F. Permeability Measurements (C. J. Duffy)

Permeability measurements in the past year have been made on core samples of gneissic rocks from the EE-2 drill hole at Fenton Hill. The effect of temperature on permeability has been measured as well as the effect of temperature cycling. Measurement of permeability at room temperature is easier, quicker, and involves fewer uncertainties than elevated temperature measurements, but because the temperature at which the samples were taken is in the 200 to 300°C range, it is important to know the effect of temperature on permeability. Figure 21 shows the results of measurements of permeability (k) at 20, 77, 131, 156, and 200°C on core EE-2 14964-1 as a function of effective confining pressure (P_e). The effective confining pressure is the confining pressure on the sample minus the fluid pressure in the sample pores. (The sample number indicates that the core was taken from the EE-2 drill hole at a depth of 14964 ft.) There is a definite decrease in permeability with increasing temperature. It will be seen later that some of this decrease may have been due to pressure cycling as the sample experiences one pressure cycle at each temperature. However, most of the effect at least up to 131°C is probably due to change in temperature.

The decrease in permeability with increasing temperature is probably due to a better fit among crystals in the rock at higher temperature. Because the minerals in the rock are generally anisotropic with respect to thermal expansion, if the temperature of the rock is changed from that at which it has texturally equilibrated, the openings between mineral grains may be expected to enlarge, thus increasing the permeability.

This change is apparently not permanent. Temperature cycling experiments have been performed which show that permeability stays constant at a given temperature during temperature cycling between 20 and 200°C.

Experiments cycling P_e have also been performed. Figure 22 shows the results of a pressure cycling experiment on EE-2 13956-1. Pressure cycling was carried out between pressures of approximately 2 and 28 MPa. A relatively steady decrease in permeability was observed during the 14 pressure cycles to which the sample was subjected. Figure 23 shows the results of a similar experiment on EE-2 13641-1. This core differs from EE-2 13956-1 in that it contains several approximately 5-mm cracks that are nearly parallel to the flow direction of the tests. This sample shows a considerably greater decrease in permeability with pressure cycling than the other sample, especially at high effective confining pressure.

The pore space through which fluid flows in these rocks is characterized by high aspect ratios. That is, they are long thin openings. These are held open by material that bridges the openings. When confining pressure in excess of the pore pressure (effective confining pressure, P_e) is placed on the sample, stress is concentrated at the bridging points. Although the stresses used in these experiments cannot fracture the rock as a whole, they are apparently sufficient to crush some of the bridging material. This results in decreased pore aperture and, consequently, reduced permeability at a given P_e . The larger decrease in permeability in the cracked sample may be indicative of more fragile bridging material. Whether this is typical of fractured rock is uncertain.

The findings indicate that pressure cycling in the geothermal loop at Fenton Hill will probably decrease the permeability of the containing rock. One difficulty with the hot dry rock concept is that it is difficult to extract heat from rock that is not quite near the fracture because of the low thermal conductivity of the rock. One method of increasing the heat, which can be extracted from a geothermal loop, may be to cycle the fluid pressure in the loop. When the pressure in the loop is lowered, water previously lost from the loop should flow back into the loop from the rock where it will

Fig. 21.
Effect of temperature on the permeability of EE-2 14964-1.

Fig. 22.
Effect of pressure cycling on the permeability of EE-2 13956-1.

Fig. 23.
Effect of pressure cycling on the permeability of EE-2 13461-1.

have been heated. Unfortunately, the pressure cycling experiments suggest that this will be a progressively slower process with each successive pressure cycle. Pressure cycling should, however, reduce the problem of water loss from the loop.

G. The Migration of Radionuclides Through Geologic Media: Laboratory Column Studies (E. N. Treher)

Elutions of radionuclides from columns of crushed tuff, granite, and argillite have been used as a simple first step in trying to relate laboratory batch-type measurements to a flowing system. Because radionuclides are often sorbed quite strongly by these materials, small columns (≤ 0.5 cm diameter by 2 to 5 cm long) are used to minimize the duration of an experiment. Even so, the elutions of some of the columns have continued for $\sim 2\frac{1}{2}$ years. The columns are loaded with ~ 5 - 10 μ l spikes of groundwater containing one or more of the radioisotopes ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{152}Eu , and ^{95m}Tc . (A few columns have also been run with uranium or neptunium.) Groundwater is pushed upward through the

column using syringe pumps at flow rates of 20 to 60 m/y, although the effects of faster flow rates were studied in some cases. The velocity of the radionuclide is measured directly and then compared with respect to the groundwater velocity (measured using HTO or nonsorbing ^{131}I) to calculate the retardation factor, R_f . The R_f is related to the sorption ratio, K_d , by the expression $R_f = 1 + (\rho/\epsilon)K_d$, where ρ is the density of the rock column and ϵ is the porosity.

Several general observations can be made from the data of approximately 40 columns. Three types of elution behavior are observed: symmetric peaks where 50% of the activity is eluted at the peak, asymmetric peaks, and no peaks--but instead a slow, usually uniform elution. When elution peaks are observed, column K_d values are generally 1 to 3 times lower than batch K_d values on the same rock for ^{85}Sr and ^{137}Cs and 2 to 5 times lower for ^{133}Ba .¹ Some of the difference between column and batch measurement results may be due to fine material (< 35 μm) present or formed during many batch measurements and not present in the columns.²

The peakless elutions have thus far been obtained only with cesium on columns with clay o

mica or zeolites present in more than trace amounts. Cesium K_d values obtained from columns of these materials are higher than the corresponding batch K_d values. Peakless elutions may be caused by an irreversible sorption of some portion of the ^{137}Cs . In all cases the batch desorption ratios on these materials are considerably higher than the sorption ratios, and this might also be explained by irreversible sorption.

Of the isotopes studied to date, $^{95m}\text{TcO}_4^-$ is the only one strongly affected by kinetics. This is not surprising since the retardation mechanism of technetium is probably by reduction of TcO_4^- to Tc(IV) , perhaps as TcO_2 , rather than by ion exchange. At flow rates of ~ 2000 m/y, in either air or in a controlled atmosphere of nitrogen with ≤ 0.2 ppm O_2 and ≤ 20 ppm CO_2 , argillite column sorption ratios are 0.30 to 0.47 mL/g. The corresponding batch sorption ratio in air is 68 mL/g. If flow rates are slowed to 14 m/y, allowing more time for reaction, the technetium R_d increases to 69 mL/g.

Europium is the only element yet studied which seems to show two distinct species. On two columns of tuff from the Nevada Test Site an initial mobile species (possible colloidal) was detected well ahead of most of the europium. On a highly zeolitized tuff, G1-2289 from Yucca Mountain Drillhole USW-G1, 9.3% of the ^{152}Eu was removed in the first 6 column volumes (CV). After 140 CV the remainder has still not been removed, although if the column R_d were similar to the batch R_d , 50% should have been removed in 110 CV. On another tuff, JA-18 from Jackass Flats Drillhole J-13, $\sim 1.8\%$ of the ^{152}Eu was removed with an $R_d = 633$ mL/g. That column is also still flowing without further elution of europium, indicating an $R_d > 2900$ mL/g. The corresponding batch sorption ratios are 1400 mL/g for sorption and 2500 mL/g for desorption. Additional measurements need to be made with europium as well as with actinides and other lanthanides, particularly when the number and size of colloidal species in the initial traced solution is well characterized.

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H. Element Migration by Interaction of Hot Dry Rock, Brine, and Working Fluid (T. Benjamin, P. Rogers, G. Bayhurst, R. Vidale, and C. Duffy)

An understanding of the interaction among minerals and fluids in the earth's crust is essential to addressing the potential problems and benefits of tapping wet and dry geothermal reservoirs and to discovering the mechanisms for formation of natural ore-forming fluids. The effects of dissolution and deposition in geothermal reservoirs must be known to permit their efficient utilization. Geothermal systems provide an analogue to the earliest stages of ore fluid formation by the leaching or dissolution of strategically important elements from minerals in contact with the aqueous fluid. Conditions could exist for economically concentrating these elements from operating power-producing geothermal systems. The initial goal of this work

is to be able routinely to obtain high-quality analytical data for a large number of major, minor, and trace elements from rock and from mineral separates as a first step in experimentation to better understand and quantify element leaching, transport, and deposition.

In pursuit of a routine procedure for the determination of the trace element distribution in rock from hot dry rock systems, new 40 element neutron activation analyses on mineral separates and whole rock samples of Fenton Hill granodiorite (8904) have been obtained. Although similar in concept and execution to the neutron activation analyses reported by Vidale et al.,¹ there are several important differences: 1) new hand-picked pure separates of biotite and magnetite replaced less pure separates; 2) new procedures for routine neutron activation of sub-gram size samples at the Omega West Reactor (OWR) have been initiated, these samples being among the first to be run; and 3) concentrations of 40 elements, a 50% increase over those reported by Vidale et al., are routinely obtained.

The present data set is considered preliminary and is not reported at this time because of two problems resulting from OWR changing to small sample analysis: 1) the glass wool used for spacing the small sample vials appears contaminated in Ti and Au yielding high and variable blanks and a corresponding problem in blank correction; and 2) the four different detection systems, though calibrated with the NBS Coal Fly Ash standard, did not yield good agreement among four small sample granodiorite (G-?) standards included with the 8904 samples. Even with these problems there are many real differences between the data of Vidale et al. and the new analyses. Most differences are factors of 2 to 4 and are subject to refinement after correction of the aforementioned problems and a second neutron activation analysis. Scandium shows a 1 to 2 orders of magnitude decrease in the new data, which will be rechecked. Following this second irradiation the samples will be dissolved and analyzed by plasma emission spectrometry and ion chromatography.

A small number of grains from each mineral separate will be retained for electron microprobe (major elements) and proton microprobe (trace elements) analyses. These analyses will not only provide a check on the neutron activation data but will also yield data on a number of additional elements.

As a very preliminary attempt, because of data limitations, to determine the magnitude of the Fenton Hill granodiorite's contribution to the element concentrations of the Fenton Hill HDR working fluid, a constrained least squares calculation was performed using the input (plus makeup) water composition, the new neutron activation whole rock (plus interstitial salts) data, and an estimate of the Jemez brine as components of the output water. As reported by Vidale et al., only nine days of the 75 day Fenton Hill run have sufficient data on both input and output compositions to attempt the three-component fit. Na, As, Br and combinations of Cs, Ca, Ba, and K from days 19, 23, 36, 38, 40, 43, 45, 47, and 50 were used. The averages and errors of the mean for the nine data sets yield estimates of $0.05 \pm 0.03\%$ and $0.18 \pm 0.07\%$ for the contributions of granodiorite and brine, respectively, to the Fenton Hill working fluid during a single pass through the system. The remainder is the input water (plus makeup) that is pumped into the system. No further conclusions or quantitative statements are warranted at this point. New water data and the repeat of the neutron activation analyses may be sufficient to attempt constrained least squares fits using the compositions of the 7 principal mineral phases from the Fenton Hill granodiorite to deduce the sources of the trace elements. Further insights into ion exchange processes and alteration phase deposition at Fenton Hill may also be obtained.

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I. Aqueous Solution Geochemistry (P. S. Z. Rogers)

1. Introduction. Aqueous solutions are important in many processes being investigated in this laboratory, including radionuclide migration, element transport in deep hydrothermal fluids, and geothermal energy utilization. Mineral alteration, element transport, and thermal effects occurring in such applications are highly dependent on the properties of the associated aqueous fluid. The determination of solution properties is thus fundamental to an understanding of these processes and is the objective of research described in this section.

The many different aqueous solutions involved in natural processes cannot all be studied experimentally because they are often complex mixtures of electrolytes and can range from dilute groundwaters to concentrated brines. A model that can predict the properties of mixed solutions, yet is based on a minimum amount of data on a few key systems, is necessary. The model also must be suitable for uses at the high temperatures and pressures encountered in many applications.

Three different models have been tested for their ability to predict the properties of aqueous solutions at high temperatures, pressures, and concentrations. They include a solution model developed by Pitzer to predict the properties of complex mixtures at room temperature, the Born equation, and the Tammann-Tait-Gibson (TTG) model. The Pitzer model was first extended to cover the high concentrations that can occur in natural brines, then was successfully tested for its ability to predict mineral solubility at high temperatures. The Born and TTG equations were examined for their ability to predict the temperature and pressure dependence of various thermodynamic functions. These projects are discussed in more detail below.

2. Aqueous Solutions at Very High Concentrations. Experimental data for aqueous solutions of a few very soluble electrolytes extend to high concentrations, with ionic strengths at saturation sometimes exceeding 25 molal. The description of aqueous solutions at these high concentrations provides a severe test of any model of electrolyte properties, and, thus, illustrates the limits of our understanding of solute interactions. The

description of concentrated electrolyte solutions is of strong practical interest for prediction of the properties of evaporite deposits, Dead Sea brines, and concentrated geothermal brines.

Pitzer and coworkers¹⁻⁶ have developed a system of equations to describe the properties of electrolyte solutions at low to moderate concentrations. Their equations include three empirically adjusted parameters, two determining the behavior of an ionic strength dependent second virial coefficient and the third representing a concentration independent third virial coefficient. They have used this system of equations to reproduce the activity properties of over 200 pure electrolytes² and to describe the properties of complex mixtures, including seawater.⁷

The properties of pure electrolytes can be reproduced up to ionic strengths ranging from 6 to 12 molal, using only the second and third virial coefficients². To extend Pitzer's model for use at even higher ionic strengths, equations have been derived to include the fourth, fifth, and higher order virial coefficients. The extended model has been tested using a recent compilation of activity data for calcium chloride,⁸ which covers an ionic strength range of 27 molal. Table XI gives the results of fitting the experimental values of the mean activity coefficient of calcium chloride with the extended model. The experimental values are

TABLE XI
ACTIVITY COEFFICIENTS OF AQUEOUS CALCIUM
CHLORIDE SOLUTIONS AT 25°C

Mean Molality	Activity Coefficient	Percent Deviation with 6 Parameters	Percent Deviation with 3 Parameters
.005	.787	.3	.2
.05	.577	.4	.1
.5	.447	.5	.3
1.0	.497	.3	.9
3.0	1.459	.5	.7
5.0	5.858	.4	1.4
7.0	18.17	.3	37.
9.0	34.20	.5	227.

listed in column 2, whereas column 3 gives the percentage deviation from those values of the results of a fit of the activity coefficients using Pitzer's model extended through sixth order. For comparison, percentage deviation values for the low concentration fit previously obtained with the unextended (third order) model² are given in column 4. The extended model gives a dramatic improvement in the quality of fit at high concentrations, without compromising agreement in the dilute region.

3. Solubility Predictions at high Temperatures. To test the effectiveness of the Pitzer model at high temperatures, predictions of the solubility of calcium sulfate in sodium chloride solutions have been compared with those obtained by Kerrisk⁹ from a number of other models commonly used in geochemical calculations. Predicted anhydrite solubilities at 200°C and 250°C are shown in Fig. 24. The upper solid line represents smoothed experimental data for anhydrite solubility at 200°C,

whereas the lower line represents the data at 250°C. The open circles give anhydrite solubilities predicted by Pitzer's model at 200°C, which are in excellent agreement with the experimental results. Other symbols in Fig. 24 represent anhydrite solubility predictions at 250°C, obtained by Kerrisk from different geochemical models. Unfortunately, anhydrite solubility predictions from Pitzer's model cannot be made above 200°C, because the required input data are not available above that temperature. Although the solubility predictions must be compared at 200°C and 250°C, it is clear that Pitzer's model gives a better representation of anhydrite solubility.

4. Electrolyte Solution Theories. Two additional solution models were examined in an attempt to find a method that might be suitable for predicting the properties of electrolyte solutions above 200°C. These models differ radically from each other and from Pitzer's model in their approach to describing solution properties. By

Fig. 24.

Comparison of predicted and experimental anhydrite (CaSO) solubilities in sodium chloride solutions. Smoothed experimental values are given by the solid lines (200°C-upper line, 250°C-lower line). Symbols represent solubilities predicted by various models.

comparing the different models, the relative importance of the various short range and long range forces present in electrolyte solutions can be determined. This leads to a better understanding of the basic properties of electrolyte solutions and may eventually result in a predictive model for high temperature aqueous solutions.

The first model examined was based on the Born equation, which gives the contribution of long range electrostatic forces to the free energy, assuming a hard sphere electrolyte of average radius R in a continuous dielectric medium with dielectric constant D ,

$$G^{el} \propto \frac{-1}{R} \left(1 - \frac{1}{D}\right)$$

Helgeson and Kirkham¹⁰ used the Born equation to calculate the electrostatic contribution to the volume and its pressure and temperature derivatives, basing extrapolations to higher temperatures on volumetric data available below 200°C. However, Smith-Magowan and Wood¹¹ recently measured the high pressure heat capacities of NaCl solutions and found that the pressure dependence at 300°C predicted by Helgeson and Kirkham is 78% too high.

To determine the cause of this discrepancy, the Born radius necessary to reproduce the high temperature heat capacities was redetermined (in collaboration with R. H. Wood, University of Delaware.) The same radius was found to reproduce recent high temperature volumetric properties, as shown in Fig. 25. At 200 bar, the agreement between the experimental volumetric properties (points) and those predicted by the Born equation (solid line) is good above ~250°C, but poor below that temperature. One explanation for this behavior is that, at low temperatures, the contributions of the long range electrostatic forces (approximated by the Born equation) and various short range forces are of about the same order of magnitude. At high temperatures, however, the effects of the electrostatic forces become very large (because of the decrease in dielectric constant) and simply overwhelm any contributions from short range forces. It is in this region that the Born equation is a successful model for solution properties.

Fig. 25.

Temperature dependence of the partial molar volume at infinite dilution (V_2^0) at 200 bar. Circles (some with error bars) represent experimental determinations. The solid line gives values predicted using the Born equation.

The extrapolated properties for NaCl solutions calculated by Helgeson and Kirkham are in error because the experimental data they considered extended only to 200°C. At that temperature, the contributions of short range forces are still significant, and the Born equation is inadequate. The Born equation also was shown to be inadequate below 300°C at higher pressures. In this region the electrostatic contribution decreases rapidly as the pressure increases, and again short range forces contribute significantly to solution properties. Thus the Born equation is an adequate model for aqueous solutions only near the saturation curve.

The second model studied is a revised version of the ITG model recently used by Leyendekkers^{12,13} at room temperature. The ITG model assumes that the orientational and electrostriction effects of the solute ions on water in the solution can be mimicked by an increase in pressure on pure water. Thus, the contribution of the water (in the solution) to any solution property can be calculated using the properties of pure water at a higher effective pressure. The difference between the experimental value of the property and the contribution of the water is assumed to be related to the intrinsic properties of the solute. Leyendekkers has shown that a single effective pressure function for each electrolyte can be used to

describe several different thermodynamic and non-thermodynamic properties. In addition, at room temperature the effective pressure function is independent of system pressure up to at least 1 kbar. This aspect of the TTG model was especially intriguing, because it would allow estimation of the pressure dependence of solution properties.

Unfortunately, attempts to extend the TTG model showed that many of the assumptions made in deriving the TTG equations were not correct at high temperatures. In particular, the effective pressure function changes dramatically with pressure at high temperatures. However, approximate values of the model parameters for sodium chloride solutions at 200 bar were obtained, and it is interesting to compare these results with those from the Born equation.

The TTG equation for the total volume of solution at system pressure P is

$$V_S^P = V_W^{P+P_e} + m V_{in}$$

where $V_W^{P+P_e}$ is the volume of pure water at the higher pressure $P+P_e$, P_e is the effective pressure function (which depends on concentration), V_{in} is related to the intrinsic volume of the solute, and m is the solution molality. The results of fitting the volumetric properties of sodium chloride with this equation are given in Table XII, which lists the effective pressure, the change in the volume of pure water in going from pressure P to $P+P_e$, and the intrinsic volume. The intrinsic volume of the solute decreases by approximately 30% from 25 to 300°C, indicating that short range forces pull the solvation sphere closer to the solute ions at high temperatures. The effective pressure remains relatively constant between 100 and 300°C; however, the change in the volume of water increases rapidly near 300°C. Again, the results indicate that electrostatic contraction of the water is the major contribution to solution properties at high temperatures and low pressures. This contribution is predominant only because of the large compressibility of water in that region.

TABLE XII
TTG PARAMETERS FOR SODIUM CHLORIDE VOLUMETRIC
PROPERTIES AT 1.0 M AND 200 BAR

T (°C)	P_e (bar)	$V_W^P - V_W^{P+P_e}$ (cm ³ /g)	V_{in} (cm ³ /mol)
25	242	.0100	29.1
50	230	.0093	29.5
100	170	.0078	27.6
150	154	.0091	26.6
200	148	.0124	22.6
250	147	.0201	19.3
300	160	.0436	19.4

5. Future Work. A calorimeter capable of operating from 0°C to 350°C will be constructed to determine the thermodynamic properties of both single and mixed electrolyte solutions. The experimental information will be used to extend suitable aqueous solution models to high temperatures and thus provide a basis for modeling more complex aqueous systems.

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VI. INORGANIC CHEMISTRY

A. Small Molecule Chemistry

1. Reduction of SO_2 with Transition Metal

Hydride Complexes (G. J. Kubas, G. D. Jarvinen, D. C. Moody, K. V. Salazar, and R. R. Ryan). The reduction of SO_2 with H_2 or CO to give sulfur and H_2O or CO_2 could be an attractive method for the removal of SO_2 from flue gases. Among the objectives of our studies of transition metal sulfur dioxide complexes we include finding metal systems that will act as catalysts for the reduction of SO_2 or will provide models for the elementary steps in a catalytic cycle. A great deal of mechanistic information has been gathered about homogeneous transition metal systems that act as catalysts for the hydrogenation of organic substrates.¹ Transition metal hydride complexes have been shown to be important intermediates in these catalytic cycles.¹ Thus, in seeking homogeneous systems to catalytically or stoichiometrically hydrogenate SO_2 , we have been studying the reactions of metal hydride complexes with SO_2 .

Solutions of the complexes $\text{RhCl}(\text{PPh}_3)_3$ and $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ are known to catalytically hydrogenate alkenes and other unsaturated compounds at 25°C under one atmosphere of H_2 .¹ We were interested to see if these known hydrogenation systems would reduce SO_2 . Under an atmosphere of H_2 at 25°C these complexes oxidatively add H_2 to give $\text{RhH}_2\text{Cl}(\text{PPh}_3)_3$ and $\text{CoH}_3(\text{PPh}_3)_3$, which are intermediates in the catalytic hydrogenation cycles.¹ Addition of SO_2 to a CHCl_3 solution of $\text{RhH}_2\text{Cl}(\text{PPh}_3)_3$ under H_2 results in rapid evolution of H_2 and formation of a dimeric complex with the composition $[\text{RhCl}(\text{PPh}_3)_2(\text{SO}_2)]_2$. The same complex is obtained by reacting SO_2 with solutions of $\text{RhCl}(\text{PPh}_3)_3$ or $\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$. The structure of the complex as determined by x-ray diffraction is shown in Fig. 26.² The Rh atoms exhibit square pyramidal coordination with SO_2 binding at the axial position. The SO_2 coordination geometry is η^1 -pyramidal and the S-O stretching frequencies of the complex (1166, 1031 cm^{-1}) and its reaction with O_2 to give a sulfate are consistent with the general properties of η^1 -pyramidal SO_2 complexes. Apparently SO_2 displaces the hydride ligands of $\text{RhH}_2\text{Cl}(\text{PPh}_3)_3$ as H_2 and this

Fig. 26.

Molecular structure of $[\text{RhCl}(\text{PPh}_3)_2(\text{SO}_2)]_2$. (Phenyl groups have been omitted for clarity.)

precludes any further interaction of the SO_2 and hydride ligands at least under these mild conditions.

Addition of SO_2 to a yellow THF solution of $\text{CoH}_3(\text{PPh}_3)_3$ results in rapid precipitation of a purple complex with the composition $\text{Co}(\text{SO}_2)_2(\text{THF})$. The same purple complex results upon addition of SO_2 to a solution of $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ or $\text{CoH}(\text{CO})(\text{PPh}_3)_3$. The loss of PPh_3 and the color change suggest an oxidation of the Co. A series of broad absorptions in the S-O stretching region between 1200 and 850 cm^{-1} suggests that the purple complex contains SO_2 bound in more than one environment or coordination geometry. The reaction of SO_2 with $\text{CoH}(\text{CO})(\text{PPh}_3)_3$ occurs slowly relative to the trihydride and dinitrogen complexes and yields crystals of the purple complex rather than a fine powder. The crystal structure as determined by x-ray diffraction has not been satisfactorily refined so far, but a very interesting coordination complex is emerging consisting of a hexamer of Co atoms, each with a coordinated THF molecule, connected by SO_2 molecules bonding in two new bridging geometries through the O atoms. The fate of the hydride ligands is not known at this point. For this Co system it seems that the formation of this very stable and nearly insoluble hexamer blocks any catalytic cycle for the hydrogenation of SO_2 .

The group VI hydride complexes Cp_2MH_2 ($\text{M} = \text{Mo}, \text{W}$) are not very active catalysts for hydrogenation

of alkenes relative to the group VIII systems discussed above, but the Cp_2MH_2 complexes readily hydrometalate electron deficient alkenes and alkynes to give stable hydrido alkyl complexes.³ The Cp_2MH_2 complexes have a base strength comparable to organic amines and form adducts with Lewis acids such as BF_3 .^{3,4} Thus we thought a donor-acceptor complex $\text{Cp}_2\text{MH}_2(\text{SO}_2)$ with SO_2 acting as a Lewis acid followed by interaction of the hydride and SO_2 ligands seemed a plausible reaction scheme.

Addition of SO_2 to a toluene solution of Cp_2MH_2 ($\text{M} = \text{Mo}, \text{W}$) at 25°C results in the rapid formation of a nearly quantitative yield of a thiosulfate complex $\text{Cp}_2\text{M}(\text{S}_2\text{O}_3)$ and water. A crystal structure determination, shown in the Fig. 27, has established the bidentate S,O-thiosulfate coordination for the Mo complex. Partial reduction of SO_2 has occurred in forming the thiosulfate and water. Heating a toluene solution of the thiosulfate complex at 100°C with excess SO_2 under 60 atmospheres of H_2 gave no apparent reaction. Formation of the stable thiosulfate complex appears to prevent further hydrogenation of SO_2 . The reaction occurs much too rapidly near 25°C to provide any details of the mechanism, and at low temperature no definitive information has been obtained. The reaction of SO_2 with the related complexes Cp_2TaH_3 and Cp_2ReH

Fig. 27.

Molecular structure of $\text{Cp}_2\text{Mo}(\text{S}_2\text{O}_3)$. (Hydrogen atoms have been omitted for clarity.)

is being carried out to better define the reaction pathway and to determine if thiosulfate formation can be avoided so that further reduction of SO_2 might be accomplished.

The stoichiometric hydrogenation reactions of the cluster hydride $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with various organic substrates have been studied extensively.⁵ This unsaturated 46 electron cluster has been shown to add a variety of two electron donors to give saturated 48 electron clusters, often involving hydrogen transfer to unsaturated portions of the donor molecule. We have been investigating the reaction of this complex with SO_2 , which is a two electron donor ligand with the potential to accept hydrogen. Of additional interest was the possibility that coordination of SO_2 to the metal atoms of a cluster complex could result in new types of SO_2 bonding and reactivity that cannot occur in a mononuclear complex.

A series of products is produced when $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ and excess SO_2 react in solution near 25°C . The first complex observable in the infrared or ^1H nmr spectra of the reaction mixture is $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-SO}_2)$. This complex has been isolated and its characterization includes a crystal structure, which is shown in Fig. 28. The SO_2 ligand acts as a two electron donor coordinating in a bridging geometry. One hydride ligand bridges the

Fig. 28
Molecular structure of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-SO}_2)$.

Os1-Os3 bond as shown. The other ligand bridges the same Os2-Os3 bond as the SO_2 but was not located in the refinement of the structure. However, its presence can be observed in the ^1H nmr spectrum and inferred from the arrangement of the carbonyl ligands around Os2 and Os3 . The structure is also closely analogous to that determined for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)$ by neutron diffraction,⁶ with SO_2 replacing the methylene bridge. The bonding in the SO_2 complex can also be described by the same qualitative molecular orbital scheme used for the methylene complex because the frontier orbitals of SO_2 and CH_2 have similar symmetry properties for interacting with the metal orbitals.

The bridging SO_2 complex is not stable in solution near 25°C and gives additional products. In the ^1H nmr spectrum the hydride resonances of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu\text{-SO}_2)$ at τ 24.2 and 28.5 gradually diminish while two new resonances at τ 4.8 and 26.1 grow in intensity. The peak at τ 4.8 is broad and is probably due to a hydroxyl proton undergoing chemical exchange at an intermediate rate. Thus we seem to be observing an interaction of a hydride ligand with coordinated SO_2 , to give some type of O-H containing species. An IR spectrum of the solid isolated from the reaction solution shows $\nu(\text{SO})$ at 1074 and 809 cm^{-1} suggesting an η^2 -bonded SO_2 ligand. We are continuing to characterize this interesting new product and hope to study the interaction of the hydride and SO_2 ligands in some detail, which has not been possible in any hydride- SO_2 systems reported to date.

The O-H containing species is not the final product in solution as the ^1H nmr spectrum at longer times continues to change and the IR spectra of solids obtained from the reaction solution show complex $\nu(\text{CO})$ absorptions in the range $2150\text{-}1900\text{ cm}^{-1}$ and broad absorptions in the $\nu(\text{SO})$ region between 950 and 850 cm^{-1} . Mass spectral data obtained from these solids have suggested the presence of $\text{Os}_3(\text{CO})_{12}$ and the sulfide cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$. This may indicate that a complex series of intermolecular reactions is occurring involving hydrogen and CO transfer. Study of this osmium system is continuing and work with related Fe and Ru systems is also being pursued.

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2. Stereochemical Control of and Reactivity of Molybdenum and Tungsten SO_2 Complexes (G. J. Kubas, G. D. Jarvinen, and R. R. Ryan). A large variety of d^6 molybdenum and tungsten SO_2 complexes has been systematically synthesized and characterized to determine the extent and nature of stereochemical controls of the metal- SO_2 bonding geometry.¹⁻⁴ The ability to control SO_2 bonding is important because we are currently placing emphasis on the reactivity of coordinated SO_2 , and the reactivity is dependent upon SO_2 bonding geometry. For d^6 complexes, the η^1 -planar and η^2 geometries have been observed whereas the η^1 -pyramidal has not and is not expected. Table XIII summarizes the

complexes we have studied and the remarkable sensitivity of the SO_2 geometry to ancillary ligand changes that we have been able to design in the complexes. Note that modification of the π -acceptor strength of just one ligand (B') complexes IV-IX leads to changes in SO_2 bonding and the coexistence of both η^1 -planar and η^2 - SO_2 isomers has been observed. These studies show that a high degree of stereochemical control has been achieved and have allowed us to formulate the following bonding principles regarding η^2 - SO_2 :

- a) The η^2 geometry involves more $\text{M} \rightarrow \text{SO}_2$ π donation and less $\text{SO}_2 \rightarrow \text{M}$ sigma donation than does the η^1 -planar case. The η^2 geometry is, therefore, generally discouraged by strongly accepting ligands and encouraged by strong σ donating ligands.

- b) The existence of a D-M-A (D = donor or weak acceptor, A = acceptor) conformation cis to SO_2 promotes η^2 bonding and dictates the orientation of the S-O_M bond; the sulfur atom lies closest to the acceptor ligand.

Table XIII also demonstrates a clear correlation between bonding geometry and $\nu(\text{SO})$. The high set of frequencies for η^1 -planar SO_2 than η^2 - SO_2 allows us to distinguish between the two without carrying out crystallographic studies.

In regard to activation of coordinated SO_2 , η^2 - SO_2 is generally more reactive than is η^1 -planar SO_2 . Also, the basicity of the terminal oxygen of η^2 - SO_2 has been demonstrated in the dimeric complex $[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{py})(\mu\text{-SO}_2)]_2$, in which the oxygen binds to a second Mo atom.² Thus, we have devoted considerable attention to the η^2 geometry and several experiments designed to promote binding of electrophiles and Lewis acids to coordinated S have been carried out. The results of the studies showed that the Mo and W η^2 - SO_2 complexes were indeed reactive; MeSO_3F converted SO_2 organo-sulfur species for example. In most cases the products of the reaction were difficult to characterize because the lability of the ancillary ligands (e.g. phosphines, pyridine) led to side reactions and/or decomposition. Thus, a study of SO_2 reactions using complexes with nonlabile ligands such as cyclopentadienide is the next logical step and should provide much cleaner products.

TABLE XIII
EFFECT OF ANCILLARY LIGANDS ON SO₂ COORDINATION GEOMETRY AND INFRARED FREQUENCIES

		A	A'	B	B'	$\nu(\text{SO})$ (cm ⁻¹)	$\nu(\text{CO})$ (cm ⁻¹)
$\eta^2\text{-SO}_2$	I	SO ₂	CO	phen	phen	1149, 935	1984, 1898
	II	SO ₂	SO ₂	bipy	bipy	1138, 873	2000, 1953
	III	SO ₂	PPh ₃	bipy	bipy	1107, 903	1898, 1805
	IV	PPh ₃	PPh ₃	SO ₂	MeCN	1138, 910	1920, 1836
	V	PPh ₃	PPh ₃	SO ₂	py	1130, 905	1928, 1820
$\eta\text{-SO}_2$ +	VI	PPh ₃	PPh ₃	SO ₂	CNBU ^t	1119, 906	1937, 1875
$\eta^1\text{-SO}_2$	VII	PPh ₃	PPh ₃	SO ₂	CNCy	1229, 1066 1119, 912 1225, 1064	1958, 1892 1931, 1872 1956, 1890
$\eta^1\text{-SO}_2$	VIII	PPh ₃	PPh ₃	SO ₂	CN(p-tolyl)	1227, 1065	1960, 1876
	IX	PPh ₃	PPh ₃	SO ₂	CO	1254, 1080	2015, 1953, 1908
	X	PPr ⁱ ₃	PPr ⁱ ₃	SO ₂	CO	1237, 1071	1997, 1931, 1889
	XI	PCy ₃	PCy ₃	SO ₂	CO	1239, 1070	1996, 1917, 1886
	XII	SO ₂	PMePh ₂	PMePh ₂	PMePh ₂	1194, 1052	1982, 1877
	XIII	SO ₂	PMe ₂ Ph	PMe ₂ Ph	PMe ₂ Ph	1173, 1043	1981, 1857
	XIV	SO ₂	CyNH ₂	CyNH ₂	CyNH ₂	1150, 1021-36	1894, 1791

An interesting series of complexes (XII-XIV) of the type Mo(CO)₂L₃(SO₂) was synthesized and found to contain η^1 -planar SO₂. The geometry was unexpected because the presence of three sigma donating ancillary ligands would appear to favor η^2 bonding. An x-ray crystal structure of Mo(CO)₂(CyNH₂)₃(SO₂) revealed that the cyclohexylamine ligands coordinate in facial fashion (Fig. 29).

The most intriguing feature of this complex was found to be its novel reactivity with oxygen:

The production of uncoordinated sulfate from SO₂ complexes is quite rare, if not unprecedented, and a catalytic method for SO₂ oxidation to sulfate would be of considerable interest. However, the mechanism may involve reaction of dissociated ligands because SO₂ and CyNH₂ were found to give

Fig. 29.

Inner coordination sphere for $\text{Mo}(\text{CO})_2(\text{CyNH}_2)_3(\text{SO}_2)$

$[\text{CyNH}_3][\text{HSO}_3]$ in DMSO, and air-oxidation of the bisulfite to sulfate was catalyzed by the molybdate coproduct of the reaction. Thus, it is probable that oxidation of the metal with concomitant ligand loss occurs initially, followed by reaction of SO_2 , CyNH_2 , and H_2O to give bisulfite and eventually sulfate. The ammonia analogue, $\text{Mo}(\text{CO})_2(\text{NH}_3)_3(\text{SO}_2)$, was also synthesized and found to be air-sensitive. However, $(\text{NH}_4)_2\text{SO}_4$ was not a product of oxidation, possibly because of the volatility of NH_3 and/or the existence of a different reaction pathway.

Summarizing, the d^6 octahedral Mo and W SO_2 complexes were discovered to be ideally suited for design of stereochemical control of SO_2 bonding geometries. Although the nature of the complexes was such that their reactions involved more than just the SO_2 ligand, valuable information was obtained for future probing of the reactivity of coordinated SO_2 .

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3. Reactivity of $\text{Pt}(\text{PCy}_3)_2$ and $\text{Pt}[\text{P}(\text{t-Bu})_3]_2$ and Their SO_2 Complexes with Small Molecules (J. M. Ritchey,* D. C. Moody, and R. R. Ryan). The study of SO_2 derivatives of zerovalent platinum complexes, and transition metal- SO_2 complexes in general, has received considerable attention in the past six years as exemplified by the 293 references cited in two recent reviews.^{1,2} At the same time, considerable effort has been focused on the synthesis and properties of two coordinate complexes belonging to the nickel triad.³ These complexes are still relatively rare, however, and no reports of their reactivity with SO_2 have appeared. The studies described below were carried out with the intent to utilize inherent coordination and electronic unsaturation of two of these complexes, $\text{Pt}(\text{PCy}_3)_2$ and $\text{Pt}[\text{P}(\text{t-Bu})_3]_2$, to promote reactions of bound SO_2 . Further, a comparison of the chemistry of these complexes has been undertaken to provide an understanding of stereochemical control and catalytic properties of these and similar complexes with small molecules including SO_2 , O_2 , H_2 , CO , CO_2 , CS_2 and C_2H_4 .

To strengthen the likelihood that $\text{Pt}(\text{phosphines})_2$ would coordinate only small molecules in a third coordination site and at the same time circumvent addition of a third phosphine, careful

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attention was paid to phosphine size. An obvious strategy is to employ ligands with large cone angles (a measure of steric bulk⁴) and to utilize variations in reactivity that accompany slight changes in the cone angles of the phosphines employed. $\text{Pt}(\text{PCy}_3)_2$ and $\text{Pt}[\text{P}(\text{t-Bu})_3]_2$ (cone angles 170° and 182° , respectively) were selected because of previously reported⁵ differences in reactivity toward H_2 , O_2 and small HX compounds.

It is important to emphasize the greatly reduced reactivity of $\text{Pt}[\text{P}(\text{t-Bu})_3]_2$ in comparison to $\text{Pt}(\text{PCy}_3)_2$ and especially with respect to platinum-phosphine analogs with smaller steric bulk. For example, conversion of Pt-SO_2 to Pt-SO_4 complexes is ordinarily a facile process in the presence of air.² Yet, contrary to the nearly instantaneous reaction of $\text{Pt}(\text{Cy}_3)_2$ and $\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2$ in air to form $\text{PtO}_2(\text{PCy}_3)_2$ and $\text{Pt}(\text{SO}_4)(\text{PCy}_3)_2$ respectively, the corresponding $\text{P}(\text{t-Bu})_3$ analogs are essentially inert. Similarly, Mingos⁶ has emphasized the ability of $\text{Pt}(\text{CS}_2)(\text{PPh}_3)_2$, PPh_3 cone angle 145° , to rapidly form the dithiocarbonate complex $\text{Pt}(\text{S}_2\text{CO})(\text{PPh}_3)_2$ in the presence of SO_2 , and Nyman⁷ has reported $\text{PtO}_2(\text{PPh}_3)_2$ to immediately form the same species with CS_2 . In contrast, we observe greatly reduced reactivity; apparently the greater phosphine bulk shuts down these reactions. We have made a systematic study of these and other reactions as outlined as follows.

A preliminary x-ray crystal structure analysis has been performed on $\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2$, the first three-coordinate platinum(0) sulfur dioxide complex to be reported. The SO_2 molecule is bound to the platinum moiety with an η^1 -pyramidal SO_2 geometry as shown in Fig. 30. Analysis of the infrared spectrum reveals $\nu(\text{SO})$ peaks at 1162 , 1029 cm^{-1} and a bending mode at 508 cm^{-1} , which are consistent with this geometry.^{2,8} It is also interesting to note the relatively short Pt-S distance of $2.26 \text{ \AA}$ observed in this three-coordinate complex as compared to the longer distances ($2.37 - 2.46 \text{ \AA}$) found for the four-coordinate $\text{Pt}(\text{O})$ complexes also containing the η^1 -pyramidal geometry. Presumably the two coordination of the phosphine ligands permits closer access of SO_2 to the platinum center.

The versatility of $\text{Pt}(\text{PCy}_3)_2$ toward CO_2 , H_2 , C_2H_4 , and CO has been examined,⁵ but not in the context of SO_2 chemistry. In the main, our work is the first organized study of this chemical reactivity, a part of which is shown below.

We have found that bis(ethylene)(tricyclohexylphosphine)-platinum(0) readily reacts with SO_2 under mild conditions and in nearly quantitative yields to form the cyclic trimer $\text{Pt}_3(\text{SO}_2)_3(\text{PCy}_3)_3$. By comparison, $\text{Pt}_3(\text{CO})_3(\text{PCy}_3)_3$ reacts slowly (days) with SO_2 to produce the same sulfur dioxide complex.

Fig. 30.

Structure of $\text{Pt}(\eta^1\text{-SO}_2)(\text{PCy}_3)_2$.
(Tricyclohexylphosphine groups indicated with a P.)

Although this SO_2 trimer is not fully characterized at this writing, it is clear from the $\nu(\text{SO})$ values of 1248 and 1077 cm^{-1} , the SO_2 is bridging rather than η^1 -pyramidal. Characteristic of transition metals with SO_2 in a bridging configuration, the oligomer does not form the sulfato complex upon exposure to oxygen. This new synthesis is more rapid and convenient and provides superior yields than the somewhat serendipitous procedure reported for the analogous $\text{Pt}_3(\text{SO}_2)_3(\text{PPh}_3)_3 \cdot \text{C}_7\text{H}_8 \cdot \text{SO}_2$ complex.⁹ A smooth reaction with $\text{Pt}(\text{PCy}_3)(\text{C}_2\text{H}_4)_2$ and CS_2 occurs, yielding what we believe to be the first platinum bridging $\eta^2\text{-CS}_2$ species. Examination of the infrared spectrum shows a band at 1113 cm^{-1} attributable to the C=S stretch, which agrees well with those found in other transition metal complexes containing a bridging CS_2 group,¹⁰ as does the absence of a C-S bending mode at 653 cm^{-1} found for the authentic $\text{Pt}(\text{CS}_2)(\text{Cy}_3)_2$ compound. Further characterization is continuing on this compound.

It is noteworthy that the carbonyl chemistry of $\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2$ and $\text{Pt}_3(\text{SO}_2)_3(\text{PCy}_3)_3$ is dependent upon the time and order of addition of the ligating moieties. We report the first example of a mixed $\text{Pt-SO}_2\text{-CO}$ complex as a result of the reaction of $\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2$ and CO over a period of days. It is not clear from the infrared spectrum [$\nu(\text{CO})$: 1834, 1777 cm^{-1} ; $\nu(\text{SO})$: 1214, 1069 cm^{-1}] whether the CO and SO_2 ligands are in terminal or bridging modes. Further study on these systems is continuing.

Finally, we are currently examining the interaction of several zerovalent platinum compounds with CO_2 . We have shown that the compound $\text{Pt}(\text{CO}_2)(\text{PCy}_3)_2$ can be prepared under mild conditions of bubbling CO_2 through a hexane solution of $\text{Pt}(\text{PCy}_3)_2$ as long as the solution is kept scrupulously free of oxygen. An earlier report¹¹ suggested that the reaction conditions required liquid CO_2 . This is the first example of a $(\eta^2\text{-CO}_2)$ -platinum complex to be reported. Bomb reactions with H_2 and $\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2$, as well as $\text{Pt}(\text{PCy}_3)_2$, H_2 and subsequent addition of SO_2 showed no catalytic effect for the platinum moiety. By contrast, we have preliminary evidence suggesting a solution of $\text{Pt}(\text{PCy}_3)(\text{C}_2\text{H}_4)_2$ is catalytically reduced with H_2 in a solution saturated with CO_2 . Further studies are underway to clarify this reaction.

It should be obvious that the small molecule reactions of $\text{Pt}(0)$ complexes are sensitive to electronic and steric controls and that the range of these reactions are rich and at the same time selective. Much investigation needs to be done to understand these interactions.

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B. Actinide Chemistry

1. Valence, Size, and Coordination Properties of Actinides Pertinent to Storage in Synthetic Materials (R. A. Penneman and P. G. Eller). We have continued to apply crystal chemical considerations to certain aspects of actinide immobilization in proposed waste forms giving special attention to americium, as it is the major contributor to nuclear waste hazards from ~ 500 to 50,000 years. As an example, application of Zachariasen's bond strength-bond formula^{1,2} to zirconolite, CaZrTi₂O₇ (a component of SYNROC), shows quite

clearly that the size/coordination requirements for trivalent actinides more closely match the eight-coordinate Ca³⁺ site than either +3 or +4 actinides in the seven-coordinate Zr⁴⁺ site. This prediction is based on the bond distance preferences of Am³⁺ and Am⁴⁺ in various known oxygen coordinated sites, i.e. we calculate these optimum bond distance requirements:

$$\begin{aligned} \text{Am}^{3+}\text{-O}_7 &= 2.43 \text{ \AA}; \text{Am}^{3+}\text{-O}_8 = 2.47 \text{ \AA}; \\ \text{Am}^{4+}\text{-O}_8 &= 2.33 \text{ \AA} \end{aligned}$$

where the oxygen subscripts denote the metal coordination numbers. Thus, in contrast to suggestions by others, we predict a strong partitioning of Am as a trivalent ion into the Ca³⁺ site of zirconolite, with vacancies or charge compensation in the Zr or Ti sites required.

In natural minerals, "impurities" or vacancies can provide charge compensation needed for substitution of a trivalent for divalent ion or tetravalent for trivalent ion. At Oak Ridge³ synthetic monazites are prepared from a lead pyrophosphate flux. Lead as Pb²⁺ is thought to play this role in their trivalent lanthanide phosphates when U⁴⁺ or Th⁴⁺ was substituted for La³⁺. A dramatic example of lattice site effects influencing valence stability is their finding the EPR signal of trivalent lead (an unusual valence for lead) in crystalline LuPO₄, with Pb³⁺ substituting for Lu³⁺. (Interpolating between Pb⁴⁺ and Pb²⁺ ionic radii to guessimate the radius of Pb³⁺, one gets an excellent fit to this site)

Although it is a general observation that strongly basic oxide matrices stabilize the higher (more acidic) americium oxidation states (such as Am(VI) in Ba₃AmO₆) over the trivalent state, exceptions can arise. For example in monazite, which favors trivalent cations of appropriate size, we predict that Am(III) will be stabilized over Am(IV). That is, even if Am⁴⁺ can be put into monazite, say by dissolving AmO₂ in monazite with high oxygen overpressure, it will be reduced by radiation effects, the more rapidly with higher specific activity isotopes. This should be true even though U⁴⁺ and Th⁴⁺ are both found in natural monazite. One could argue that the trivalent state of thorium is unavailable, but U³⁺ is certainly an attainable

oxidation state. Also there may be cases, e.g. with curium, in which the energy to produce the tetravalent state from the trivalent one is sufficiently large that radiation effects will cause reduction even in a site strongly favoring tetravalent ions.

Because the elements plutonium, americium, and curium have profoundly different valence stabilities in a variety of chemical situations, we anticipate differences when they are incorporated in oxide matrices and exposed to radiation (self radiation or other). We can anticipate both oxidation and reduction to occur.

When complexed by aqueous heteropoly tungstates and molybdates, the stabilization of plutonium(IV) over plutonium(III) is about one volt compared to the aqueous potentials.⁴ This amount of stabilization will greatly stabilize Pu(IV), stabilize Am(IV) to about the normal Ce(IV/III) value, but should not be sufficient to stabilize Cm(IV) over Cm(III) against reduction by radioactivity or other constituents in the crystal. However, we do suggest that valence stabilization effects in selected solids can be chosen so as to favor certain oxidation states.

Divalent americium can be prepared in some solids, for example, from the reaction of excess metal with halides, but Am^{2+} is such a powerful reducing agent that it is not known in aqueous solution. Yet Am^{2+} has been detected when Am^{3+} in dilute CaF_2 solid solution is cooled to liquid helium temperatures. The electrons ejected in the lattice by alpha bombardment can, at low temperatures, reduce Am^{3+} ions to Am^{2+} ions as demonstrated unequivocally by EPR.⁵ Increasing temperatures causes loss of the Am^{2+} signal.

A lattice effect caused by the longer bond distances required by actinide oxygen bonds is illustrated by the following. In classic perovskite, CaTiO_3 , the Ti^{4+} -oxygen distance is half the cubic cell edge, because the $\text{M}^{4+}\text{-O}_6$ octahedral bonds lie along the cube edges. In the barium analog BaTiO_3 , the Ti-O distance is ~ 2.0 Å.

In the barium actinide perovskite BaAmO_3 , we estimate per Zachariasen's formulas that the Am^{4+} -O bond distance should be 2.22 Å, which is much longer than the 2.17 Å distance obtained from the cell edge of putative "cubic" BaAmO_3 and BaPuO_3 . The praseodymium analog BaPrO_3 , originally reported as cubic, has been found by neutron diffraction to have lower symmetry, with the PrO_6 octahedra tilted off the "cubic" axes.⁶ This change in symmetry allows the Pr-O distances to lengthen to 2.22-2.23 Å, agreeing with our estimate of the longer distance required for $\text{Pr}^{4+}\text{-O}_6$ (2.23 Å). Thus, we predict that further work will show that the Am-O and Pu-O distances are actually close to values observed in the praseodymium compound and that these structures are not actually cubic, but are of lower symmetry.

Changes in crystal structure or site occupancy may be expected with radiation damage as an actinide III-IV valence change requires a ~ 0.15 Å change in each bond distance.⁷ Such valence changes may bring about lattice disruption, metamictization, or stabilization of alternate phases. Adjustment to these effects are likely to be different in special cases. For example, where the coordinating oxygens are immobilized by being covalently attached to silicate, phosphate, etc., oxygen mobility will be greatly lessened. This is in contrast to simple oxides, where statistical oxygen vacancies could more readily permit mixed valences, e.g., a ThO_2 solid solution containing both Am_2O_3 and AmO_2 . We estimate that Am^{3+} in six coordination has nearly the same Am-O distance as Th-O displays, eight coordinated in ThO_2 .

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2. The Synthesis and Structure of a Mixed Valent Uranium Complex: Tetra- μ -phenoxy-di- μ_3 -oxo-[bis(triphenoxytetrahydrofuranuranium(V))bis-(tetrahydrofurandioxouranium(VI))] (A. J. Zozulin, D. C. Moody, and R. R. Ryan). The alkoxides of uranium (IV), (V), and (VI) have received considerable attention, with the primary emphasis dating back to the Manhattan Project and the search for volatile uranium compounds suitable for uranium isotope separation. In recent years a wealth of information in this area has appeared. In contrast, there has been no report of an uranium(III) alkoxide. Since our initial discovery of a soluble form of uranium (III) chloride, $UCl_3(THF)_x$ (THF = tetrahydrofuran),¹ we have been interested in the

coordination and reaction chemistry of $U(III)^2$ and have recently begun a study to synthesize uranium(III) alkoxides.

Our attempts at synthesizing these complexes has involved a metathesis reaction of $UCl_3(THF)_x$ with the appropriate lithium, sodium, or potassium alkoxide salt. Two general types of reactions have been observed, with the least common type exemplified by the reaction with NaOMe where a stable uranium(III) alkoxide salt was formed, $NaU(OMe)_3Cl$. The most common result of these attempts, however, was partial oxidation of the uranium and the generation of a solution containing a mixture of $U(III)$ and $U(IV)$ products. Our work in this area established that in general the uranium(III) alkoxides suffer from a redox instability as well as a thermal instability, both giving rise to $U(IV)$ products.

This type of reaction was observed with sodium phenoxide. The addition of three equivalents of NaOPh to a THF solution of $UCl_3(THF)_x$ leads to an immediate color change (purple to red-brown) and the precipitation of NaCl. When a quantitative chloride analysis is performed on the NaCl by-product, only 50 to 60% of the theoretical yield is obtained, whereas analyses of the uranium product consistently showed the presence of chloride. The addition of ether, however, results in a quantitative precipitation of sodium chloride. In view of the insolubility of sodium chloride in THF, these facts suggest a possible initial uranium salt formation, which is disrupted upon addition of diethyl ether. We have thus far been unsuccessful at characterizing the products of this reaction and no uranium(III) phenoxide, the desired product, has been isolated. However, during these studies the ethereal solution was exposed to molecular oxygen, and an interesting reaction was observed that resulted in a dark red-brown solution, from which the title complex (I) was isolated.

A single crystal x-ray diffraction study established the molecular structure shown in Fig. 31. The compound exists as a tetrameric unit with crystallographically imposed I symmetry, composed of two uranium(V) atoms, $U(2)$, and two uranium(VI) atoms, $U(1)$, connected via four bridging phenoxides and two triply bridging oxygens. Each uranium atom has a

single coordinated THF molecule. The U(V) atoms are also bonded to three terminal phenoxides, whereas the U(VI) atoms exist as a uranyl moiety. The coordination polyhedron around each uranium atom can be regarded as a distorted pentagonal bipyramid. The U-U contacts are relatively short with $U(1)U(2) = 3.818(4)$ Å and $U(1)U'(1)$ and $U(2)U'(2) = 3.854(4)$ Å. The THF oxygen-uranium distance for the uranyl group is $2.42(2)$ Å and is similar to bond distances found for coordinated THF in other uranyl complexes.^{3,4} A considerably longer distance [$2.53(2)$ Å] is observed for the THF oxygen-uranium(V). The bridging phenoxides show an average U-O bond length of $2.42(2)$ Å as compared to $2.07(2)$ Å for the terminal phenoxides. Finally, the triply bridging oxygens show distances of $2.08(2)$ Å for the unique $U(2) - O(3)$, suggesting a bond order of one by comparison with the terminal alkoxide distances, and $2.28(2)$ Å for the average $U(1) - O(3)$.

From the crystal structure it can be seen that this complex contains uranium in both the +5 and +6 oxidation states. This represents the first structure determination of a uranium alkoxide containing uranium in two oxidation states. By summing the formal charges of the ligands around each uranium atom, U(1) would represent uranium in the +6 oxidation state while U(2) exists as U(V). The magnetic

susceptibility of the complex also suggests the presence of a uranium(V) ion. The compound obeys a Curie-Weiss plot at low temperatures with a calculated moment of 1.10 BM. Assuming there is little or no contribution to the moment from +6, this value is then consistent with moments reported for other uranium(V) complexes.⁵ The oxidation states may also be calculated from Zachariasen's bond length-bond strength relationships.^{6,7} In the present structure the oxidation states of each uranium atom were calculated to be 6.09 and 5.51 for U(1) and U(2), respectively. Abnormally high values for the +5 oxidation state have been obtained in calculations performed in this laboratory on U(V) compounds containing U-O-U bonds. This suggests a better correlation of Zachariasen's formalism to U⁺⁶ complexes than U⁺⁵ and may be due in part to more abundant crystallographic data available on bond lengths in U⁺⁶ compounds as compared to U⁺⁵ compounds.

In conclusion, the attempted synthesis of uranium(III) phenoxide complexes and subsequent air oxidation has led to the isolation and characterization of a unique mixed valent alkoxide complex, I. An earlier report of an unusual red uranyl alkoxide, $UO_2(OC_4H_9)_2 \cdot 4C_4H_9OH$, isolated from the air oxidation of $U(OC_4H_9)_4$, was characterized only by chemical analysis.⁸ In light of the data presented herein, it appears likely that the previously reported red uranyl alkoxide also exists as a mixed valent complex and not as a pure uranyl alkoxide.

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Fig. 31.
Coordination around the uranium atoms in I.

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3. The Structure of $\gamma(\text{NH}_4)_2\text{UF}_6$. A Crystallographic Tour de Force (R. R. Ryan and R. A. Penneman). The $(\text{NH}_4)_2\text{UF}_6$ system undergoes a remarkable series of structural changes over quite a narrow temperature range ($\sim 70^\circ$); this implies very small energy differences among these four structures (α , β , γ , and δ). When we first made this observation, no single crystal data were known.

The structure of the low temperature (α) phase was determined by us¹ several years ago and was found to contain linear chains of uranium atoms coordinated by eight fluorines as a square antiprism. The similar compound Rb_2UF_6 consists of chains of fluoride dodecahedra.² These two compounds exhibit closely related chain structures. The Rb-compound consists of infinite chains of $[\text{UF}_8]$ dodecahedra linked by edges of type m; the NH_4 -containing compound consists of chains of antiprisms linked by s edges on opposite square faces (see Fig. 32). The uranium positions as well as the nitrogen and rubidium positions are equivalent in the two structures. The fluorines in $(\text{NH}_4)_2\text{UF}_6$ are distorted

Fig. 32.

Projection of idealized eight-coordinate polyhedra. a) square antiprism, b) dodecahedron.

from the dodecahedral arrangement in Rb_2UF_6 so as to make maximum use of the H---F hydrogen bonding. This behavior suggests that the dodecahedron provides the energetically lower ground state configuration for this structure type.

Besides the α -phase, $(\text{NH}_4)_2\text{UF}_6$ exhibits at least three higher temperature phases,³ β , γ , δ . All of these phases have U-U distances of $\sim 4 \text{ \AA}$ and, therefore, contain (UF_x) in chains. The diffraction pattern of $\gamma(\text{NH}_4)_2\text{UF}_6$ shows a sub-cell that is similar to the α phase but exhibits weak reflections caused by scattering from a larger super-cell. Problems of this kind are a difficult crystallographic challenge in that scattering from the sub-cell contains little information about the super-cell structure. We now have solved the structure of $\gamma(\text{NH}_4)_2\text{UF}_6$ by accurately measuring the weak reflections, refining the sub-cell on the intensities (instead of the conventional structure of factor refinement) and sorting out the multiplicity of fluorine peaks (in the difference maps) by using a population analyses.

We find that the γ -structure consists of infinite chains of alternate antiprisms and dodecahedra, the common edges being the ℓ edges for the antiprisms and the G edges for the dodecahedra (Fig. 32). It is clear that the phase changes in these materials involve interconversions between the most common eight-coordination types: dodecahedron $\leftrightarrow$ antiprism. Of the several octacoordinate structures that contain linear chains of actinide fluoride polyhedra, only three have been accurately determined using three dimensional x-ray

data. All of these structures have been found to contain polyhedra of either the dodecahedron or antiprism type. Our study of $\gamma(\text{NH}_4)_2\text{UF}_6$ is the first to establish the coexistence of these two polyhedron types in the same crystal.

The different molecular arrangements available for eight coordination have been the subject of considerable attention. Eight coordination frequently occurs in actinide fluoride and oxide complexes, with the preponderance of these octacoordinate polyhedra being either the square antiprism, symmetry (D_{4d}), or the dodecahedron (D_{2d}) with triangular faces. Of the remaining idealized eight-coordinate polyhedra, some are not represented and others have but few representatives in this class of compounds.

The dodecahedron requires a larger radius ratio than the antiprism (i.e., 0.665 vs 0.645), and it is tempting to say that it is favored over the antiprism for the large actinide elements. An attempt was made by Hoard and Silverton⁴ to quantify the energy relationship between the square antiprism and the dodecahedron. The main conclusion of their study was that no significant difference exists between the ground state energies of the two types of polyhedra. The experimental evidence supports the conclusion that these two polyhedra are roughly equivalent in energy; the choice between them, in the actinide fluoride structures, is apparently decided by the packing forces. In the present case the coordination polyhedra are dictated by rotational reorientation of the NH_4^+ ions to participate in different N-H...F hydrogen bonding schemes.

The antiprism can be characterized by two parameters, i.e. l/s , the ratio of the length of the side of a triangular face to that of the edge of the square face, and θ , the angle between the $\bar{4}$ axis and the vector from the central ion to one of the ligands (see Fig. 32). Hoard and Silverton established the most favorable values for these parameters, based on their model, to be $l/s = 1.057$ and $\theta = 57.3^\circ$. The hard sphere model for the antiprism demands $l = s$ and $\theta = 59.25^\circ$.

Three parameters are necessary to characterize the dodecahedron with triangular faces (see Fig. 32). Hoard and Silverton chose for these parameters:

θ_A , the angle between the M-A bond vector and the $\bar{4}$ axis of the polyhedron; θ_B , the corresponding angle made with the M-B bond vector, and the ratio of the bond lengths, M-A vector/M-B vector. The most favorable values for these parameters are $\theta_A = 35.2^\circ$, $\theta_B = 73.5^\circ$ and $M-A/M-B = 1.03$. The corresponding values for the hard sphere model are $M-A = M-B$, $\theta_A = 36.9^\circ$ and $\theta_B = 69.5^\circ$.

It takes only a small distortion of the antiprism to bring it to the dodecahedral conformation; in crystal structures for which the site symmetry of the central ion is low as is often the case, it is a moot question as to which is the better idealized geometry for the description of the polyhedron. It has been the practice to use the parameters chosen by Hoard and Silverton to distinguish between the two polyhedra. This procedure has recently been criticized by Lippard and Russ⁵ who propose that different parameters be used in making this decision. The parameters they suggest are θ_{LR} , the angle between best planes through the atoms labeled AAB and through B'B'A'A' (interpenetrating trapezoidal planes), and (d) the average deviation of the ligand atoms from these planes. It should be noted that these parameters, while helpful, amount essentially to a rejection test and do not provide sufficient criteria for assigning a distorted polyhedron to one of the idealized polyhedra. We suggest a different and perhaps more objective criterion for testing the degree of deviation of a polyhedron from an idealized geometry is to find the best least squares fit of idealized polyhedra to the actual atom positions. A comparison of the sum of the squares of the residuals for the geometries to be tested then provides a meaningful parameter for making the choice of a suitable idealized geometry.

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4. Crystal Chemical Studies of Actinide

Molybdates (P. G. Eller, T. L. Cremers, R. A. Penneman, and A. Rosenzweig*). In the first Divisional Report,¹ we described the structure of low temperature (orthorhombic) uranium(IV) molybdate and noted its structural resemblance to some other (seemingly unrelated) binary oxides (see Fig. 33). Because of the possible pertinence of actinide molybdates to the PUREX "dissolver residue" problem, we have continued the characterization of the several reported actinide molybdate phases. In addition, these "oxide matrices" are typical of synthetic minerals being suggested for long term nuclear waste storage.

It is worthy of note that much of the previously published work in this area contains substantial errors, particularly in the positions of the light atoms and, hence, give an entirely erroneous view of the coordination. We believe that our work has established the correct structures in this area of possible importance to processing and also to actinide storage in synthetic minerals.

Hexagonal thorium molybdate was prepared¹ by skull melting of the oxides at 1200°C (see Fig. 34).

niversity of South Florida.

Fig. 33.

The structures of UMo_2O_8 , UVO_5 and U_3O_8 viewed normal to the sheets comprising the structures. In each structure, parallel sheets are connected by a 4.1 Å U-O-U linkage. A marked similarity also exists in the in-plane edge sharing of coordination polyhedra, particularly for the first two structures.

Crystals from the solidified melt were studied by single crystal x-ray crystallography. Crystal data: Hexagonal - $P6_3$, $a = 17.574(4)$, $c = 6.224(1)$ Å, $Z = 9$, $R = 0.032$ for 745 reflections with $I \geq 2\sigma(I)$.

Our study produced a much more accurate, more satisfactory geometry for the Th coordination and showed that the twinned P3 model proposed for this phase is incorrect.² Molybdate tetrahedra, which bridge to both six- and nine-coordinate thorium polyhedra, were found. In Fig. 35, the trigonal prismatic Th polyhedron is shown viewed parallel to the threefold axis.

Single crystals of orthorhombic $\text{Th}(\text{MoO}_4)_2$ were obtained by heating the hexagonal form at 800°C for one week, followed by slow cooling (1.5 days). An x-ray structure investigation confirmed the rough structure previously proposed by Thoret.² Space group - $Pbca$, $a = 10.318(5)$, $b = 9.737(4)$, $c = 14.475(6)$ Å, $Z = 8$, $R = 0.027$ for 2620 reflections with $I \geq 2\sigma(I)$. The structure is that of a true molybdate, containing MoO_4 tetrahedra with each oxygen shared by one Th and one Mo. The thorium coordination (Fig. 36) is that of a nearly regular square antiprism. There is no simple structural relationship to the hexagonal form.

Plutonium(IV) molybdate, PuMo_2O_8 , has been reported in two different orthorhombic forms, one form being isostructural with orthorhombic $\text{Th}(\text{MoO}_4)_2$ (described above) and one form having an unknown structure. The structurally undetermined form (and its dihydrate) can be obtained by aqueous precipitation and is claimed to be isomorphous with the natural mineral sedovite.⁵

Fig. 34.

Stereoplot of the structure of hexagonal thorium molybdate, viewed parallel to the unique axis.

Fig. 35.

The trigonal prismatic Th polyhedron in hexagonal thorium molybdate, viewed parallel to the threefold axis.

Fig. 36.

A view of the nearly regular square antiprismatic thorium coordination in orthorhombic thorium molybdate.

Sedovite has been described by Sidorenko and Skvortsova and allegedly has the composition UMo_2O_8 .^{3,4} The mineral is very rare, and the above authors do not give a specific locality for its occurrence. The lattice dimensions obtained by them by application of Ito's method to powder diffraction data are: $a_0 = 3.36 \text{ \AA}$, $b_0 = 11.08 \text{ \AA}$, and $c_0 = 6.42 \text{ \AA}$ for orthorhombic symmetry. Two lines of their pattern, however, could not be indexed to these lattice constants. The density is given as approximately 4.2 gm/cm^3 , but no optical data are given other than that the refractive indices are greater than 1.789.

Two problems arise from these data: (1) the cell volume and density suggest an unlikely cell content of ca. one UMo_2O_8 formula unit/cell; and (2) the short a axis requires U-U distances having the improbably short value of $3.36 \text{ \AA}$. We presume that either the lattice dimensions, or the composition, or the density, or some combination of the three are in error.

A sample of sedovite, allegedly from the type locality, was obtained from a private collection. The dark brown crystals are extremely small laths whose maximum dimension is not more than $80 \mu\text{m}$ and whose smallest dimension is at least an order of magnitude less. A powder pattern of this material agrees exactly with that published by Sidorenko and Skvortsova, but attempts to obtain single crystal patterns have thus far proved unsuccessful.

Crystal morphology and partial optical properties indicate that the symmetry is not greater than monoclinic. Furthermore, the morphology suggests that the short axis of the reported cell should be doubled. The complete powder pattern was successfully indexed on the basis of a monoclinic cell with $a_0 = 6.42 \text{ \AA}$, $b_0 = 11.08 \text{ \AA}$, $c_0 = 6.72 \text{ \AA}$, $\beta = 91.53^\circ$ (the a and c axes of Sidorenko and Skvortsova have been interchanged). This reindexing of the cell overcomes the short U-U distance problem and resolves the problem of unit cell contents by giving two molecules/unit cell.

Optically the crystals display an inclined extinction of the slow vibration direction to the crystal elongation. The extinction angle varies

from 7° to 20° for light from $5000 \text{ \AA}$ to $5800 \text{ \AA}$ wavelength, and less markedly, from 20° to 25° , between $5800 \text{ \AA}$ and $6400 \text{ \AA}$.

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VII. ISOTOPE SEPARATION AND ANALYSIS

A. Separation of Sulfur Isotopes by Distillation (T. R. Mills)

At present, separated sulfur isotopes can be produced by methods based upon transport processes (electromagnetic separation and liquid thermal diffusion¹) in very limited quantities (tens of grams) at a cost of $\geq \$400$ per gram of isotope. It appears probable that use of a different separation process will be necessary to produce sizeable amounts (hundreds of grams) at lower costs.

The separation approach taken for this work is the low temperature distillation of compounds containing sulfur. An 8-m-long distillation column 25 mm in diameter has been built specially for

sulfur investigations. The column is in a vacuum jacket with multiple layers of aluminized mylar around it for thermal radiation heat rejection. Temperature control of the sulfur-containing material is obtained by using liquid nitrogen as primary refrigerant to cool a secondary refrigerant system. Either a propane-ethane or a propane-propylene liquid mixture is used for the secondary refrigerant. The column is packed with stainless steel Propak packing and has 118 theoretical plates.

Hydrogen sulfide is the only working material used thus far. This column and another column used previously in unreported work (1974) have been operated at pressures from 40 kPa to 120 kPa. The isotope separation has been measured by analyses of H_2S from the top and bottom of the column using the CEC 21621 mass spectrometer. The separation of ^{32}S from ^{34}S , expressed in terms of relative volatility, α , has varied from 1.0014 to 1.0008.

Although the mass spectrometric analyses of H_2S directly appear to be repeatable and sound, the standard gaseous form for mass spectrometer analysis is sulfur dioxide. To confirm the present results, repeats of earlier runs are under way with the chemical conversion done by a modification of the method of Kaplan.²

Following completion of H_2S studies, other sulfur compounds will be distilled, with SF_4 being the likely next compound to be studied for isotope separation.

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B. Separation of Stable Isotopes (I. R. Mills, R. C. Vandervoort, and M. Goldblatt)

The stable isotope separation program has the objectives of providing separated stable isotope of carbon, oxygen and nitrogen (ICONs) for research purposes and also of developing new or improved techniques for incorporating the separated isotope into commonly desired chemical forms. Isotopic materials are sold at cost to Los Alamos investigators or to the general research community through the Mound Facility. The value of isotopic product produced for Mound sales during FY 1981 was \$667K.

The isotopes are separated by cryogenic distillation of CO for carbon isotopes and of NO for nitrogen and oxygen isotopes. During FY 1981, the quantities of isotopes separated were: 0.8 kg ^{12}C at 99.95% enrichment, 2.7 kg ^{13}C (90%), 5.9 kg ^{13}C (99%), 0.4 kg ^{15}N (60%), 1.6 kg ^{15}N (98%), 0.1 kg ^{17}O (20%), and 0.1 kg ^{17}O (50%). Actual production was considerably below full capacity because of attempts to match production to demand.

Most of the isotopically enriched CO or NO is converted to other labeled compounds for use by researchers. The reactions used were summarized in the FY-1980 CEC Division annual report.¹ Table XVI summarizes the forms and amounts of labeled compounds prepared in FY 1981.

TABLE XVI
ISOTOPICALLY LABELED COMPOUNDS MADE IN FY-1981

Product	Quantity (mol)	Product	Quantity (mol)
$^{12}CO_2$	17	$^{15}NH_3$	86
$^{13}CO_2$	372	$(^{15}NH_4)_2SO_4$	9
$^{13}CH_3OH$	66	$(^{15}NH_2)_2CO$	0.3
$^{12}C^{17}O_2$	0.1	$K^{15}NO_3$	6
$^{12}C^{16}O^{18}O$	17	$H^{15}NO_3$	9
$^{13}C^{16}O^{18}O$	0.2	$H_2^{17}O$	10
$K^{13}CN$	8	$^{17}O_2$	1
$^{15}N_2$	14	$^{18}O_2$	2.5

A major program of improving performance of NO isotope plant was undertaken in FY 1981. A new NO feed system was designed and built. All NO gas handling hardware, including purifiers and cryogenic traps, was examined and helium leak tested with repair or replacement of parts as needed. As a result of this sizeable effort, many previously plugged drawoff lines in the cryogenic isotope columns were opened, some of them for the first time since initial startup of the columns. The NO plant can truly be said to be operating better now than when it was new.

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C. Nitric Oxide Isotope Plant Feed System

(T. R. Mills, B. B. McInteer, M. Goldblatt, R. C. Vandervoort, J. G. Montoya, and D. E. Armstrong)

The Los Alamos nitrogen and oxygen separation plant requires a feed stream of nitric oxide containing some level of ^{15}N , ^{17}O , and ^{18}O to be extracted. The heavy isotopes are enriched in the plant, and a NO stream substantially depleted in these isotopes is withdrawn from the top of the plant. The isotopically depleted NO may be either converted to product or disposed of, subject to demand for it. Recently the sole proven supplier of NO discontinued production; thus, an alternate feed supply was needed. We have chosen an innovative method that does not require either purchase or generation of NO.

The only other system presently used for producing ^{15}N -enriched product is the NO- HNO_3 chemical exchange system (Nitrox system),¹ which relies on an isotope effect when NO and HNO_3 approach chemical equilibrium. The oxygen isotopes also show an isotope effect, although the system is normally not used for oxygen isotope separation.

Ability of NO and HNO_3 to rapidly exchange isotopes suggested our approach to promote isotopic

exchange between NO depleted of heavy isotopes and HNO_3 of normal isotopic abundance. In a counter-current flow column the NO gas can be enriched to nearly normal NO gas, and the nitric acid solution will be highly depleted of heavy isotopes.

The feed system that was designed and put into operation is shown in Fig. 37. The heart of the system is the exchange column (Scrubber 1), a 1.2-m-long, 100-mm-diam glass column filled with stainless steel Propak packing. Calculations for equimolar NO and HNO_3 flow indicate that the NO will be enriched from 0.01% to 0.34% ^{15}N , whereas the HNO_3 will be depleted from 0.37% to 0.04% ^{15}N in the column. Mass spectrometric analyses of the NO and HNO_3 have shown this degree of exchange. We have also observed efficient exchange of oxygen isotopes such that the NO stream exiting the exchanger is of approximately the normal oxygen isotopic mixture.

Most of the remaining parts of the new feed system are for gas purification. Nitrogen dioxide is an important part of the exchange process; the exchange occurs more quickly at high acid concentrations because of the presence of NO_2 as an intermediate between NO and HNO_3 .¹ However, NO_2 must be removed from the feed NO stream, and a water scrubber column (Scrubber 2) identical to the

Fig. 37.
Nitric oxide isotope plant feed system.

exchange column is used. Nitric acid and nitric oxide are produced in the scrubber column by the reaction:

The gas exiting the scrubbing column is then pure, but wet, NO. Water vapor is removed by a condenser (not shown) and a silica gel drying bed. A cryogenic distillation column is used to separate nitrogen gas introduced to the NO from other flows in the plant as well as to provide extra protection against NO₂ or water that has passed through other purifiers. The highly pure normal NO is then fed to the isotope separation column.

Nitric oxide is removed from the overall plant because of isotopic production, losses from the purifiers, or gases dissolved in the waste nitric acid. (The liquid is a brilliant blue color, indicating dissolved N₂O₃.) Makeup NO is generated by adding sulfur dioxide to nitric acid. The SO₂ reacts with the acid to yield NO and sulfuric acid waste.

The mixture of waste nitric and sulfuric acids is stored temporarily before being sent to the chemical dump, although the HNO₃ also has possible utility as a depleted ¹⁵N product.

The new system was put into use in August 1981 and has worked very well. Additional work is under way to improve the chemical analysis of the waste HNO₃ so that we may obtain better data on the rather complicated chemical equilibrium system of HNO₃, N₂O₄, N₂O₃, NO, and H₂O between the liquid and gas phases.

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D. The Los Alamos Facility for Automatic Nitrogen Analysis (B. B. McInteer and J. G. Montoya)

Separated nitrogen isotopes, which are produced in this country only at Los Alamos, are widely used as tracer materials in field studies of the nitrogen cycle in agricultural and other research. Such studies involve many hundreds of samples of plants, soils, water, or animal tissue requiring isotopic nitrogen analysis. Processing these samples to an appropriate chemical form and their resulting isotopic analysis has represented for many years a limitation in the use of separated nitrogen isotopes. Especially, the nitrogen isotopic analysis has been performed in a few specialized laboratories with a total capacity estimated to be 10,000 samples per year.

In 1980, Los Alamos announced the development of an automated instrument capable of analyzing several hundred samples per day for isotopic nitrogen.¹ The equipment was designed to accept movable trays of small polyethylene vials that were loaded with samples in the form of ammonium sulfate solution. The vials were flushed with Freon-12 gas to remove air. Sodium hypobromite reagent solution was then added to oxidize the ammonium ion to nitrogen gas. A small cryogenically cooled U-trap removed the Freon and other contaminants from the nitrogen gas sample, which was then expanded into an inlet manifold where the sample pressure was measured and adjusted. Upon connection to the mass spectrometer, the ratio of the mass-29 peak (¹⁵N¹⁴N) to the mass-28 peak (¹⁴N₂) was measured. Analyses were of good quality, were rapid, and required only 0.025 mg of nitrogen per sample.

As part of the testing and demonstration phase of this program the Laboratory offered to perform such analyses free of charge to all workers. The response to this service has been remarkable. In 1980 about 4000 samples were analyzed. During 1981 about 20,000 samples from forty laboratories engaged in university and governmental research have been analyzed. Some workers are using labeled nitrogen for the first time, whereas others have a mass spectrometer available but too many samples for it. All users regard the service as important. Thus, the continuation of a central facility for performing such analyses seems necessary.

Technical progress on the equipment has continued. All samples are performed with duplicate aliquots. If the percent of ^{15}N is measured to be x_1, x_2 with a mean value, $\bar{x}$, then the criterion for acceptability is

$$\text{if } \bar{x} > 0.366, \text{ then } x_1 - x_2 < 0.008 \bar{x} ;$$

$$\text{if } \bar{x} \leq 0.366, \text{ then } x_1 - x_2 < 0.0029 .$$

Otherwise, the analysis is rejected. Most samples satisfy this criterion by a wide margin, but when nitrogen is scarce in a sample, or if the equipment malfunctions, this quality control avoids serious anomalous errors. Also, a simplified microvalve has been designed, built, and tested successfully. A new automatic report format for the user is now in use. But especially revealing of the emphasis of the program has been development of the sample trays themselves.

1. Initially, separate vials (0.15 ml) were placed in a preparatory tray of 130 vials. After the samples were pipetted, the vials were dried by a gas stream and then were manually transferred to a master tray that was part of a modified plotter. This system proved arduous to load and expensive in vial costs.
2. The second system, still in use, involves trays with 260 fixed vials. The plotter moves a metal frame to which a tray can be attached or removed. This has permitted trays that require 8 to 9 hours to process. Two trays may be done per calendar day.
3. The next system, still being developed, is based on disposable commercial polystyrene trays containing 96 wells each. This system will provide for automatic tray changing so that a stack of seven trays can operate around the clock. But the most novel feature of this new system is that the user will fill and dry his own trays, keeping his own record of separate samples, still in duplicate, and will interpret individual samples. The analytical facility will be responsible only for identifying the tray itself. The required methodology for filling, drying, and mailing these

trays is being developed collaboratively with Dr. R. D. Hauck, Tennessee Valley Authority, Fertilizer Research and Development Center, Muscle Shoals, Alabama.

The objective of the Los Alamos ICONs program is to encourage the use of stable isotopes by the scientific community. This analytical center promises to fill that objective amply.

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E. Developments in Mass Spectrometry (V. M. Armijo, G. W. Butler, A. J. Gancarz, S. J. Knight, G. W. Knobeloch, F. O. Lawrence, L. Z. Liepins, R. E. Perrin, D. J. Rokop, and W. R. Shields)

The mass spectrometers in CNC-7 that are operating and those in the process of being modified or constructed are designed to make the following measurements: 1) high-precision isotopic ratio measurements; 2) large dynamic range measurements; and 3) analysis of relatively small numbers of atoms. In this progress report we summarize the advances made this year in three areas, each of which utilizes one or more of the design features. These include the search for naturally occurring ^{244}Pu , high-precision isotopic analyses of uranium on relatively small samples, and (n,2n) cross section measurements made in support of the nuclear weapons research effort.

In our continuing search for ^{244}Pu the approach that we have adopted is to look in rocks formed in diverse geochemical environments. In all of these rocks the chemical conditions of formation were such that plutonium is predicted to have been preferentially concentrated. We are examining both sedimentary and igneous rocks; the sedimentary rock

is a phosphate-rich rock from the Pliocene Bone Valley Formation, Florida, and the igneous sample is monazite, a cerium-thorium-rare earth mineral from Kangankunde, Africa.

The analysis involves chemical separation of the plutonium from very large amounts of material and subsequent mass spectrometric analysis of the small (10^6 or 10^7) number of atoms. The chemical separations must be done with extreme care and cleanliness to enable successful mass spectrometric analysis and to avoid the introduction of extraneous plutonium.

The greatest problem in the mass spectrometric measurement of small numbers of ^{244}Pu atoms is interferences at the 244 mass position which are due to scattered ions and isobaric hydrocarbon molecules. The scattered ions are primarily scattered alkali-metal ions. This problem has been alleviated largely by electrodepositing the plutonium onto the rhenium ionizing filament and overplating the plutonium with rhenium. The electrodeposition effects a final Pu-alkali metal separation. The overplating increases the ionization efficiency by creating a diffusion barrier. With this method, the filament can be heated to higher temperatures than under normal conditions when the sample would directly evaporate.¹ The ionization efficiencies for 10^{-12}g Pu samples range from 0.2% to 0.8%.

The Florida phosphate rocks generally contain 50 to 200 ppm U. At these levels it is commercially profitable to recover the uranium. In the recovery process the dissolved rock is contacted with a mixture of kerosene, octyl-phosphoric acid and octyl phenol. Under the conditions of this process the plutonium is extracted into this organic mixture. We processed and analyzed two samples of the mixture each equivalent to 24 kg of rock and determined an upper limit of less than 83 ^{244}Pu atoms per gram of rock.

These rocks are marine sediments. Hence, it is important to understand the behavior of plutonium in the ocean in order to explore the implications of the data. Plutonium has a residence time in the ocean of less than 300 years, and the removed plutonium is deposited in sediments.² This residence time is short relative to the mean life of ^{244}Pu . Therefore, the deposition rate is virtually the same as the flux rate of ^{244}Pu to the

ocean. We assume that all plutonium is deposited in phosphate minerals. Because phosphorous in the ocean is in steady state and the flux of dissolved phosphorous is known, we calculate a ^{244}Pu flux of $<2.8 \times 10^{15}$ atoms/yr.

If this flux is all galactic cosmic ray ^{244}Pu and includes the flux to the earth's land surface then the ^{244}Pu flux to the surface of the earth is $<1.7 \times 10^{-11}$ atoms $\text{cm}^{-2} \text{sec}^{-1}$. It is possible to calculate a flux for comparison using cosmic-ray and element abundance data. The galactic cosmic ray flux of VH nuclei calculated from the formula of Fleischer et al. (1975) is 1.07×10^{-3} particles $\text{cm}^{-2} \text{sec}^{-1}$ of the VH nuclei (i.e., $Z \geq 90$ approximately 97% are iron. Satellite, balloon, and Skylab measurements indicate a flux of nuclei with $Z \geq 90$ relative to the iron flux of 6.7×10^{-7} .⁴ Approximately 17.6% of the $Z \geq 90$ nuclei are ^{244}Pu , and about 50% of these are destroyed in transit through the earth's atmosphere. The calculated flux to the earth's surface is 6×10^{-11} particles $\text{cm}^{-2} \text{sec}^{-1}$. This is in reasonable agreement with the value inferred from our ^{244}Pu measurements.

Alternatively, the flux of $<1.7 \times 10^{-11}$ atoms $\text{cm}^{-2} \text{sec}^{-1}$ could be primordial plutonium released during weathering and erosion. If all the plutonium-bearing minerals in the $1.54 \times 10^{16} \text{g}$ of rock eroded each year are dissolved, then crustal rocks contain less than $7 \times 10^{-23} \text{g}$ $^{244}\text{Pu}/\text{g}$ rock. Furthermore, if all the ^{244}Pu was concentrated in the crust of the earth, then the average terrestrial concentration is less than $3 \times 10^{-25} \text{g}$ $^{244}\text{Pu}/\text{g}$ earth. This value is a factor of 1000 less than that reported by Fields et al.³ for the earth, but a factor of 10 greater than the abundance inferred from meteorite data.

The analyses of the monazite samples are still in progress and no final ^{244}Pu concentrations are available.

A variety of investigations in CNC Division, including for example weapons radiochemical diagnostics and the Oklo natural fission reactor investigation, have necessitated the development of a method for accurate isotopic analysis of small uranium samples. The method developed is electrodeposition of uranium on degassed zone-refined rhenium filaments that are overplated with rhenium. We

investigated the effects of voltage, electrolyte molarity and pH, and time on the thermal ionization efficiency, stability of the ion beam, and uranium mass fractionation. The optimal parameters ascertained permit analysis of 10 ng of uranium at ionization temperature of $1620 \pm 10^\circ\text{C}$ and an ionization-transmission efficiency of 1.5×10^{-4} . The isobaric interferences are less than or equal to the background of the measuring system, 0.05 counts per second. Accuracies achieved on 10 ng of NBS U-500, a 1:1 ^{235}U : ^{238}U isotopic standard, are 0.05% to at the 95% confidence level.

Integral to determining thermonuclear yields by using neutron reactions on radiochemical detector elements to measure neutron fluences are accurate values of the cross sections. Typically, we determine cross sections for (n,xn) reactions at neutron energies ranging from 7.5 to 28 MeV using radiochemical techniques. However, the fraction of the target that has undergone an (n,xn) reaction can, in principle, be measured mass spectrometrically. This requires the ability to measure large isotopic ratios because the product to target ratios generally range from 10^{-6} to 10^{-10} .

We recently completed the determination of the cross section for the reaction $^{209}\text{Bi}(n,2n)^{208}\text{Bi}$ at 14.9 MeV using both conventional radiochemical and mass spectrometric techniques. The latter required measuring a $^{208}\text{Bi}/^{209}\text{Bi}$ of 1.1×10^{-6} . The values of the cross sections were 2.197 ± 0.054 b using radiochemistry and 2.147 ± 0.054 b using mass spectrometry. This excellent agreement validates the use of mass spectrometry for determining nuclear reaction cross sections.

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VIII. ATOMIC AND MOLECULAR COLLISIONS

A. Dynamics of Molecular Photodissociation (D. S. Moore, D. S. Bomse, and J. J. Valentini)

The dissociation of a molecule into atoms or smaller molecular fragments through the absorption of light is an important process in atmospheric chemistry, laser isotope separation, combustion, chemical synthesis, astrophysical chemistry, and chemical lasers. Despite the importance of molecular photodissociation to this wide range of phenomena, our understanding of the energetics and dynamics of photodissociation is not at all well developed.

Our lack of knowledge about the photodissociation process is a direct consequence of the difficulty encountered in measuring the nascent electronic, vibrational, and rotational energies of the photofragments. These energy distributions provide our only direct link to the dynamics of photodissociation, but have seldom been experimentally accessible because the distributions are rapidly degraded by collisions of the photofragments with other molecules. Even in low pressure gases collisions occur very frequently (every 100 ns at 1 torr).

To obtain these nascent energy distributions, one must probe the fragments before they have collided with other molecules. This requires measurement techniques with time resolution better than 100 ns, coupled with photodissociation effected simultaneously on the same time scale.

We have developed a technique that uses pulsed laser photodissociation, coupled with pulsed Coherent Anti-Stokes Raman Spectroscopy (CARS), to measure the collision-free photofragment electronic, vibrational, and rotational energy distributions. CARS is a very general, sensitive, and highly time-resolved spectroscopic technique based on the Raman effect, an inelastic light scattering process. The spectra one obtains using CARS reveal the molecular energy distributions of the photofragments.

A typical CARS spectrum of a molecular photofragment, oxygen from photodissociation of ozone, is shown in Fig. 38. The oxygen was produced by photodissociation of ozone (2 Torr pressure) at a wavelength of $5320 \text{ \AA}$. The spectrum, recorded within 6 ns of the dissociation, indicates that the oxygen photofragment is produced only in the ground electronic state, with a large amount of rotational and vibrational excitation.

The vibrational and rotational state distributions extracted from the CARS spectrum are shown in Fig. 39. The distributions are significantly non-Boltzmann, with a peak in the rotational distributions at or near $J = 31$. These dramatically non-Boltzmann distributions indicate that the dissociation process is a direct one, not proceeding through a long-lived excited state, and that the geometry of the excited state is nonlinear.

Fig. 38.

CARS spectrum of molecular oxygen produced in the photodissociation of ozone at $5320 \text{ \AA}$. Grid at the top of the figure identifies the rotational and vibrational levels for each spectral line. Prominent feature between 1545 and 1560 cm^{-1} is due to molecular oxygen impurity in the ozone.

Fig. 39.

Vibrational and rotational state distributions for molecular oxygen extracted from the spectrum (Fig. 38).

Detailed information such as this about the photofragment energy distributions is being used by other scientists at Los Alamos who are interested in the theoretical modeling of photodissociation.

B. Photoionization of H_2S and of Mixed Clusters with H_2O and CH_3SH (N. C. Blais and E. A. Walter, University of New Mexico)

A photoionization mass spectrometer is used to identify ion species formed at measured wavelength of ionizing ultraviolet light. The reagents are introduced into the ionization region by means of a supersonic free jet that cools most of the degrees of freedom of the reagents to temperature in the range 10 K to 100 K . In addition to low temperature molecules, clusters of the reagents of various sizes are also formed, the distribution of which depends on the details of the expansion process. In this work we report a continuing series of experiments using H_2S , H_2O and CH_3SH as reagent.

The appearance potential of the fragment $(\text{H}_2\text{S}\cdot\text{H})^+$ was measured. This fragment arises from reaction between moieties of the H_2S dimer when it is irradiated by photons of wavelength shorter than $1209 \text{ \AA}$. Using the values of the ionization thresholds for the clusters $(\text{H}_2\text{S})_n$ that we measure earlier¹ for $n = 1$ to 7 , we obtain the energy diagram for the thermochemical properties of H_2S shown in Fig. 40.

Fig. 40.

The energetics for the formation of ionized clusters and ionic fragments formed in the H_2S system.

Mixed clusters of $\text{H}_2\text{S}\cdot\text{H}_2\text{O}$ were formed in our supersonic free jet expansion source and the appearance potential of the $\text{H}_2\text{S}\cdot\text{H}_2\text{O}^+$ ion was measured. A value almost identical to the H_2S dimer was found, $9.74 \pm .03$ eV. This is evidence that the bonding of water to hydrogen sulfide perturbs the ionic ground state levels to the same extent as does H_2S .

Mixed clusters of $\text{H}_2\text{S}\cdot\text{CH}_3\text{SH}$ were also formed, and the appearance potential of the ground state of the $\text{H}_2\text{S}\cdot\text{CH}_3\text{SH}^+$ was measured to be $9.20 \pm .03$ eV. This is about 0.24 eV below that of CH_3SH^+ . The perturbation of the ground state of CH_3SH^+ by cluster formation is much less than for H_2S , which is

about .74 eV. A discontinuity in the ion yield spectrum also occurs at about 9.83 eV, which may correspond to the ionset of ionization of the H_2S moiety of the cluster. Evidence to justify this assumption must await obtaining the spectrum of $(\text{CH}_3\text{SH})_2$ in the same energy region. Figure 41 shows the ion yield curve for $(\text{H}_2\text{S}\cdot\text{CH}_3\text{SH})^+$.

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Fig. 41.

The ion yield spectrum for the formation of mixed cluster ions $(\text{H}_2\text{S}\cdot\text{CH}_3\text{SH})^+$ from polymers of H_2S and CH_3SH .

IX. MOLECULAR SPECTROSCOPY

A. Development of the CARS Method for Measurement of Pressure and Temperature Gradients in Centrifuges

(A. H. Zeltmann and J. J. Valentini)

Coherent Anti-Stokes Raman Spectroscopy (CARS) is a very sensitive technique that has been successfully used to obtain molecular spectra in gas and liquid systems.¹⁻³ CARS can also be used as a powerful analytical spectroscopic technique for making accurate concentration and temperature measurements with spatial resolution on the order of 0.1 mm and temporal resolution on the order of 10 ns. As an analytical method CARS has been applied to the measurement of spatially resolved hydrogen concentrations in flames,⁴ determination of temperature, concentration, and spatial distribution of N_2 , O_2 , and CO in flames,⁵ measurement of vibrational and rotational temperatures in an electric discharge,⁶ and thermometry in sooting flames⁷ and hydrogen plasmas.⁸ CARS has recently also been applied to the study of transient phenomena such as photodissociation.⁹

CARS has been applied to the spectroscopic study of several volatile hexafluorides, including UF_6 .¹⁰ A proposal¹¹ to apply CARS to the measurement of UF_6 in gas centrifuges led to the experiments described here. We have shown, with a series of experiments, the feasibility of applying the CARS technique to the measurement of UF_6 concentration in a gas centrifuge under anticipated conditions of pressure, temperature, device geometry, and materials of construction. Measurements show that the resultant CARS signals are properly related to system parameters as suggested by underlying theory and related phenomenological equations.³

The CARS experiment involves a four-wave mixing process in which two pump photons at frequency ω_p and one at the Stokes frequency, ω_s , are mixed in a sample and produce a fourth photon at the anti-Stokes frequency, $\omega_{as} = 2\omega_p - \omega_s$. This mixing occurs for all materials, but is enhanced if $\omega_p - \omega_s$ coincides with a Raman frequency of the sample. McDowell¹² found Raman active fundamentals of UF_6 at 667.1 cm^{-1} ($\nu_1(A_{1g})$), and 534.1 cm^{-1} , $\nu_2(E_g)$.

We have shown that our CARS signal intensity conforms to the theoretical equation⁴ for four-wave mixing phenomena,

$$I_{as} = C \cdot N_{\text{UF}_6}^2 \cdot p_p^2 \cdot p_s$$

where C consists of fundamental constants and intensive properties of the medium, N_{UF_6} is gas density and p_p and p_s are laser intensities at the pump frequency and at the Stokes frequency. The dependence of signal intensity on laser power is shown in Table XV. The results show that there is a third-order dependence on laser power, i.e., the dependence of the power in the pump laser squared and the power in the Stokes laser to first power.

Table XVI lists data on the dependence of CARS signal on UF_6 pressure and laser intensity. Column 2 shows the CARS amplitude, normalized with respect to laser intensity to the third power, as a function of UF_6 pressure. The pressure range is that expected in centrifuge operations. The results shown in Table XVI indicate a second-order dependence of CARS signal on N_{UF_6} . The CARS signal

TABLE XV
CARS SIGNAL AS A FUNCTION OF LASER INTENSITY AT
CONSTANT PRESSURE UF₆ PRESSURE, 10.0 TORR

P _D	Laser Power		Signal Power, I _{as} mW	I _{as} /P _D ² P _S ² Arbitrary Units
	KW	P _S		
532.1 nm	551.7 nm	513.8 nm		
179	73	10.2	4.4	
204	94	12.0	3.1	
221	134	22.7	3.5	
225	154	30.3	3.9	
243	181	36.5	3.4	
227	209	58.5	3.6	

TABLE XVI
CARS SIGNAL AMPLITUDE FOR VARIED PRESSURE
AND LASER POWER

N _{UF₆} Torr.	Laser Power		Signal Power, I _{as} mW	Normalized CARS Signal, I _{as} /P _D ² P _S ² N _{UF₆} ² Arbitrary Units
	KW	P _S		
	532.1 nm	551.6 nm	513.8 nm	
5.6	262	265	35.6	6.2
10.0	277	209	58.5	3.6
17.7	767	80	30.3	4.3
37.0	96	45	24.6	4.3

intensity was as expected, about seven orders of magnitude lower than the intensity of the lasers used to generate it. The apparatus is diagrammed in Fig. 42.

Factors that can limit the use of CARS, such as nonresonant background interference with the signal, will not be a problem in gas centrifuge experiments. Raman resonances from other molecular species likely to be present in the centrifuge are far removed in wavelength from the UF₆ resonance, so good spectral discrimination against other species is easily achieved. The signals do not appear to saturate at higher power levels, although this has not been thoroughly investigated.

CARS appears to be an excellent technique for determination of pressure in a centrifuge. Of particular significance is the high signal level compared with other spectroscopic methods. With CARS, there is near unit signal collection efficiency, good discrimination against background, and no

Fig. 42.

CARS apparatus for gas centrifuge measurements.

interference from fluorescence. The method has high wavelength resolution as the CARS signal bandwidth is determined solely by the laser line-width and should allow accurate determinations of pressure with high sensitivity. Because our experiments indicate that such measurements can likely be made in only a few laser pulses at a 10 pulse-per-second repetition rate, these pressure and temperature measurements can also be made quite rapidly. There is no experimental barrier to the use of CARS for extremely accurate measurements of temperature and pressure gradients in an operating centrifuge.

Our experiments have also shown that there are a number of techniques by which the quantitative determinations can be improved with little extra effort.

1. Install telescopes in the main laser paths to limit beam divergence.
2. Optimize the dichroic filter.
3. Use a doublet achromat lens with a short focal length.
4. Insert a third narrow band filter in the detector path.

5. Use a high quality boxcar integrator as a detector.
6. Make all signal power measurements on a ratio basis relative to some stable signal.

Figure 42 diagrams the principal elements of the CARS experiments. Two laser beams whose photons are separated in energy by the energy $\nu_1(A_{1g})$, a normal mode of UF_6 , are superposed by means of a dichroic mirror. These beams are made collinear by passing through widely separated irises and brought to a focus within the cell containing UF_6 . The combined laser signals and generated CARS signal are reflected off the centrifuge rotor wall. The more intense laser beams are substantially absorbed by a pair of narrow band filters tuned to 514 nm, the anti-Stokes signal wavelength. Further discrimination is obtained by a 1/4 m-monochromator tuned to the monochromator signal wavelength. The signal amplitude is measured by a photomultiplier tube in a cooled housing. The laser beams are monitored by partial reflection from a quartz flat into a photodiode.

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- B. High Resolution Studies of Guest-Host Interaction and Dynamics in Low Temperature Impurity Doped Solids (L. H. Jones and B. I. Swanson)
- Using high resolution vibrational spectroscopy, we have demonstrated¹⁻⁴ for the first time that dynamic exchange among equivalent sites for

impurities in low temperature matrices occurs on a microsecond time scale. This unexpected observation has led us into a thorough examination of guest-host interactions for molecules isolated from each other in low temperature matrices. An understanding of such interactions and resulting dynamics is essential for correct interpretation of energy relaxation studies and estimation of perturbations on force fields for molecules, radicals, and ions isolated in bulk solids. We have in the past year directed our attention to studies of the details of such interactions as described in the following sections.

1. Dynamic exchange and isotope effects. We previously reported⁵ dynamic site exchange for SF_6 in xenon matrices with a kinetic isotope effect. An explanation for such a surprising observation was not presented. At this time we can report that the exchange barrier for the two isotopes ($^{32}\text{SF}_6$ and $^{34}\text{SF}_6$) is about the same (17 cm^{-1}); however, the high temperature exchange rate is faster for the heavier isotope (40 ps for $^{34}\text{SF}_6$ compared with 54 ps for $^{32}\text{SF}_6$). Another anomaly is observed in this system; namely, from the observed intensities it is apparent that the transition dipole moment change for ν_3 of $^{34}\text{SF}_6$ is less than that of $^{32}\text{SF}_6$. This suggests a different mode character for the two isotopes, possibly arising from perturbation by nearby vibrational levels, such as $\nu_5 + \nu_6$ (some 60 cm^{-1} lower than ν_3 for $^{32}\text{SF}_6$ but only $\sim 43 \text{ cm}^{-1}$ lower for $^{34}\text{SF}_6$). At this time, we do not know whether this anomaly exists in the gas phase; accurate gas phase intensity measurements are not reported for $^{34}\text{SF}_6$. However, the kinetic isotope effect is likely to arise from the same difference in mode character as the intensity anomaly. The results of this study have been published.⁶ A clear understanding of this and other isotope effects³ for SF_6 in low temperature matrices requires further study.

2. High temperature annealing effects using a xenon overcoat. We have discovered that deposition of a layer of pure xenon over an argon or krypton matrix allows one to heat the matrix to significantly higher temperatures than without the overcoat without serious loss of matrix.⁷ This

has led to some interesting observations on the effects of annealing; in this report we shall discuss the high temperature annealing effects for SF_6 in argon matrices. In Fig. 43 we show the vibrational spectrum for the ν_3 mode of SF_6 in argon. The lower curve shows the absorption for a matrix annealed at 30°K with deposition of 10 to 20 μm of pure xenon over the matrix. This is identical with previous observations of matrices annealed at 30°K without the xenon overcoat. We note at this point that as such a matrix (without the xenon overcoat) is heated above 34°K, we observe rapid loss of argon and a residue of neat SF_6 . However, the middle and upper curves in Fig. 44 show that with a xenon overcoat one can anneal for 30 min at temperatures as high as 42K without serious loss of argon. At 43K we start to see significant loss of argon in a few minutes.

Fig. 43.

Absorbance for the ν_3 mode of $^{32}\text{SF}_6$ in a matrix of concentration $\text{Ar}/^{32}\text{SF}_6/^{34}\text{SF}_6 = 20,000/1/1$. Spectra recorded at 9°K after indicated annealing.

Fig. 44.

Expanded spectra for the same matrix as Fig. 43, recorded at 9°K.

Our conclusion is that the evaporation of argon is inhibited by the xenon overcoat and is controlled by the rate of diffusion of argon through xenon, which of course increases with temperature. We note from Fig. 44 that the 39K annealing leads to disappearance of most of the less prevalent sites and we are left with two or three sites giving sharp absorption features. Heating further, to 42K, leads to decrease of the two low frequency peaks but actual increase in the intensity of the high frequency doublet which we previously showed arises from site symmetry splitting on one site.^{1,3} Thus, we believe that the high frequency doublet arises from SF_6 molecules in the most stable site. We predict that if a single crystal of argon with a low concentration of SF_6 were formed from a liquid solution and cooled to 9K, we would see in this region only absorptions from the high frequency doublet.

Another interesting phenomenon is observed in these studies. We note in Fig. 43 that a broad absorption centered at about 937 cm^{-1} increases with high temperature annealing. This is more obvious from an examination of Fig. 44. This is a spectrum of an argon matrix containing nearly equal amounts of $^{34}\text{SF}_6$ and $^{32}\text{SF}_6$. The ordinate is expanded to

emphasize the growth of the broad features center at about 919.7 cm^{-1} for $^{34}\text{SF}_6$ and 937.8 cm^{-1} for $^{32}\text{SF}_6$. The prominent, sharp features are off scale in this figure. One would normally assign such features that grow with annealing to aggregates of two or more adjacent SF_6 molecules. However, this cannot be the case, as the feature in question for $^{32}\text{SF}_6$ is of identical position and shape for a matrix with natural isotopic abundance of ^{32}S (~96%) as it is for the 50-50 mixture in Fig. 4. If this feature arose from aggregate, it would show a shift in position and broadening from coupling of the $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$ vibrational coordinates. Furthermore, we note that with annealing some minor, sharp peaks grow in, arising from dimers and indicating that higher aggregation does not occur. The weak, sharp features from $929\text{--}930\text{ cm}^{-1}$ arise from $^{33}\text{SF}_6$.

We are convinced that these broad features for the two isotopes arise from monomer SF_6 molecules that were on the sites that disappear on annealing. A definitive clarification of the origin of the broad features must await further study. However, two other observations must be in accord with this explanation. First, we note that the spectra in Fig. 44 result from a matrix deposition at 9°K. If a similar mixture is deposited at the same rate at 20K and overcoated with xenon, the broad features of Fig. 44 are very much weaker—barely perceptible. Also, spectra of this same matrix of Fig. 44 taken at higher temperature (30K) show significant narrowing of these broad features.

3. Matrices of SOF_2 in noble gas solids: Equilibria among different sites. We have made infrared absorption studies of SOF_2 and some of its isotopic species that show unique reversible temperature dependence. The least complex example is that of SOF_2 in a xenon matrix. In Fig. 45 we show the ν_1 stretching mode for normal SOF_2 in a xenon matrix at a dilution of 1/5000. These spectra were recorded at the indicated temperatures after annealing at 60K; they are completely temperature reversible. At low temperature, there are two dominant sites. As temperature is raised, these sites decrease in intensity while a third peak grows in. The only explanation is that an equilibrium exists among these sites within a given trapping cage.

Fig. 45.
Reversible temperature dependent spectra for SO stretch of SOF_2 in a xenon matrix; host/guest ≈ 5000 .

The intensities observed indicate rather significant changes in relative stability as a function of temperature. Such equilibria have not been reported before and offer a further probe into understanding guest-host interactions. At 50°K the peaks coalesce, indicative of phase exchange among these sites.

4. The role of rotation in matrix phenomena: Vibrational dephasing for CH_3F and CD_3F in argon and krypton matrices. For certain small molecules such as HCl and DCl, there is evidence in the literature for rotation in low temperature matrices. Recently Gauthier-Roy, et al.⁸ presented spectra of CH_3F and CD_3F in neon, argon, and krypton matrices for which they interpret certain weak features as caused by rotational transitions. They conclude that CH_3F undergoes slightly hindered rotation at low temperatures in rare gas solids. Abouaf-Marguin and Gauthier-Roy⁹ use this suggestion of rotational structure as support for the interpretation of their vibrational energy relaxation studies.⁹ Essentially, they follow the relaxation rate to the ground state after pulsed excitations of ν_3 with a CO_2 laser. They observed much faster relaxation for CH_3F than for CD_3F , which they interpret as proving that the rate-determining step is a transfer of energy from an excited vibrational level to a high J rotational level. We have looked into this problem because CH_3F is somewhat large to replace a rare gas atom, and we feel any rotation should be highly hindered. In Fig. 46 we show the spectrum of the ν_3 mode for a rather thick (100 μm) matrix of $\text{Ar}/\text{CH}_3\text{F} = 10,000$. Even though the main ν_3 peak is way off scale, no structure is seen on the high frequency side contrary to predictions of theory for free or hindered rotation. The evidence for rotation presented by Gauthier-Roy, et al.⁸ was for extremely thick and concentrated matrices. We feel that they were misassigning weak absorptions that actually arose from aggregates as they observed much stronger aggregate peaks in nearby regions. We conclude that CH_3F and CD_3F do not undergo rotation in low temperature rare gas solids but undoubtedly have a local site phonon mode that is part libration and part translation.

In Fig. 47 we present the ν_3 modes and their reversible temperature dependence for CH_3F and CD_3F in argon and krypton matrices. We note that the CD_3F absorption is much broader than that of CH_3F , particularly in krypton. Furthermore, all peaks broaden considerably as temperature is raised. The difference in width for the two isotopes is partly due to difference in mode character and partly due

Fig. 46.

Spectrum for ν_3 of CH_3F in argon annealed at 30°K, recorded at indicated temperatures. $\text{Ar}/\text{CH}_3\text{F} = 10,000$, thickness = 100 μm .

to rapid relaxation of ν_3 to ν_6 for CD_3F .⁹ The broadening with temperature is indicative of vibrational dephasing by a low frequency, local site phonon mode. In Fig. 48 we present spectra of the ν_5 mode of CD_3F in argon and krypton. This shows amazing broadening with temperature--much greater than for ν_3 or the other modes. The great variability of temperature broadening for the different modes can only be explained as arising from vibration dephasing. Because we do not believe methyl fluoride rotates in matrices, we propose an alternative explanation of the vibrational energy relaxation. We feel that vibrational energy is transferred into a continuum of librational levels, overlapping from broadening, rather than into discrete rotational levels. A report¹⁰ on this work has been accepted for publication.

Fig. 47.

Temperature reversible spectra for methyl fluoride ν_3 mode of indicated matrices.

Fig. 48.

Temperature reversible spectra for methyl fluoride ν_5 mode of indicated matrices.

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X. MUONIC X-RAYS

Density Effects in Muonic Atom Cascades in Nitrogen
(J. D. Knight, C. J. Orth, M. E. Schillaci, R. A. Naumann, and F. J. Hartmann)

The observed variation of the muonic x-ray intensity pattern for an element in the gas phase as a function of gas density, i.e., as a function of frequency of collisions with neighbors that can replace electrons lost by Auger processes, offers a tool for the study of the muonic atom deexcitation cascade. With our collection of muonic x-ray spectra of N_2 measured at 0.77, 5.0, and 20 atm and in the liquid state, and in a mixture with oxygen (5 atm N_2 + 5 atm O_2), we have been attempting to fit the intensity patterns with simple cascade models. A convenient model for this purpose is incorporated in the cascade program of Akylas and Vogel;¹ one usually starts with the assumption that the muons are all captured into the ℓ substates of a single principal quantum number n in some modified statistical distribution and allows the deexcitation cascade to proceed, controlling the initial electron population and the rate of refilling of electrons lost by Auger steps. For muons stopping in N_2 we have started the cascade with the following conditions: muon population at $n = 14$, distributed in ℓ by the function $P(\ell) = e^{\alpha\ell}/(2\ell + 1)$ with α adjustable, electron population and K-electron refilling rate adjustable, and L electrons either set at constant population or not replaced when ejected by an Auger step. In fitting possible calculated cascades to the data, we have also imposed the constraint that the K-electron refill rate must be proportional to the gas density.

Our calculations are compared with the experimental data in Fig. 49 where we show the $K\beta/K\alpha$, $K\gamma/K\alpha$, $K\delta/K\alpha$, and $K\epsilon/K\alpha$ muonic x-ray intensity

Fig. 49.

Muonic Lyman intensity ratios as a function of K-electron refilling width (smooth curves) compared with experimental x-ray intensities for N_2 gas targets. The set of points marked 10 atm refers to N muonic x-rays from a 5 atm N_2 + 5 atm O_2 target.

ratios as a function of K-electron width ($1 \text{ eV/h} = 1.519 \times 10^{15} \text{ s}^{-1}$), with an approximate best fit for the four gas pressures plus liquid N_2 . Our angular momentum distribution parameter $\alpha = 0.14$ at $n_{\text{init}} = 14$, and the initial electron population is given by $1s^2 2s^2 2p^2$ (i.e., a muonic N atom minus one electron). We note that the experimental data for the gas targets are fitted reasonably well by the calculations, except for the $K\gamma/K\alpha$ and $K\delta/K\alpha$ ratios at the lowest pressure. Even with the L electron shell kept full, it was not possible to obtain a good fit for the liquid N_2 target without adjusting the muon angular momentum distribution at capture. It is interesting that the data are fitted as well as they are, considering that the cascade as used does not take into account the time distribution of electron-replacing collisions relative to the progress of the cascade, multiple collisions during the cascade, etc..

One may ask, "are the K widths fitted here realistic?" If we set the kinetic energy of the muonic N atom at 6 eV (from repulsion of two singly-charged ions) and the $N\mu^+ - N_2^0$ collision radius at 3.89 Å, we may estimate the travel time

of the $N\mu^+$ at 20 atmospheres to be about $4.5 \times 10^{-13} \text{ s}$, corresponding to a width of $1.5 \times 10^{-3} \text{ eV}$. The best fit value of the K width from Fig. 49 comes out to be $3.6 \times 10^{-3} \text{ eV}$, a not unreasonable value in view of the crudeness of our assumptions.

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XI. NUCLEAR COSMOCHEMISTRY AND GEOCHEMISTRY

A Tritium and Neutron Production Rates in Meteoroids (R. C. Reedy)

Cosmic-ray particles produce a large number of neutrons when they bombard extraterrestrial objects that have diameters greater than a few centimeters. These neutrons induce spallogenic reactions (which require incident particle energies above about 1 MeV), like $^{24}\text{Mg}(n,\alpha)^{21}\text{Ne}$, or neutron-capture reactions (by very low-energy neutrons), like $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$. The concentrations and distributions of cosmogenic nuclides made by such reactions can be used to determine the history of meteoritic or lunar samples when they were exposed to cosmic rays. Neutron-capture reactions have production-rate-versus-depth profiles that are considerably different from those for spallogenic reactions, and so studies of nuclides made by both types of reactions are valuable in unfolding a sample's exposure history.

The large Kirin meteorite, which fell in China in 1976, provides an excellent example of the use of both spallogenic and neutron-capture-produced nuclides in studying the cosmic-ray-irradiation history of an extraterrestrial object.¹ The measured ^{60}Co activities in a number of samples varied by a factor of four, a range expected for neutron-capture reactions in large objects.² However, the long-lived and stable nuclides showed much less variation with depth and their concentration-depth profiles were inconsistent with the ^{60}Co -inferred depths, indicating that they were formed in a different

radiation geometry. These data for cosmogenic nuclides and calculated production-rate profiles imply that the present Kirin meteorite body was knocked out of a much larger object $\sim 10^5$ years ago.¹

Production-rate profiles for both spallation³ and neutron-capture⁴ reactions have been calculated for the moon. A number of models are available that can calculate production-rate profiles for spallogenic nuclides in meteorites.⁵⁻⁸ Neutron-capture rates were estimated for meteoroids² by using a simple slowing-down model. However, better production-rate profiles for neutron-capture reactions are needed for meteoroids of various sizes and chemistries.

Recently, Spergel and co-workers⁹ have started to do detailed neutron-transport calculations for meteoroids. These neutron-transport calculations require, as input, the distribution of source neutrons as a function of depth and energy. The energy spectrum of source neutrons in meteoroids is like that in the moon and is fairly well known.⁴ The work reported here estimates the absolute source strengths and depth distributions of neutrons in spherical stone meteoroids of various sizes from calculated tritium production rates.

Neutron production rates in meteoroids should be calculated using cross sections for neutron production and using particle fluxes, like the methods used for the sun.¹⁰ However, neutron-production cross sections are not available for many of the major elements in meteorites. Because the excitation functions (cross sections as a function of energy) for producing neutrons are similar in shape to those for making tritium,¹⁰ I decided to use tritium production rates to get relative neutron production rates in the moon and meteorites.

The excitation functions for the reactions making ^3H and the galactic-cosmic-ray particle fluxes in the moon were from Reedy and Arnold.³ For a meteoroid with a radius of 70 g/cm^2 (about 20 cm), the particle fluxes determined for the St. Severin chondrite⁶ were adopted. For meteoroids with other radii, the fluxes were derived from the flux-shape parameters of Bhandari *et al.*⁷ and normalized to the St. Severin fluxes. The ^3H production rates of Trivedi and Goel,⁸ hereafter denote for spherical chondrites were also used.

(Trivedi and Goel used ^3H activities measured in several thick-target bombardments and the model of Kohman and Bender⁵).

The calculated ^3H production-rate-versus-depth profiles are shown in Fig. 50 for several meteoroids with radii from 20 to 300 g/cm^2 , plus in a semi-infinite plane (infinite radius). These profiles are qualitatively similar to those in TG, showing ^3H production rates, $P(^3\text{H})$, which monotonically increase with depth for radii $\leq 70 \text{ g/cm}^2$ and which mainly decrease with depth for large radii ($\sim 300 \text{ g/cm}^2$ or larger). However, compared to TG's profiles, the ones calculated here increase less rapidly near the surface and decrease slower with increasing depth for large radii. The absolute production rates are about 0.5 of those of TG. In lunar samples, the ^3H production rates calculated with these parameters are 0.7 of the measured ^3H activities.¹¹ Both ^3H and ^3He are made by similar reactions, and calculated ^3He production rates in meteorites are also low by a similar factor.¹²

Fig. 50.
Calculated production rates of ^3H as a function of depth in meteoroids of various radii.

As noted by TG, measured ^3H activities in meteorites extend over a large range of values, which they give as 400 to 800 dpm/kg. However, many lower ^3H activities have been measured (e.g., 210-310 dpm/kg for four meteorites¹³). I feel that the ^3H production rates given by TG are slightly too high, and that the actual ^3H production rates in meteorites are probably about 1.4 times those reported here. Because of the similar shapes for the excitation functions for making ^3H and neutrons, these ^3H production-rate-versus-depth profiles can be used for the relative neutron-production profiles in spherical meteoroids.

The lunar ^3H production-rate-versus-depth profile was integrated over depth, and the total ^3H production rate was 27.5 atoms/min/cm². About half of the lunar ^3H is produced in the top 100 g/cm². For meteoroids of various radii, the total ^3H production rate was calculated and then divided by the surface area (using a density of 3.5 g/cm³ to get dimensions in centimeters). The ^3H production rates ranged from 2.0 to 17.0 atoms/min/cm² for radii of 20 and 300 g/cm². The total ^3H production rates per unit surface area calculated with the TG ^3H profiles were 2.2 and 1.1 times the above values for 20 cm and infinite radii, respectively.

The source strengths of cosmogenic neutrons per unit surface area, S_n/A , were calculated for meteoroids using these ^3H production rates per unit area by normalizing to the lunar neutron source strength of 12.8 neutrons/cm²s.¹⁴ Figure 51 shows S_n/A as a function of meteoroid radius. A very large meteoroid (infinite radius) would have a source strength of 14.1 neutrons/cm²s, which is 1.1 times the lunar value because of the higher flux of galactic-cosmic-ray particles at several AU from the sun.⁶ Also shown in Fig. 51 are the neutron source strengths calculated from the TG ^3H -production data, but normalized to my result for a 70 g/cm² (20 cm) radius. Using this normalization, TG's production profile for ^3H in the moon would imply a source strength for an infinite radius of only 6.5 neutrons/cm²s. The deviations at large radii are due to big differences in the rate with which ^3H production decreases with increasing depth.

Fig. 51.

Source strengths of neutrons produced by cosmic rays per unit surface area in meteoroids of various radii, as calculated from ^3H production profiles. The crosses indicate values calculated from the profiles of Fig. 50; $S_n/A = 14.1$ neutrons/cm²s for infinite radius. The dots represent neutron source strengths calculated with the ^3H production profiles of Trivedi and Goel and normalized to the value at 70 g/cm² (the circled cross); $S_n/A = 6.5$ neutrons/cm²s for infinite radius.

For depths greater than 100 g/cm², my and TG's ^3H production rates decrease with e-folding lengths of 148 and 74 g/cm², respectively.

For radii less than 200 g/cm², the relative source strengths in meteoroids as a function of radius probably are determined quite well because both sets of ^3H -production profiles gave similar results. I feel that the relative source strengths for larger radii, and thus the absolute source strengths for all radii, which are determined from my ^3H production rates are fairly good. However, I plan to do additional calculations, including some using neutron-production cross sections, to check and improve these neutron-source-strength calculations. Comparisons of calculated production rates for neutron-capture-produced radionuclides (e.g., ^{60}Co) with measured activities will help to establish the absolute values of the neutron source strengths.

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- B. A Search for Anomalous Iridium Concentrations in Late Cretaceous and Early Paleocene Deposits in Northern New Mexico (C. J. Orth, J. S. Gilmore, J. D. Knight, C. L. Pillmore,* R. H. Tschudy,* and J. E. Fassett**)

The great extinction of floral and faunal taxa that marked the end of the Cretaceous Period 65 million years ago is a puzzle that has challenged scientists for decades. Although a variety of speculations have been offered to account for this great dying, the first good physical evidence for what might have happened has been provided by the Alvarez et al.¹ discovery of anomalously high iridium (Ir) concentrations at the planktonic Cretaceous-Tertiary (K-T) boundary in uplifted marine sedimentary rock sequences in Europe and New Zealand.

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Iridium is several thousand times scarcer in the earth's crust than it is in asteroids, meteoroids, and probably comets, so Alvarez and his colleagues reasoned that a large asteroid struck the earth 65 million years ago, and the impact hurled asteroidal and crustal material into the stratosphere, blocking out the sunlight for several months. As a result, photosynthesis was suppressed, food chains terminated at their origins, and Ir-rich dust settled out over the entire earth.

The objective of this work is to locate and characterize Ir abundance anomalies at the K-T boundary in continental deposits in the San Juan and Raton Basins, and at several more distant sites. All Ir anomalies reported thus far have occurred in pelagic sediments and were subjected to possible marine enrichment processes, thereby weakening the asteroid impact arguments.

Our approach is to analyze samples from rock outcrops and drill cores that span the K-T boundary using neutron activation analysis. We are collaborating with paleontologists and geophysicists from several universities to home in on the boundary using vertebrate fossil, paleomagnetic, and palynological techniques; the zone we seek is expected to be only a few centimeters thick. At Los Alamos the samples are dried, pulverized, and irradiated with neutrons at the Omega West Reactor to convert some of the Ir to 74-d ^{192}Ir , which can be detected with high sensitivity. On selected samples we perform radiochemical purification of Ir, which increases the detection sensitivity a hundred fold.

We have located a strong Ir abundance anomaly at the palynological K-T boundary in core samples taken at a site in York Canyon, about 50 km west of Raton, New Mexico. Here the Ir concentration reached 5000 parts per trillion (ppt) compared with about 20 ppt in strata above and below. The anomaly occurs at precisely the same stratigraphic level, 256 m below the surface, where several Cretaceous pollen species became extinct, and where the ratio of angiosperm (flowering plant) pollen to fern spores decreases abruptly from 30 to 0.1. The ratio recovers to about 10% of its previous value within 20 cm of succeeding sediments. The Ir and pollen/spore results are shown in Figs. 52 and 53.

Fig. 52.

Ir abundances (solid circles) and ratios of angiosperm pollen to fern spores (triangles) as a function of core depth and lithology. The plotted Ir abundances in parts per trillion (ppt) are derived from radiochemically separated samples. The curve through the pollen data is drawn to guide the eye.

Fig. 53.

Expanded view of the data of Fig. 52 in the vicinity of the Ir anomaly and the pollen break. The Ir abundances are given by the histogram and the angiosperm pollen/fern spore ratios by the solid circles. The curve is drawn to guide the eye. The lithologic symbols are the same as in Fig. 52 except for coal, which is shown by stipple.

The $^{244}\text{Pu}/\text{Ir}$ atom ratio is $\leq 1 \times 10^{-7}$, about two orders of magnitude lower than would be expected from a supernova event.

This is the first observation of the anomaly in conjunction with the palynological K-T boundary and in fresh-water sediments. Although our evidence supports the hypothesis that the excess Ir came from an extraterrestrial (solar system) source which caused the great dying, it is also possible that the excess could have been due to eruptions from deep within the earth.

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XII. NUCLEAR STRUCTURE AND REACTIONS

A. Decay Scheme of ^{37}S (J. W. Starner and M. E. Bunker)

The decay of 5.1-m ^{37}S to levels of ^{37}Cl has been reinvestigated, using sources prepared by neutron activation of natural sulfur (0.017% ^{36}S) and isotopically enriched sulfur (~80% ^{36}S). The investigation was prompted by three factors: (1) the availability of the highly enriched sample, on loan to Oak Ridge National Laboratory from a European laboratory, (2) the likelihood that previously unknown gamma-ray transitions would become observable, using the enriched material, and (3) theoretical interest in the level structure of ^{37}Cl , which has a magic number ($N=20$) of neutrons.

The investigation was conducted with Ge(Li) detectors having a resolution of ≤ 2 keV FWHM at 1 MeV. In addition to the four gamma rays previously reported,¹ we have observed three additional low-intensity transitions of energy 1169.1, 3086.3, and 4396.3 keV. The 3086.3- and 4396.3-keV gamma rays are presumed to be ground-state transitions because levels of these approximate energies are known from charged-particle reaction data.² Through parameter Ge(Li)-Ge(Li) coincidence measurements, we have established that the very weak (0.034%)

1169.1-keV gamma ray populates the known 3103.6-keV level, establishing a new level in ^{37}Cl at 4272.7 keV, of spin $7/2^-$ or $9/2^-$. These measurements also confirm that the previously-known 906.3-keV gamma-ray feeds the 3103.6-keV level (see Fig. 54).

Several large-scale shell-model calculations have been made for ^{37}Cl , the most recent and most successful being that of Hasper,³ which utilized the Oak-Ridge/Rochester shell-model code. These calculations predict a $7/2^-$ state at 4.1 MeV, which probably corresponds to the level we have established at 4.272 MeV.

Fig. 54.
Decay scheme of ^{37}S .

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B. Nuclei Far From Stability Using Exotic Targets

(J. B. Wilhelm, G. E. Bentley, K. E. Thomas, R. E. Brown, E. R. Flynn, J. Van der Plicht, L. G. Mann and G. L. Struble)

Study of nuclei far from stability is usually accomplished using conventional targets with exotic reactions and/or sophisticated detection techniques. With the advent of the high intensity meson factories such as LAMPF, a new possibility has emerged for the production of macro quantities of off stability isotopes using spallation reactions to provide nuclear target materials. Using the beam stop area at LAMPF, we have developed extensive facilities to irradiate a variety of target materials for the radiomedical isotope program. As a by product of this effort, many isotopes of interest for nuclear studies are potentially available at the few mg level. A typical irradiation cycle is for ~ 4 months during which time a beam fluence of $\frac{1}{2}$ -1 A-hr impinges on targets of 10 to 20 gm/cm². For heavy element targets such as Ta the spallation yield results in the production of neutron deficient isotopes over a wide range of mass number (Fig. 55) throughout the rare earth region. With an irradiation of a target of 10 gm/cm² with a total fluence of 0.5 A-hr of protons, a cross section of 1 mb results in the production of ~ 100 μ g of product. This product must be extracted from the extremely radioactive target and, in general, must be isotope-separated to obtain adequate purity levels for nuclear structure studies.

Fig. 55.

Cross section for cumulative yields of mass chains for the reaction $p + ^{181}\text{Ta}$. The solid curve is a cascade calculation followed by statistical evaporation for 570 MeV incident protons.

In addition to isotopes produced with spallation reactions on Ta, there is interest in several light elements. Production targets of Cu, V and Si have been irradiated in the primary proton beam. For these lighter elements the lower charged particle Coulomb barrier results in more equivalent proton and neutron emission. The yields are, therefore, not as skewed toward the neutron deficient region. Table XVI summarizes these isotopes and indicates the production yield expected in a typical LAMPF irradiation cycle (~ 4 months). In all cases 10s to 100s of micrograms are expected, and this should be adequate feed material to produce usable nuclear targets. Properties associated with these isotopes can yield information regarding the nucleosynthesis process in stars and the processes involved in supernova explosions. Through

TABLE XVI
PRODUCTION OF LIGHT ISOTOPES

Isotope	$t_{1/2}$ (a)	Target	Production/Cycle (μ g)
^{60}Fe	3×10^5	Cu	20-200
^{44}Ti	47	V	20-200
^{32}Si	~650	V	30-300
^{26}Al	7×10^5	Si	50-500

the use of the $(t, {}^3\text{He})$ reaction, information can be acquired on the low lying 1^+ levels and thus some insight for the Gamow-Teller decay strength, which is important for understanding isotopic production in nucleosynthesis and in supernova. The extension of these studies to the most neutron rich isotopes is important and, therefore, measurements on ^{60}Fe (3×10^5 a) is of special interest. The (t, p) reaction on ^{60}Fe would provide an extension of available information on level structure for the nuclear synthesis codes.

The (p, γ) measurements on ^{26}Al (7.3×10^5 a) are also of astrophysical interest. Recent measurements of the isotopic content of ^{26}Mg in meteorites has led to discrepancies in the theories of nucleosynthesis and the origin of the solar system. By directly measuring the (p, γ) cross section on this isotope, we can investigate the nature of this apparent discrepancy. Studies on ^{44}Ti (47a) can provide insight into level structures in this region and are also important for nucleosynthesis systematics. Another unique isotope for study is ^{32}Si (~650a). This very neutron rich isotope permits examination of the nuclear region that bridges the gap between the deformed s-d shell and the closed N=20 neutron shell. Using (t, p) , (t, α) and $(t, {}^3\text{He})$ reactions this region could be investigated in detail.

For each isotope to be studied, chemical processing techniques have to be perfected for operation in remote hot cells to efficiently extract microgram quantities from up to kilogram samples. In general these chemically isolated products have to be isotopically separated onto thin target backings. This requires development of ion source

technology and the availability of a separator that can safely handle the radioactive feed material and be adequately decontaminated following the separation. As a long term development, shorter lived isotopes will become more attractive for potential target material. This will necessitate rapid handling throughout the processing and coordination with accelerator scheduling to maximize the usefulness of the target.

C. He-Jet Transport of Fission and Spallation

Reaction Products (M. E. Bunker, B. J. Dropesky, W. L. Talbert, Jr. (X-5), R. J. Gehrke,* and V. J. Novick*)

The feasibility of utilizing a He-jet transport system coupled to an isotope separator to study short-lived radionuclides far from stability produced with the high-intensity H^+ beam at LAMPF via high-energy proton-induced fission and spallation reactions, is under investigation. The ultimate objective of this research program would be to determine the masses, spins, and moments of highly unstable nuclei, and in favorable cases, to study the nuclear structure of these nuclei.

The properties of nuclei far from beta stability are of great theoretical interest because such data help guide improvements in nuclear models and provide new insight into nucleosynthesis of the elements. The data also have practical applications in such areas as reactor decay-heat calculations. Although the study of these highly unstable nuclei is a very active field, especially in Europe, there are a number of elements that have remained virtually inaccessible because of target limitations--limitations that do not exist with a He-jet system.

The basic idea of He-jet transport is that the reaction products recoiling from a thin target foil are first stopped in flowing aerosol-loaded He gas. The radioactive atoms then attach themselves to the aerosol particles and are swept out of the reaction chamber to a remote station via a small-diameter capillary tube. A major advantage of the technique is that essentially all elemental species ejected from the target can be transported to the ion

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source of a remote isotope separator where, according to recent experiments in the U.S. and Europe, most elements--even refractory elements like Mo, Tc, Pd, Ru, and Rh--can be successfully ionized. In contrast, the targets used at existing major on-line separator facilities at proton accelerators, such as the ISOLDE facility^{1,2} at CERN, have to be massive to compensate for the relatively low beam currents available ($\leq 5 \mu\text{A}$), and the only elements that can be studied are those that can readily diffuse out of these elevated-temperature targets (which does not include the refractory elements). In the He-jet technique, very thin targets ($\leq 10 \text{ mg/cm}^2$) are used, with the result that very high beam currents are required to produce a sufficient number of atoms for detailed nuclear studies. The LAMPF accelerator is, in fact, uniquely capable of providing the high product yields needed for mounting the proposed He-jet-coupled separator facility.

The initial experiments conducted at LAMPF in 1981 have demonstrated that fission products and spallation products ejected from thin U, Ta, and Rh targets bombarded with up to 3 μA of 800-MeV protons can be rapidly and efficiently transported over large distances using a relatively simple He-jet system. A 1-liter target chamber was installed in a cave near the end of the H^- beam line and was typically operated at a pressure of 2 atm absolute. Helium containing NaCl aerosol was flowed into the target chamber and back to a collection station 41 m from the target. The return flow was made through 1.6-mm ID capillary tubing. With a He flow rate of 30 cm^3/s and an aerosol generator temperature of 660°C, total transport efficiencies of between 40 and 50 % were observed for all non-gaseous elements ejected from the targets. The time delay from beam turn-on to the arrival of the first activity at the collection station was measured to be about 3 s. These initial results are very encouraging. The next step in the program will be to design and test a prototype He-jet target chamber capable of efficient operation in the main LAMPF 800-MeV H^+ beam, where the current is typically 400 μA . In a parallel effort, our collaborators at Idaho National Engineering Laboratory

will continue to develop improvements in the coupling of He-jet systems to isotope separator ion sources.

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D. Fission Probabilities for Actinide Nuclei

Excited by the ($^{12}\text{C}, ^8\text{Be}_{\text{g.s.}}$) Reaction

(E. Cheifetz, H. C. Britt, and J. B. Wilhelmy)

We have demonstrated the feasibility of using the $^{12}\text{C}, ^8\text{Be}_{\text{g.s.}}$ reaction to determine fission probability information in the 7 to 16 MeV excitation energy region. Direct reactions of the type (p,p'), (d,p), (t,p), ($^3\text{He},d$), ($^3\text{He},t$), (α,α') and ($^7\text{Li},\alpha$) have been extensively used to study fission barriers and fission probability distributions in actinide elements. The attractive features of using direct reactions are that a projectile of a single energy yields a fission probability distribution over a broad excitation energy range and that the use of different reactions permit the investigation of many different fission nuclides from a single target. However, each direct reaction is applicable for P_f measurements only over a limited energy region and, therefore, it has been useful in some cases to investigate the same nuclear system using a variety of reactions.

Theoretical interest is often centered on the properties of the even-even nuclei. The majority of target nuclei available in the actinide region are even Z elements, and the direct reactions currently available to reach the higher excitation energies have been centered on the ^3He (5-11 MeV region) and ^7Li (12-20 MeV region) projectiles, which result in the formation of odd Z isotopes.

We have, therefore, investigated the use of the ^{12}C , $^8\text{Be}_{\text{g.s.}}$ reaction that, when starting with an even-even target, gives fission probability information on even-even actinide isotopes. To obtain accurate excitation energy information for the actinide nucleus, it is necessary that the direct reaction does not give internal excitation energy to the ejectile. The ^8Be formed in the reaction is unstable with the ground state having a 90 keV positive Q value and a 10^{-16} s. $t_{1/2}$ for decay into two alpha particles. The higher excited states in ^8Be have extremely short half lives and larger positive Q values and, if formed in the direct reaction, decompose into two alpha particles in the presence of the heavy actinide nucleus and result in a broad angular dispersion of the outgoing alpha particles. However, the $^8\text{Be}_{\text{g.s.}}$ isotopes formed have sufficient life times to be fully accelerated by the Coulomb field and with the relatively small Q value available for decay result in the emission of two alpha particles that are highly correlated in their direction of motion with a maximum opening angle of 6° and almost the same kinetic energy.

To measure these correlated particles, we have used a three counter telescope consisting of a $40\text{ }\mu\text{m}$ ΔE detector, a $500\text{-}\mu\text{m}$ annular detector, and a $700\text{-}\mu\text{m}$ back detector as shown in Figure 56. The

Fig. 56.

Experimental arrangement. All detectors are shown to scale.

$^8\text{Be}_{\text{g.s.}}$ signal was the detection of coincident particles having nearly the same energy in the back and an ular detector. With this $^8\text{Be}_{\text{g.s.}}$ signal fission fragments were measured in coincidence using solid state detectors positioned to measure fragments emitted at $\sim 0^\circ$ and 90° with respect to the heavy element recoil direction. From this information fission probabilities were determined for the $^{232}\text{Th}(^{12}\text{C}, ^8\text{Be}_{\text{g.s.}})$ and $^{236}\text{U}(^{12}\text{C}, ^8\text{Be}_{\text{g.s.}})$ reaction, which provide fission probability information for ^{236}U and ^{240}Pu , respectively. These results are shown in Figure 57 along with results obtained from (t,p) and (n,f) studies to produce the same fissioning nucleus. These results establish the feasibility of using this new technique and provide a method to extend studies into the heavier even-even actinide region to higher excitation energies than are currently available.

Fig. 57.

Fission probability as a function of excitation energy for two compound systems: (a) ^{236}U , full circles are current experimental results, continuous line are experimental results of ^{234}U (t,pf) and the dashed line is $\sigma_f/3.1$ for neutron induced fission of ^{235}U ; (b) ^{240}Pu circles are current experimental results, continuous line are results of ^{238}Pu (t,pf), and dashed line is $\sigma_f/3.1$ for ^{239}Pu (n,f).

E. Comparison of ^{252}Cf Spontaneous Fission with $^{250}\text{Cf}(t, pf)$ (J. Weber, H. C. Britt, and J. B. Wilhelmy)

The detailed characteristics of the mass and kinetic energy distribution for fragments from the fission of actinide nuclei continues to be of experimental and theoretical interest. One of the most intensively studied fission systems is that of the spontaneous fission of ^{252}Cf . Because this has become a primary standard we wished to investigate the dependence of the fission variables on nuclear excitation energy in the ^{252}Cf compound nucleus. For access to the isotope we have used the $^{250}\text{Cf}(t, pf)$ reaction. The ^{250}Cf target was prepared by isotope separation onto a $60 \mu\text{g}/\text{cm}^2$ C foil and had a thickness of $\sim 50 \mu\text{g}/\text{cm}^2$. Because accurate comparisons with the $^{252}\text{Cf}(sf)$ were desired, a thin spontaneous fission source of $\sim 10^4$ f/min was used. This was prepared by the self transfer method onto a $\sim 100 \mu\text{g}/\text{cm}^2$ Ni foil.

The experimental arrangement consisted of a ΔE -E counter telescope system to measure the direct reaction protons (and thus obtained the ^{252}Cf excitation energy) and two pairs of solid state fission fragment detectors located at $\sim 0^\circ$ and 90° with respect to the ^{252}Cf recoil direction. A 16-MeV triton beam was used, which resulted in a useful excitation energy region between 5 and 9 MeV for the induced fission. Results of the comparison of the excited and spontaneous ^{252}Cf are presented in Fig. 58 for the yield, average kinetic energy release, and standard deviation of the kinetic energy release as a function of heavy fragment mass. The major features are that the mass distribution moves in the direction of increasingly symmetric fission, the TKE is increased in the symmetric region and the width of the TKE is broader at all mass divisions.

The most remarkable effect of excitation energy on the fission of ^{252}Cf is the increase in yield of a component with $M \sim 132$ and an increased TKE. This behavior is in marked contrast to results for lighter actinides where increasing the excitation energy enhances a symmetric mass division that occurs with a relatively lower TKE. This result would be consistent with the enhancement in induced fission of a compact scission shape

Fig. 58.

Yield, average total kinetic energy, and variance of the average total kinetic energy as a function of mass for ^{252}Cf spontaneous fission and for results of the $^{250}\text{Cf}(t, pf)$ reaction summed over the excitation energy range 5-9 MeV.

involving a spherical $M = 132$ shell. However, an increase in yield for such a configuration with excitation energy is contrary to the usual qualitative expectations concerning the relative importance of shell configurations as excitation energy increases. The results could also be explained by a mass dependent change with excitation energy in the kinetic energy of the fragments at scission. In view of the current preference of a one body dissipation model in the theory of fission dynamics, this hypothesis would seem even less compelling than the shell hypothesis. In any case, the results seem surprising and qualitatively different from results for lighter

ctinides. A detailed understanding will await a quantitative theoretical treatment of fission dynamics.

Another interesting feature of the results is in the region $M \sim 146$. Here it is seen that the TKE is about equal for induced and spontaneous fission as compared with a difference of ~ 2 MeV for masses above and below this region. Similar results have also been observed for ^{246}Cm and ^{250}Cf . This difference could be consistent with the hypothesis that in this mass region for spontaneous fission the scission configuration contains a compact shape involving a deformed shell in the region $Z = 42$, $N = 60, 62$ in the nascent light fragment as has been postulated and that with increasing excitation energy this fragment becomes more prolate. This interpretation is consistent with the apparent observed trend where for induced fission the TKE decreases monotonically whereas for spontaneous fission there appears to be a bulge near $M_H = 146$, $M_L = 106$. Again, these speculations can only be confirmed by a quantitative dynamical fission theory.

F. Symmetric Fission Yields for ^{231}Th from the $^{230}\text{Th}(d, pf)$ Reaction (A. Sicre, G. Auchampaugh, H. C. Britt, A. Gavron, Y. Patin, J. Van der Plicht, and J. B. Wilhelmy)

Recent experimental studies have suggested separate barriers for symmetric and asymmetric fission in the radium, actinium and thorium region. In addition, there have been attempts to look for structure in excitation functions for symmetric fission yields in the $n + ^{232}\text{Th}$ reaction and the $^{232}\text{Th}(\alpha, \alpha' f)$ reaction. These experiments have given contradictory results and have generally been hampered by poor statistics in the low yield symmetric fission region. A search for gross structure in the excitation function for symmetric fission yields near threshold would provide yet another test for the hypothesis of two independent paths to fission. We have attempted to gain additional information on this question by measuring the symmetric and asymmetric yield in the 6-12 MeV excitation energy range in ^{231}Th excited by the $^{230}\text{Th}(d, pf)$ reaction.

A 17-MeV deuteron beam from the Los Alamos FN Tandem Van de Graaff was used to bombard a $200 \mu\text{g}/\text{cm}^2$ ^{230}Th target that had been evaporated onto a $50 \mu\text{g}/\text{cm}^2$ C foil. The outgoing protons were measured using a solid state ΔE -E telescope located at 80° with respect to the beam axis. The fission fragment energies were measured in coincidence with particle signals from the telescope in two pairs of heavy ion semiconductor detectors located at $\sim 0^\circ$ and $\sim 90^\circ$ with respect to the recoil axis of the ^{231}Th . Approximately 200K proton fission coincidence events were recorded in the experiment. The measured fragment kinetic energies were converted to preneutron emission fission masses using standard kinetic energy and neutron emission calibration procedures. The raw and background corrected data are shown in Fig. 59 summed over all nuclear

Fig. 59.

Mass yields of the reaction $^{230}\text{Th}(d, pf)$ summed over excitation energies $6 \text{ MeV} < E_x < 13 \text{ MeV}$. Circles: raw data; squares: after correction for the random events.

excitation energies populated in the (d,pf) reaction. The region of interest is the symmetric fission area and it is populated only at the 10^{-3} fission level. A gate has been put on the symmetric mass region ($113 \leq M \leq 118$) and this yield studied as a function of nuclear excitation energy. The results are presented in Fig. 60 and hint at some gross oscillatory structure in the symmetric yield. However, the data are severely limited by poor statistics, and the gross peaks seen at 8.5 and 10 MeV are not significantly established. This experiment represented approximately 5 days of beam time, and a major improvement in technique would be required to improve the quality of the data. With this experiment we have observed, as we had in previous measurements in the Ra region, a different threshold for asymmetric (~ 6.2 MeV) and symmetric ($\sim 7-8$ MeV) fission. This is consistent with gross mass distribution feature being already established at the saddle point.

Fig. 60.

Yield of nearly symmetric fragment masses as a function of excitation energy. Results have been corrected for random events.

G. A Comparison of the Fissions of Uranium-238 Induced by 350-MeV Positive Pions and 500-MeV Protons (W. Faubel,^{*} B. J. Dropesky, R. S. Rundberg, R. J. Prestwood, B. P. Bayhurst, and C. J. Orth)

Prior to this study, the only radiochemical investigation of pion-induced fission of uranium was that reported by Russell,¹ who irradiated very thick targets of uranyl nitrate with 122-MeV negative pions. He observed that a single-peaked symmetric mass distribution resulted, similar to that for 134-MeV proton-induced fission. The purpose of the present study was to examine the features of the fission of ^{238}U induced by positive pions that range in energy across the (3,3) pion-nucleon resonance (~ 180 MeV) and compare the features with 500-MeV proton-induced fission. We were particularly interested in looking into the production of neutron-deficient isotopes of fission product elements that had been reported² for high energy proton-induced fission of ^{238}U and ^{232}Th . Because the energy deposition mechanism could be expected to be different for the two probes (i.e., absorption of the rest mass of the pion (140 MeV) in the one case vs higher incoming momentum in the proton case), a comparison of the yields of the neutron-deficient species might provide some insight into these mechanisms.

Foils of depleted uranium were irradiated with 100-, 190-, and 350-MeV π^+ in the P^3 channel and with 500-MeV protons in Line B of the Clinton P. Anderson Meson Physics Facility (LAMPF). The targets ranged in thickness from 54 to 475 mg/cm^2 and were irradiated for 8 to 20 h in the pion beam and for 1 to 10 min in the proton beam. The particle fluences were determined with aluminum monitor foils by measuring the yield of 15-h ^{24}Na and using the well-established cross sections for the $^{27}\text{Al}(\pi^+, X)^{24}\text{Na}$ and $^{27}\text{Al}(p, Y)^{24}\text{Na}$ reactions. Following the irradiations, a small measured fraction (activity-wise) of each ^{238}U target was assayed by standard high resolution $\text{Ge}(\text{Li})$ γ -ray spectrometry techniques. The remainder of each target was dissolved and radiochemical isolation of about a dozen elements from Ga to Nd was carried out. Each of

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these purified elemental fractions was assayed by spectrometry to determine the yields of both the neutron-deficient and neutron-rich isotopes.

The yields of the barium isotopes as a function of pion energy, as shown in Fig. 61, are illustrative of some of the general features learned in this study. The yields of the neutron-rich fission products ^{139}Ba and ^{140}Ba , associated with low-energy asymmetric fission, decrease as the pion energy is increased. On the other hand, the yields of the neutron-deficient species (^{131}Ba , ^{133}Ba) are substantially lower than those of the neutron-rich isotopes, and their values increase as the pion energy is increased. These products obviously result from a predominantly high energy mode of fission, as had been reported in the case of proton-induced fission.² These observations regarding the Ba isotopes are equally true for the symmetric fission region (Ag) and for the light wing of the fission product distribution (Ga and As).

In our comparison of pion- and proton-induced fission of ^{238}U , another interesting observation is illustrated in Table XVII. Here we list the measured cross sections for the neutron-deficient ^{131}Ba and neutron-rich ^{140}Ba and their ratios as a function of pion and proton kinetic energy. We note that the ratio of ^{131}Ba to ^{140}Ba decreases with decreasing particle energy, as expected from the remarks above, but, more interestingly the ratios for the pion case correspond rather well with the ratios for protons having about 150 MeV more kinetic energy. This leads one to the conclusion that at the three pion energies studied, the absorption of the rest mass energy of a pion (140 MeV) must be playing an important role in the nuclear excitation process. Thus, in our detailed comparison of the yields of essentially all products measured in common for 350-MeV pions and 500-MeV protons, we have observed that within the uncertainties of our measurements the yields are the same for both the neutron-rich and neutron-deficient fission products. Therefore, whereas we expected the mechanisms for energy deposition to be different for fast positive pions and protons, the net effect of the processes involved results in a very similar distribution in excitation energies.

Finally, a few more general observations can be cited from our study of fast π^+ -induced fission

TABLE XVII
RATIOS OF NEUTRON-DEFICIENT TO NEUTRON-RICH
BARIUM ISOTOPES

Pion-Induced Fission			
T_{π^+} (MeV)	$\sigma^{131}\text{Ba}$ (mb)	$\sigma^{140}\text{Ba}$ (mb)	$\sigma^{131}/\sigma^{140}$
350	2.5	9.0	0.28
190	1.8	23.4	0.13
100	1.4	21	0.07

Proton-Induced Fission			
T_p (MeV)	$\sigma^{131}\text{Ba}$ (mb)	$\sigma^{140}\text{Ba}$ (mb)	$\sigma^{131}/\sigma^{140}$
500 ^a	2.25	9.5	0.24
350 ^b	2.5	16	0.16
250 ^b	1.1	17.5	0.06

^aPresent work.

^bRef. 2.

Fig. 61.

Cross sections for the barium isotopes as a function of pion kinetic energy.

of ^{238}U . (1) When we sum the cross sections of all products measured as a function of pion energy, we observe that the fission cross section is higher at 190 MeV than at 350 MeV by 30 to 40% and than at 100 MeV by 10 to 20%. These sums represent only about 25% of the total reaction cross section because we did not measure every elemental fraction and could not measure the stable isotopes; however, there is no obvious reason that those products we measured are not representative of the total picture. Therefore, we conclude that the (3,3) pion-nucleon resonance is exhibiting its influence even in the complex processes involved in fission. (2) The pion interaction in uranium results in predominantly symmetric fission, centered at $A \sim 110$, with no major change in the overall distribution apparent between 100 and 350 MeV, despite the increase in yields of neutron-deficient products. (3) We have observed very large cross sections (57 to 97 mb) for the single-nucleon-removal reactions yielding $^{237}\text{U} + ^{237}\text{Pa}$, despite the competition from fission.

A detailed report on the results of this study is presently being drafted for publication in the *Physical Review C*.

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H. Pion-Nucleus Reactions

1. Cross Sections for the $^{12}\text{C}(\pi^\pm, \pi N)^{11}\text{C}$ Reactions From Threshold to 100 MeV (G. W. Butler, B. J. Dropesky, C. J. Orth, R. E. L. Green, ^{*}R. G. Korteling, ^{*} and G. K. Y. Lam ^{**}). The cross sections for the primary pion beam monitor reactions $^{12}\text{C}(\pi^\pm, \pi N)^{11}\text{C}$ (20.4 min) at energies of 100 MeV and below were measured by activation techniques at the TRIUMF meson facility in Vancouver, B. C., Canada. The excitation functions for these reactions had previously been determined over the energy range from 40 to 600 MeV at the Clinton P. Anderson Meson Physics Facility (LAMPF).¹ However, the low energy cross sections in that work had large relative uncertainties associated with them because of difficulties in reliably measuring the electron and muon contamination in the pion beam at these energies. The much more favorable duty factor and the shorter pion channel at TRIUMF, compared to LAMPF, made it advantageous to remeasure these cross sections at that facility.

The measurements made at TRIUMF were carried out at their biomedical pion channel, which provided useable pion fluxes even at the lowest energies. The experimental techniques employed were essentially the same as those used in the earlier LAMPF study. A two-element, plastic-scintillator telescope was employed to measure the flux of particles that passed through the carbon target during an irradiation. The targets were 3.2-mm-thick by 38-mm-diam disks of plastic scintillator containing 91.6% carbon by weight. These disks were the same diameter as the first scintillator of the counter telescope and were taped to its upstream face during the irradiations. No correction was made for the 1.11% ^{13}C content of the carbon; that is the results reported here technically apply to natural carbon.

Upon tuning the channel to the desired pion charge and energy, a measurement of the composition of the beam was made. The pion beams always contain some muons that come from the decay of the pions and directly from the pion production target

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and also some electrons that come mainly from the production target. Protons can also be present in the π^+ beam, but these were removed by differential momentum degradation. The scintillator telescope counted all three particles (π , μ , and e), and in addition was used to obtain a time-of-flight (TOF) spectrum, which provided the abundance of each component in the beam and thus the π to total particle ratio needed for our cross section determination. Only the pions bring about the nuclear reaction resulting in ^{11}C production.

After the beam composition was determined, a target irradiation was carried out, normally ranging from 20 to 40 min (one to two half-lives of the ^{11}C) in duration. The irradiated target was transported to a counting area where the disk was optically coupled to the face of a photomultiplier tube, covered with a special cap to ensure that all positrons from the ^{11}C decay were annihilated as close as possible to the scintillator disk, and taped over to render the assembly light tight. This assembly was then placed in contact with the face of a 75-mm-thick x 75-mm-diam NaI(Tl) scintillator inside a lead shield.

The ^{11}C positrons were selfdetected by the plastic scintillator, and the annihilation quanta were detected in the NaI(Tl) scintillator, which had an electronic window set to include only the 511-keV photopeak pulses. Each sample was counted for at least three half-lives using standard β - γ coincidence circuitry. The ^{11}C disintegration rate was calculated from the net β^+ , γ , and β^+ - γ coincidence rates.

The computed cross sections for the $^{12}\text{C}(\pi^\pm, \pi\text{N})^{11}\text{C}$ reactions are listed in Table XVIII along with the values determined earlier at LAMPF. Although the new cross sections certainly fall within the uncertainties associated with our earlier numbers, they are consistently lower than the previous values. Over the energy range from 90 to 40 MeV, the new π^+ cross sections range from 4% to 26% lower and the π^- cross sections range from about 2% to 42% lower than our earlier cross sections.

These more precise values for the low energy cross sections of the primary reactions used to determine pion fluxes by activation techniques will have a significant impact on the work of physicists in calibrating various pion monitoring instruments

TABLE XVIII
CROSS SECTIONS FOR THE $^{12}\text{C}(\pi^\pm, \pi\text{N})^{11}\text{C}$ REACTIONS

Energy (MeV)	Earlier Cross Section ^a (mb)	New Cross Section ^b (mb)
π^+		
30		3.5 $\pm$ 0.3
40	8.8 $\pm$ 1.9	6.5 $\pm$ 0.4
50	13.7 $\pm$ 2.6	10.3 $\pm$ 0.6
60	19.0 $\pm$ 3.2	14.6 $\pm$ 0.8
70	23.6 $\pm$ 3.4	20.1 $\pm$ 1.0
80	27.6 $\pm$ 3.3	25.2 $\pm$ 1.3
90	31.5 $\pm$ 3.0	29.8 $\pm$ 1.5
100	35.0 $\pm$ 2.6	33.5 $\pm$ 1.7
π^-		
30		1.8 $\pm$ 0.2
40	5.7 $\pm$ 2.3	3.1 $\pm$ 0.3
50	8.1 $\pm$ 2.9	6.1 $\pm$ 0.3
60	11.6 $\pm$ 3.7	10.6 $\pm$ 0.6
70	17.5 $\pm$ 4.8	16.4 $\pm$ 0.8
80	23.8 $\pm$ 5.5	24.5 $\pm$ 1.2
90	30.6 $\pm$ 5.8	30.0 $\pm$ 1.5

^aRef. 1.

^bThese new values from the present work are recommended for future use.

and of the biomedical people in establishing absolute doses in pion therapy, in addition to all our nuclear chemistry studies of pion-nucleus reaction cross sections.

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2. Study of Core Polarization in ^{18}O via the Pion Double-Charge-Exchange Reaction $^{18}\text{O}(\pi^+, \pi^-)^{18}\text{Ne}(g.s)$ (L.-C. Liu). Among all the nuclear probes currently available at high intensity, the pion is unique in that it has 3 charge states and can change up to 2 units of charge in a nuclear reaction without altering its other intrinsic quantum numbers. Because in a pion-induced double-charge-exchange (DCE) reaction the pion interacts with at least two nucleons, it has long been hoped that pion DCE reactions would yield information on nucleon-nucleon (N-N) correlations inside a nucleus.

Several pion-nucleus DCE experiments have been performed at LAMPF.¹⁻³ In the case of the reaction $^{18}\text{O}(\pi^+, \pi^-)^{18}\text{Ne}(g.s)$, differential cross sections were determined between 5° to 40° for pion energies 164 and 292 MeV (Fig. 62). Because the ground states of ^{18}Ne and ^{18}O are isobaric analogs, this DCE process is a coherent one and should be well accounted for by diffractive scattering theories. The simplest consequence is that the first diffraction minimum, $\theta_{\min}$, should occur at a smaller angle for the higher incident particle energy. However, inspection of Fig. 62, shows just the opposite, well outside of experimental error. This paradox has puzzled many researchers. To date, there appears to be general agreement that with any reasonable assumptions about neutron and proton density distributions and pion optical potential parameters, the $\theta_{\min}$ cannot be brought to less than 30° at 164 MeV.⁴ This also seems to be independent of whether a coupled-channel formalism⁵ or a Glauber-type multiple-scattering theory⁶ is used in the calculations. Using a strong-absorption model, Seth has shown² that to produce $\theta_{\min} \sim 20^\circ$ at 164 MeV a radius of 4.8 fm is needed for ^{18}O . (The established experimental value is ~ 3.6 fm.) It was also observed that N-N short-range correlations are unimportant at this energy.⁶

In all these considerations, however, the DCE reaction was always conceived as being due to two sequential single-charge-exchange events. In addition, a simple shell model was used for the nuclear structure of ^{18}O . In the past we stressed the importance of including other irreducible two-nucleon processes (e.g., the true pion absorptions) in the calculation of pion-nucleus reactions.⁷ Using our coupled-channel theory,⁷ we found in this

study that even with simple shell model nuclear wave functions the inclusion of irreducible two-nucleon processes will cause the $\theta_{\min}$ to move from $\sim 30^\circ$ (short dashed curve) in to $\sim 23^\circ$ (dot-dashed curve) at 164 MeV, and from $\sim 21^\circ$ out to $\sim 22^\circ$ at 292 MeV. Furthermore, we found that as long as we use nuclear wave functions obtained from the assumption of an inert ^{16}O core,⁸ it is not possible to cause any further appreciable change of the position of $\theta_{\min}$. On the other hand, if we assume the existence of core-polarization and introduce into the valence neutron wave function of ^{18}O a collective state component arising from 4p-2h excitation, we are able to move the $\theta_{\min}$ further toward the experimental values (the solid curves). As we know, the need for core polarization has long been established in the analyses of inelastic transitions caused by electron scattering from oxygen isotopes.⁸ However, the DCE processes connecting two double-analog nuclei involve transitions that are absent in experiments employing electrons or nucleons. We believe that pion-nucleus DCE reactions represent a valuable new tool for nuclear structure studies. On the other hand, we also note that such studies can be meaningful only if we include those two-nucleon processes that were not previously contained in the conventional two sequential single-charge-exchange reaction mechanism.

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Fig. 62.

Angular distributions for the reaction $^{18}\text{O}(\pi^+\pi^-)^{18}\text{Ne}$ (g.s.). The data denoted by $\bullet$ were due to Seth et al.,² those denoted by $\circ$ and $\square$ were from Greene et al.³ Theoretical results obtained with and without the addition of new "irreducible" two-nucleon processes are respectively shown as the dot-dashed and short dashed curves. The solid curves contain core polarization, the sequential single-charge-exchanges, and the new two-nucleon processes.

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3. A Product Recoil Study of the $^{12}\text{C}(\pi^{\pm}, \pi N)-^{11}\text{C}$ Reactions over the Energy Range 90 to 350 MeV

(R. S. Rundberg, G. C. Giesler, B. J. Dropesky, A. A. Caretto,* and N. T. Porile**).

The study of the pion-nucleon knock-out reactions $^{12}\text{C}(\pi^{\pm}, \pi N)^{11}\text{C}$ has attracted a great deal of both experimental and theoretical interest. On the basis of the free-particle pion-nucleon cross sections and a simple nucleon knock-out model, the ratio of the cross sections for the π^{-} -induced reaction to the π^{+} -induced reaction at the (3,3) resonance (180 MeV) had been predicted to be 3. An early experimental ratio was reported¹ to be unity. We have more recently determined² that the ratio is 1.59 ± 0.07 , considerably different from the predicted value.

The most successful attempt, to date, to account for this discrepancy is the semiclassical transport model of Sternheim and Silbar.³ This model enables one to estimate the probability that the outgoing nucleon (neutron or proton), after having been struck by the incident pion, will undergo charge exchange before exiting the nucleus.

An inherent assumption in these comparisons of experimental cross sections with predictions based on free-particle pion-nucleon cross sections is that the mechanism involves a simple pion-nucleon knock out similar to quasi-free scattering. However, conceptually there are two major mechanisms by which a pion- (or proton-) induced nucleon-removal reaction might take place. (A) Direct Knock-Out (DKO), whereby the incident pion strikes a bound nucleon causing its ejection. The incident particle and the struck nucleon exit the nucleus without further interaction, leaving a residual nuclear excitation energy of less than about 10 MeV, in order to preclude subsequent nucleon evaporation. (B) Inelastic Scattering followed by Evaporation (ISE), whereby the incident pion inelastically scatters off a bound nucleon transferring between 10 and 20 MeV to that nucleon. The nucleon subsequently evaporates, which de-excites the nucleus and produces the nucleon-removal product.

Mechanism (A) would predict a relatively isotropic angular distribution for the recoiling ^{11}C nucleus, whereas mechanism (B) would predict a peak in the angular distribution at close to 90° to the direction of the incident pion.

We have chosen the relatively simple thick-target thick-catcher technique, employed previously^{4,5,6} for studies of the $^{12}\text{C}(p, pn)^{11}\text{C}$ reaction, to learn some of the features of the recoil properties of the $^{12}\text{C}(\pi^{\pm}, \pi N)^{11}\text{C}$ reactions. The experiment involved irradiations of target-catcher stacks with pions followed by assay of the induced ^{11}C activity. The irradiations were performed at the P^3 and LEP channels of the Clinton P. Anderson Meson Physics Facility (LAMPF). The pion energies ranged from 90 to 350 MeV, and the exposures lasted about 30 min.

The target stacks consisted of a 14.3 mg/cm^2 thick graphite foil sandwiched between $25\mu\text{m}$ ($\sim 5 \text{ mg/cm}^2$) thick beryllium catcher foils of the highest available purity. Beryllium guard foils protected the stack from externally produced ^{11}C recoils. The stacks were irradiated in two different orientations to the beam at each energy. In experiments designed to yield the projected forward and backward ranges, the stack was mounted perpendicular to the beam direction, whereas in those designed to yield the perpendicular ranges, it was mounted at 10° to the beam.

Following irradiation, the ^{11}C activity in the target and catcher foils was assayed with a $\gamma\text{-}\gamma$ coincidence counter consisting of two NaI(Tl) scintillation detectors mounted on opposite sides of the target foil. The efficiency-calibrated system was set to count the 511-keV quanta resulting from annihilation of the 20.4-min ^{11}C positrons.

The disintegration rates of the various foils were used to obtain the average projected ranges of ^{11}C in carbon, designated FW, BW, and PW. The quantities F, B, and P are the fraction of the total number of ^{11}C nuclei recoiling into the forward, backward, and perpendicular catchers, respectively, and W is the surface thickness of the target. In the case of the 10° runs, the value of P represents the average of the results obtained for the two catchers.

The energy dependence of the projected range is displayed in Fig. 63. We see that the projected

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Fig. 63.

Energy dependence of the average projected ranges of ^{11}C from the $^{12}\text{C}(\pi^\pm, \pi\text{N})^{11}\text{C}$ reactions. FW, PW, and BW correspond to the forward, perpendicular, and backward ranges, respectively.

forward ranges decrease with increasing pion energy, the projected perpendicular ranges are largely independent of energy, and the projected backward ranges increase with bombarding energy. Furthermore, the energy dependence of FW and BW is markedly stronger for incident π^- than for π^+ .

Our results constitute the first determination of recoil ranges of $^{12}\text{C}(\pi^\pm, \pi\text{N})^{11}\text{C}$ reaction products, and they may be compared to similar results previously obtained for the $^{12}\text{C}(p, pn)^{11}\text{C}$ reaction induced by protons of comparable energies.^{4,5,6} Within the limits of uncertainty, the FW and BW

values are equal, but the values of PW are significantly larger in the proton reaction, particularly at the lower energies.

Analysis of our pion reaction data is underway in terms of a two-velocity vector representation of the reaction and based on a quasi-free scattering model for describing on a microscopic level how momentum is transferred from the incident pion to the carbon nucleus. The velocity and kinetic energy of the recoiling nucleus will come from this analysis. In addition, a comparison with calculations based on the intranuclear cascade code ISOBAR plus the evaporation code DFF will be made. From these analyses, we expect to be able to conclude something about the contributions of the DK0 and 1SE processes to the nucleon-removal reactions in the carbon as a function of pion energy and pion charge.

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4. Excitation Function for the Pion Single Charge Exchange Reaction $^{13}\text{C}(\pi^+, \pi^0)^{13}\text{N}$ (g.s.)

(D. J. Vieira, G. W. Butler, R. S. Rundberg, N. Imanishi,* G. C. Giesler, and B. J. Dropesky). The study of pion single charge exchange (SCE) reactions is currently a topic of strong interest and activity in intermediate-energy nuclear science research because it helps to test and refine our understanding of how pions interact with nuclei. Of all the SCE reactions studied to date^{1,2} perhaps the most intriguing is the $^{13}\text{C}(\pi^+, \pi^0)^{13}\text{N}$ (g.s.) reaction. Because the ground state of ^{13}N is the analog of the ^{13}C ground state and to the extent that the nuclear structure of these states is similar, this reaction minimizes uncertainties arising from nuclear structure models and allows a more direct probing of the pion-nucleus SCE interaction. Furthermore, because the ground state is the only particle-bound state of ^{13}N , which decays by positron emission with a half-life of 9.96 min, activation techniques can be used to measure this specific charge exchange transition probability between the ground states of these two nuclei.

The earliest measurements of this reaction cross section were by Chivers *et al.*,³ who reported a cross section of 3.0 mb in the pion-nucleon (3,3) resonance region of 180 MeV. In a later study involving the measurement of this reaction cross section over the energy range of 70 to 250 MeV, Shamaï *et al.*⁴ observed a relatively flat excitation function with a cross section of 0.95 mb reported near 180 MeV. A number of theoretical calculations of this reaction have been performed using a variety of different models;^{1,2,5-8} however, all of these approaches predict a relatively low cross section ranging from 0.2 to 0.5 mb at 180 MeV. Because of this unexplained discrepancy between theory and experiment and the suggested possibility⁹ that the cross sections of Shamaï could be too large

due to contributions from the secondary reaction $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$, we decided to reinvestigate this SCE reaction.

Our measurements reported here were performed at LAMPF where both the low-energy pion (LEP) channel and the high energy (P^3) channel were used to provide pions in the energy range of 50 to 190 MeV and 120 to 350 MeV, respectively. Pion fluxes of $(0.4-6) \times 10^8$ π/sec were obtained at the LEP channel with a momentum acceptance of $\pm 2\%$, whereas $(1-15) \times 10^8$ π/sec with a momentum spread of $\pm 3.5\%$ were utilized at the P^3 channel. A typical spot size had dimensions of 2 cm vertically by 3 cm horizontally. Protons were removed from the pion beam using a differential absorption technique, whereas positron, electron, and muon beam contaminants cause no appreciable interference because the lepton reaction cross sections are known to be very small.¹⁰

Several ^{13}C targets were fabricated using 99.3% isotopically enriched ^{13}C powder pressed into thin disks using a 10% by weight admixture of 90% enriched ^{13}C polyethylene as binder. The resulting targets had a ^{13}C enrichment of 93.4%, a diameter of 4.92 cm, and areal thicknesses ranging from 48 to 195 mg/cm^2 . For an irradiation, a target (or set of targets) was placed in a thin polyethylene bag, which prevented potential contamination of the target by recoil activities produced by pions interacting with the surrounding air or exit window of the beam channel. Irradiation periods ranged from 5 to 20 min. A plastic scintillation detector mounted out of the beam but in the vicinity of the target was used to monitor any beam intensity variations that occurred during the course of the irradiation. If any variation occurred, an appropriate correction was applied to the calculated cross section.

The pion intensity was measured by simultaneously irradiating a Pilot B plastic scintillator disk (with the same diameter as the target), which was located downstream of the ^{13}C target and outside of the polyethylene bag. The plastic scintillator was activated by the $^{12}\text{C}(\pi^+, \pi^+ \text{N})^{11}\text{C}$ reaction whose cross sections over the energy range of interest are well known.¹¹ After the irradiation, the scintillator was counted in a $\beta^+-\gamma$ coincidence system and the disintegration rate for the 20.4-min ^{11}C activity was extracted from decay cur

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analysis. Combining this information with the known cross section, the incident pion flux was obtained.

After irradiation, the ^{13}C target was removed from the polyethylene bag, and the β^+ activity present in the target was measured in an annihilation γ - γ coincidence counter. This counter consisted of two 7.6 cm by 7.6 cm Na(Tl) detectors with a 0.16-cm-thick copper plate placed in front of each detector to insure that all the positrons were stopped and annihilated immediately. This arrangement afforded maximum counter efficiency and prevented the summing of two annihilation quanta in a single detector. To further increase the sensitivity of the system, the counter was completely surrounded by 10 cm of lead to reduce counter background. The absolute efficiency of this system was determined by counting activated Pilot B disks on this counter as well as on the absolute β - γ counter mentioned earlier. Counting of the activated targets started 2 to 5 min after the end of bombardment and continued for 1 to 2 h. The resulting decay data were analyzed with the standard decay code CLSQ.

For π^+ irradiations of ^{13}C , a two-component fit to the data gave the best results. Both the 9.96-min half-life of ^{13}N and the 20.4-min half-life of ^{11}C were clearly observed. The latter activity arises from reactions such as $^{13}\text{C}(\pi^+, pn)^{11}\text{C}$ and $^{13}\text{C}(\pi^+, \pi^+ 2n)^{11}\text{C}$ or the $^{12}\text{C}(\pi^+, \pi^+ N)^{11}\text{C}$ reaction on the 1.6% ^{12}C present in the target. Searches for shorter- or longer-lived decay components failed to improve the fit. However, when π^- irradiations were carried out, and the counting of the target was started as soon as possible after the end of bombardment, a weak short-lived component resulting from 2.04-min ^{15}O was observed instead of ^{13}N . One expects the ^{13}N activity to be absent because π^- interactions with ^{13}C cannot produce ^{13}N ; however, the presence of ^{15}O indicated that the target was contaminated by an element heavier than carbon. Chemical analysis of the outer portion of one target confirmed this suspicion by yielding 0.5 to 1.3% oxygen by weight. Further chemical analyses failed to reveal any significant amounts of nitrogen or other heavier elements. Assuming the above oxygen contamination, we calculated that the observed yield of ^{15}O was

entirely consistent with the measured cross section of the $^{16}\text{O}(\pi^-, \pi^- n)^{15}\text{O}$ reaction.¹² From this, we concluded that oxygen was the only contaminant of any consequence in our targets.

Because of the relatively small level of oxygen contamination present, we decided to apply a small correction to our data that subtracted out the effects resulting from pion reactions with oxygen. To facilitate making this correction, we measured the oxygen contamination in each target by determining the disintegration rate of ^{15}O produced by 190 MeV π^- irradiations. Combining this information with the known $^{16}\text{O}(\pi^-, \pi^- n)^{15}\text{O}$ cross section at 190 MeV, we determined the oxygen present in each target. We found this number ranged from 0.5 to 1.0%, entirely consistent with the previous chemical analysis results. To check the cross-section measurements for pion reactions on oxygen and to extend those measurements to higher and lower pion energies where we would need to correct our data, we undertook a series of irradiations on $\sim 200\text{-mg/cm}^2$ boric acid (H_3BO_3) targets at positive pion energies ranging from 50 to 350 MeV. Cross sections for the following reactions were obtained: $^{16}\text{O}(\pi^+, \pi^+ N)^{15}\text{O}$, $^{16}\text{O}(\pi^+, X)^{13}\text{N}$, and $^{16}\text{O}(\pi^+, X)^{11}\text{C}$, where X is used to represent any combination of emitted particles that will yield the final product. With the use of these numbers and the determined oxygen contamination present in each target, a ^{15}O decay component was calculated for each irradiation. This calculated ^{15}O component was then introduced in the decay curve analysis as a known component and the data were refitted. Finally, a small correction was applied to our measured ^{13}N yield to subtract out the amount of ^{13}N produced directly from pion reactions with oxygen via the $^{16}\text{O}(\pi^+, X)^{13}\text{N}$ reaction. In all, the total amount of the above corrections reduced the ^{13}N cross section by typically 0.1 mb.

Figure 64 shows the observed dependence of the ^{13}N cross section at 164 MeV incident π^+ energy as a function of target thickness. These data were compiled from measurements using a single target or various combinations of stacked targets. Within the uncertainties of the measurements, no significant increase in the cross section is observed with increasing target thickness. For comparison, a measurement by Shamai *et al.*⁴ at 160 MeV is also

Fig. 64.

The observed cross section at 164 MeV for the $^{13}\text{C}(\pi^+, \pi^0)^{13}\text{N}$ (g.s.) reaction as a function of target thickness.

plotted (open circle). Extrapolation of our data to the target thickness of their measurement would appear not to be consistent with their determination. However, since performing these measurements, we realize that determining the contribution to the measured (π^+, π^0) reaction product yield due to the secondary (p, n) reaction may be more complicated than we initially expected. More detailed calculations of these effects are in progress, and we will simply state that secondary contributions to the measured ^{13}N cross sections are estimated to be no larger than 0.1 mb.

The measured excitation function of the $^{13}\text{C}(\pi^+, \pi^0)^{13}\text{N}$ (g.s.) reaction is shown in Fig. 65. These values are found to be consistently smaller than those reported in Ref. 4 by 30 to 50%, but our result at 164 MeV is in good agreement with the integrated cross section determined from angular distribution measurements using the LAMPF π^0 spectrometer.¹³ Additional data, not shown in Fig. 65, at 140, 180, 210, and 300 MeV are still being analyzed.

Of the numerous theoretical calculations of this reaction using a variety of different models,^{1,2} we have chosen four different calculations as representative of current models. These included the fixed-scatterer calculations of Gibbs et al.,⁵ the distorted wave impulse approximation

(DWIA) predictions of Lee and Kurath,⁶ the covariant coupled-channel calculation of Liu,⁷ and the isobar-hole predictions of Hirata.⁸ However, none of the above calculations are found to be in good agreement with the observed excitation function. In particular, all the calculations underestimate the reaction cross section in the region of the (3,3) resonance by a factor of ~2. Because pions interact so strongly with nuclear matter in this energy range, this discrepancy tends to indicate that other more complicated reaction mechanisms should be included in these calculations. Furthermore, the sharp dip observed at ~70 MeV is not correctly predicted, although the fixed scatterer prediction does show a similar minimum at a somewhat lower energy. The interpretation¹⁴ of this minimum is expressed as a result of two competitive elements: the fundamental SCE cross section (i.e., $\pi^+ + n \rightarrow p + \pi^0$), which increases with pion energy in this region, and the distortion of the pion waves (or the loss of the pions to other reaction channels), which also increases with energy in this region. Together, these factors combine to produce a minimum. Moreover, the interference between $\underline{s}$ and $\underline{p}$ partial waves can increase or decrease the depth of this minimum. Thus, this reaction may prove useful in determining the interplay of $\underline{s}$ and $\underline{p}$ waves in the charge exchange process.

We believe that further theoretical efforts in interpreting these measurements will contribute to the improvement of our understanding of the pion-induced single charge exchange reactions.

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Fig. 65.

Measured excitation function (solid data points) for the $^{13}\text{C}(\pi^+, \pi^0)^{13}\text{N}(\text{g.s.})$ reaction. Four theoretical excitation functions are shown as per the indicated code.

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I. Spallation Reaction Cross Section Measurements Using RbBr (P. M. Grant, D. A. Miller, J. S. Gilmore, and H. A. O'Brien)

The measurement of medium-energy spallation cross sections is an important activity of the Medical Radioisotopes Research Group as it utilizes the high intensity proton beam at LAMPF for the production of radioactive nuclides for biological and physical research. Knowledge of the formation cross sections of isotopes of interest allows the calculation of estimated production yields in thick targets, the monitoring of remote processing chemical yields, and an evaluation of isotopic interferences.

We are currently using a RbBr target to produce ^{68}Ge and are developing additional chemical recovery schemes for several other medically-interesting nuclides that are also produced in this target. These include ^{75}Se for biomedical compound labeling, the $^{72}\text{Se} - ^{72}\text{As}$ generator, ^{67}Ga for tumor localization and detection of inflammatory disease, and ^{62}Zn for computed emission tomography of the prostate and pancreas.

Three pressed RbBr pellets having dimensions of 13 mm diameter, 5 to 6 mm thickness, and between 2 and 3 grams weight, were fabricated. Each pellet together with Al monitor foils were irradiated with $(800 \pm 5)\text{-MeV}$ protons to an integrated intensity of approximately $1 \mu\text{A-hr}$ at the nuclear chemistry targeting station in LAMPF's Area B. Two of the three pellets were separately dissolved in 6 M HCl, and suitable counting aliquots were subsequently removed, diluted, and placed in a standard geometry for quantitative analyses via gamma ray spectrometry.

It was impossible to measure ^{68}Ge in the original solution because the low-intensity, 1077-keV gamma photon from the $^{68}\text{Ge} - ^{68}\text{Ga}$ equilibrium decay was effectively masked by the more abundant 1077 keV peak from the decay of ^{86}Rb . Because ^{86}Rb emits

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only this one gamma and photons associated with $^{73}\text{Ge} - ^{68}\text{Ga}$ decay have extremely low intensities, a mathematical apportionment of the 1077-keV peak activity via multiplicity correlation analysis is not feasible. Thus, a radiochemical separation of germanium was required.

Under the conditions of distillation from 6 M HCl media, only isotopes of Ge, As, and Se volatilize from the solution. Assays of the distillates in conjunction with measured distillation yields allowed cross-section determinations for several isotopes of these three elements.

The third RbBr pellet was chemically processed for the determination of ^{67}Cu and ^{67}Ga cross sections. It was not possible to separate these nuclides by counting the untreated original solution because of their similar half lives and effectively identical gamma photon emissions. The copper procedure entailed ion exchange, a number of sulfide precipitations, and several $\text{Fe}(\text{OH})_3$ scavenges, whereas the gallium separation involved several solvent extraction and precipitation steps.

The cross sections for the production of 40 nuclides by the irradiation of RbBr with 800-MeV protons are listed in Table XIX. The samples were periodically counted from the day of irradiation until approximately $t_0 + 1.25$ years. The spectral data were reduced with the GAMANAL code, and the reported values are weighted averages obtained from repetitive counts of the Al monitors and experimental solutions. The quoted uncertainties are one standard deviation of the measured values and do not include uncertainties associated with the monitor cross sections, spectrometer efficiency calibration, photon intensities, etc.

XIII. RADIONUCLIDE PRODUCTION AND SEPARATIONS

A. Radioisotope Production Developments (G. E. Bentley, J. W. Barnes, K. E. Thomas, M. A. Ott, F. W. Seurer, T. P. DeBusk, F. J. Steinkruger.

The Medical Radioisotope Group (CNC-3) is responsible for developing medium energy proton accelerator-produced isotopes in sufficient quantities for evaluation as biomedical tracers and diagnostic for evaluation as biomedical tracers and diagnostic

TABLE XIX
SPALLATION CROSS SECTIONS FOR THE REACTIONS
OF RbBr WITH 800-MeV PROTONS

Nuclide	Cross Section (mb)	Type
^{88}Y	0.3 ± 0.2	IY
^{85}Sr	4.3 ± 0.9	CY
^{83}Sr	3.0 ± 0.5	CY
^{82}Sr	2.1 ± 0.2	CY
^{86}Rb	19 ± 1	CY
^{84}Rb	50 ± 2	CY
^{83}Rb	42 ± 1	CY
^{82m}Rb	12 ± 2	IY
^{81}Rb	14 ± 1	CY
^{82}Br	4.9 ± 0.4	CY
^{80m}Br	23 ± 2	IY
^{77}Br	49 ± 2	CY
^{75}Br	12 ± 6	CY
^{75}Se	67 ± 2	CY
^{73}Se	22 ± 1	CY
^{72}Se	12 ± 0.4	CY
^{76}As	14 ± 4	IY
^{74}As	29 ± 0.9	IY
^{71}As	27 ± 1	CY
^{69}Ge	35 ± 2	CY
^{68}Ge	19 ± 1	CY
^{67}Ga	41 ± 1	CY
^{65}Zn	39 ± 2	CY
^{62}Zn	2 ± 1	CY
^{67}Cu	1.6 ± 0.08	CY
^{64}Cu	16 ± 0.9	IY
^{61}Cu	7.8 ± 0.6	CY
^{60}Co	9.1 ± 0.7	CY
^{58}Co	18 ± 0.8	CY
^{57}Co	13 ± 0.5	CY
^{59}Fe	1.8 ± 0.1	CY

TABLE XIX (cont)
SPALLATION CROSS SECTIONS FOR THE REACTIONS
OF RbBr WITH 800-MeV PROTONS

Nuclide	Cross Section (mb)	Type
⁵⁶ Mn	3.0 ± 0.2	CY
⁵⁴ Mn	1.1 ± 0.4	IY
⁵² Mn	2.7 ± 0.1	IY
⁵¹ Cr	7.9 ± 0.5	CY
⁴⁸ V	2.3 ± 0.09	CY
⁴⁶ Sc	2.2 ± 0.1	CY
^{44m} Sc	0.8 ± 0.2	IY
⁴⁴ Sc	0.6 ± 0.1	IY
⁷ Be	4.1 ± 0.7	CY

IY = Independent Yield
CY = Cumulative Yield

imaging agents. Target irradiations are performed at the Isotope Production Facility at the Clinton P. Anderson Meson Physics Facility (LAMPF). Target preparation and processing is accomplished at the CNC-3 hot cell facility.

Inserting thick targets (up to 2.0 cm) in the LAMPF primary proton beam places stringent requirements on the design of the target package. The accelerator is presently operating at a nominal current of 500 μ A with an energy of 800 MeV. Depending upon which targets are in the proton beam upstream of the Isotope Production Facility, our production targets receive from 50% to 75% of the nominal beam current. This requires that each target package be capable of dissipating ~10 kW of beam power via water cooling.

A substantial effort during fiscal year 1981 has been invested in designing target encapsulation that can withstand the hostile environment present during irradiations. This effort has included the manufacturing of special machining cutters so that all-aluminum target holders may be fabricated, replacing the previously used stainless steel/aluminum holders. The design and fabrication of

a new holder now permits the target to be inserted through the side instead of the top (see Fig. 66). This moved the metal closure seal away from localized heating caused by the accelerator beam impinging upon the seal area, thus minimizing cooling water leaks. Various target cladding systems have been designed and fabricated that allow the containment of a variety of different materials, including pure metals, metal oxides, and salts. Targets for the production of ¹²⁷Xe and ¹²³I from La₂O₃, CsCl, and CsI have been prepared such that they may be opened and heated while under vacuum to facilitate complete recovery of the produced rare gas radioisotopes.

Targets irradiated during FY 1981 and the major radioisotopes produced are listed in Table XX. The amounts of each radionuclide shipped in FY 1974 through 1981 are shown in Fig. 67. Radioisotope shipments to extramural users are listed in Table XXI. The total number of radioisotope shipments as a function of fiscal year is shown in Fig. 68.

Fig. 66.
Radioisotope Production Side-Loading Target Holder.

TABLE XX
TARGETS IRRADIATED AT THE ISOTOPE PRODUCTION
FACILITY DURING FY 1981

Target Material	Number Irradiated during 1981	Principle Isotope(s) Produced
Al	2	^{22}Na
CsCl	4	^{123}I , ^{127}Xe
CsI	2	^{123}I , ^{127}Xe
In	2	^{109}Cd
La_2O_3	4	^{127}Xe
Pb	2	^{178}W , ^{191}Os
Mo	13	^{77}Br , ^{82}Sr
Ni	3	^{52}Fe
RbBr	8	^{68}Ge
Si	1	^{26}Al
ZnO	1	^{67}Cu
TOTAL	42	

TABLE XXI
ISOTOPE SHIPMENTS FOR FY 1981

Nuclide	mCi	Shipments
^{22}Na	683	2
^{48}V	2	2
^{52}Fe	20	1
^{99}Fe	1.2	1
^{67}Cu	110	2
^{68}Ge	212	8
^{77}Br	4600	63
^{82}Sr	4200	28
^{88}Y	8	1
^{88}Zr	150	1
^{127}Xe	3200+	4
$^{145,146}\text{Sm}$	240	1
$^{146,148,150,151,153}\text{Gd}$	1500	1
^{172}Hf	1	1

Fig. 67.

Millicuries of radionuclides purified and shipped by CNC-3.

Fig. 68.

Total number of isotope shipments.

B. Irradiation and Separation Methods for ^{127}Xe
(J. W. Barnes, M. A. Ott, T. F. DeBusk, and F. H. Seurer)

Xenon-127 ($t_{1/2} = 36.4$ d) is used in clinical medicine for lung function studies and brain blood flow measurements. Brookhaven National Laboratory began distributing this nuclide several years ago; but as a result of increasing demand coupled with a restricted accelerator operating schedule, BNL has requested that Los Alamos develop a backup production capability for ^{127}Xe .

The one-piece stainless steel target container developed for ^{123}Xe (^{123}I) production was used to irradiate both CsCl and CsI salt targets. However, the copper seals failed during the longer irradiation times required to produce ^{127}Xe . We are experimenting with a new encapsulation system for salt targets that consists of a 7.6-cm by 1.9-cm-diam cylinder of copper with welded ends (see Figs. 69 and 70). Each cylinder holds about 35 g of CsCl , and three cylinders are placed in a single target holder. To date, no leaks have been detected for irradiations of two weeks duration.

Fig. 69.

Welded copper cylinders positioned inside-loading target holder.

A new stainless steel vacuum line was built and installed in the hot cell for ^{127}Xe . Its operation is far superior to the previous glass vacuum system.

During this fiscal year, 8 targets were irradiated, and ~4 Ci of ^{127}Xe were sent to BNL in 4 shipments.

C. Production of Microcurie Amounts of ^{26}Al

(K. W. Thomas and the Los Alamos Medical Radioisotopes Group)

1. Introduction. Aluminum-26 is a nuclide of immense interest in the field of cosmochemistry. In particular, it is one of the primary nuclides used to determine the production rate of cosmic-ray-produced nuclides in meteorites and, by virtue of its long half life, to date those meteorites. For this use an accurate value of the half life of ^{26}Al is extremely important. There has been some speculation that, in fact, its half life is not as well known as previously believed.^{1,2} A redetermination of the ^{26}Al half life would be of great interest to cosmochemists. Also connected with the importance of ^{26}Al to this field is its production and disintegration rate by cosmic rays. A study of the $^{26}\text{Al}(n,p)^{26}\text{Mg}$ and $^{26}\text{Al}(p,\gamma)^{27}\text{Si}$ reactions as well as any number of other nuclear reactions would be a useful contribution to this problem. Other applications of ^{26}Al include studies of its hyperfine structure and the isotope shift in the optical emission spectrum for use in an ultra-sensitive analysis program; use as a tracer to measure the mass transfer of Al^{+3} ions in liquid extraction studies; and, once the half life is confirmed, use as a gamma-ray counting standard. For these reasons an effort was made to produce ^{26}Al in high yield.

Nuclear spallation yields a broad spectrum of reaction products that are primarily neutron deficient and generally unavailable in useful amounts from other sources. The isotope of interest must be isolated from many diverse radioactive species in addition to gram-kilogram quantities of target material, generally without adding any carrier of the element in question. Further, due to the intense radioactivity of the targets after

Fig. 70.

Welded copper cylinders in aluminum frame used for salt target irradiations.

irradiation, these chemical separations must be carried out in a hot cell.

2. Experimental. The Los Alamos Meson Physics Facility (LAMPF) is a proton linear accelerator with design objectives of 800-MeV maximum energy and 1-mA average current. It is presently operating at close to full energy and approximately 600 μ A of current, of which 50 to 75% is available at the main beam stop and the Isotope Production Facility.

The target consisted of a single crystal of electronics-grade silicon measuring 1.47 cm thick and 5.34 cm in diameter and weighing 63 g. It was

housed in a stainless steel container and sealed with a copper "O" ring. This target was cycled in and out of the Isotope Production Facility at LAMPF during a two-yr period. Approximately 10^{23} protons having an energy of 500 to 700 MeV were received by the silicon during the irradiation. The target read ~50 R/hr at several centimeters 6 months after the end of bombardment.

In a hot cell, the silicon was dissolved in a 1:1 mixture of ultrapure, concentrated HF and HNO₃ at 100°C. The silicon was removed by distillation as SiF₄ during the target dissolution. The dissolution was carried out slowly over a several day period resulting in a dissolution volume of 600 mL.

This solution was taken to dryness in a teflon beaker several times with HF, then with fuming HNO_3 , and finally with concentrated HClO_4 . After slurring the precipitate with HClO_4 and transferring to a 40-ml Vycor centrifuge tube, the slurry was heated in an open furnace to 200°C until completely dry. The residue was taken up in 10 to 15 ml of purified 0.25 M oxalic acid/0.1 M HCl. The oxalic/HCl acid solution was previously run through an anion exchange column identical to the one described below.

An anion exchange column 10.5 cm high by 2.2 cm i.d. was prepared using MP-1, 200-400 mesh resin. The free column volume was 44 ml, and the column was preconditioned starting with concentrated HCl and proceeding down to water and finally with the 0.25 M oxalic acid/0.1 M HCl solution.

The dissolved residue was loaded onto the column and the flow rate was determined by gravity (~ 40 ml/hr). The column was rinsed with 10 ml of the oxalic acid solution, 70 ml of water, and 60 ml of 0.1 M HCl. These washes removed a significant amount of ^{22}Na and ^7Be . The aluminum was eluted with 150 ml of 6 M HCl.

The major contaminants in this preliminary ^{26}Al fraction were ^7Be , ^{22}Na , ^{46}Sc , ^{75}Se , ^{88}Y , $^{172}\text{Hf/Lu}$ and ^{175}Hf . With the exception of the ^7Be and ^{22}Na , these contaminants came from the hot cell in which the chemistry took place. This fraction, in 150-ml volume, read 500 mR/hr at contact, but was considered low enough in activity to be removed from the hot cell for further purification.

After taking the ^{26}Al fraction slowly and carefully to dryness (AlCl_3 is somewhat volatile), it was redissolved in 0.25 M oxalic acid/0.1 M HCl and run through a second anion column using the same procedure just described. Further separation from ^7Be and ^{22}Na was achieved, but little improvement was to be expected from the other contaminants.

Removal of the ^{46}Sc , $^{172}\text{Hf/Lu}$, and ^{88}Y and a great reduction in ^{75}Se contamination was achieved by several extractions with bis-2-ethyl-hexylorthophosphoric acid (HDEHP). The ^{26}Al fraction was taken up in 1 M HCl and extracted with an equal volume of 10% HDEHP/toluene for 5 min. The aqueous fraction (^{26}Al) was washed with toluene, the organic fraction was washed with 1 M HCl, and this acid wash was further washed with toluene.

The aqueous fraction and the acid wash were combined and the entire extraction procedure was repeated.

As a final clean-up step, the ^{26}Al fraction was taken to dryness several times with fuming HNO_3 and concentrated HClO_4 and run through the anion exchange column as before except ~ 50 ml of 0.25 M oxalic acid/0.2 M HCl was used as a wash after loading instead of just 10 ml. This improved the ^7Be separation.

3. Results. Approximately 11 μCi of ^{26}Al were recovered. Chemical yield is conservatively estimated at 90%. Extra care was taken to avoid the addition of any aluminum carrier; however, due to the production of stable aluminum in the target during the irradiation, the ^{26}Al is not carrier-free. Table XXII lists the remaining contaminants at day 204.9(81) MST in the ^{26}Al fraction relative to the dpm of ^{26}Al present. In addition to the ^{26}Al , 2.1 Ci of ^{22}Na and 1.5 Ci of ^7Be , corrected to the end of bombardment, were obtained. The decontamination factors of the ^{26}Al from these nuclides were $>10^{14}$ and $>10^{11}$, respectively.

TABLE XXII
CONTAMINANTS IN THE ALUMINUM-26

Nuclide	dpm/dpm ^{26}Al (204.904 (81))	$t_{1/2}$
^{56}Co	$<0.034^a$	77d
^{75}Se	0.031	120d
$^{77}\text{As} (^{77}\text{Br})$	0.019	1.61d (2.37d)
^{88}Y	0.002	106d
^{110m}Ag	0.015	253d
^{114m}In	0.044	49.5d
$^{172}\text{Hf} (^{172}\text{Lu})$	$<0.04^*$	1.87y (6.7d)
^{183}Re	0.119	71d
$^{184,184m}\text{Re}$	0.01	38d (169d)

^aUpper limit only.

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D. Production and Recovery of ^{123}Xe (^{123}I) (J. W. Barnes, M. A. Ott, T. P. DeBusk, G. E. Bentley, P. M. Wanek, and F. H. Seurer)

A study to determine the optimum parameters for the production of ^{123}I was initiated. The principal strategy is to form 2-hr ^{123}Xe in an appropriate target, isolate the radioxenon as rapidly as practical following end-of-bombardment (EOB), allow ^{123}Xe to decay to ^{123}I , transfer the remaining xenon nuclides, and recover the radioiodine. The major interference arises from the simultaneous production of 17-hr ^{125}Xe , which decays to 60-d ^{125}I . The production variables being studied include 1) target material; 2) irradiation time; and 3) time allowed for radioxenon to decay to radioiodine.

A new target container was fabricated out of stainless steel. It was capable of being coupled to a vacuum line system and contained a thin copper seal that could be punctured while attached to the vacuum system. The vacuum line contained four cold traps, one of which was used to remove volatile species other than radioxenon released from the target container. The remaining three cold traps permitted a study of the $^{125}\text{I}/^{123}\text{I}$ ratios at different growth times following removal of the radioxenons from the target.

The results following a one- and a two-hour bombardment of CsI are shown in Table XXIII. Although these results were obtained under conditions that were less than optimum, nonetheless the $^{125}\text{I}/^{123}\text{I}$ ratios obtained in the first traps are

TABLE XXIII
PRELIMINARY BATCH METHOD ^{123}I AND ^{125}I
RESULTS FROM DECAY OF RADIOXENOUS
PRODUCED IN A CsI TARGET

Length of Irradiation	1 hour	2 hours
<u>Trap #1</u>		
Decay Period	EOB + 1.35 h to	EOB + 1.30 h to
	EOB + 4.35 h	EOB + 4.30 h
$^{125}\text{I}/^{123}\text{I}$ dpm at T_0	0.003	0.004
<u>Trap #2</u>		
Decay Period	EOB + 4.35 h to	EOB + 4.30 h to
	EOB + 6.35 h	EOB + 6.30 h
$^{125}\text{I}/^{123}\text{I}$ dpm at T_0	0.008	0.008
<u>Trap #3</u>		
Decay Period	EOB + 6.35 h to	EOB + 6.30 h to
	EOB + 8.35 h	EOB + 8.30 h
$^{125}\text{I}/^{123}\text{I}$ dpm at T_0	0.038	0.022

encouraging. New irradiation containers and vacuum lines have been constructed, and additional experiments are planned when LAMPF resumes operation in 1982.

E. The Chemical Isolation of Spallogenic Selenium from RbBr (F. J. Steinkruger)

Selenium-72's daughter, ^{72}As , has been suggested as a useful brain scanning agent; however, separation from parent ^{72}Se is considered difficult.¹ Wong et al. have suggested that ^{75}Se may be an appropriate radiolabel for the study of the biodistribution of proline.² In the separation of ^{68}Ge from a RbBr target, isotopes of selenium ($^{*}\text{Se}$) and arsenic ($^{*}\text{As}$) are codistilled with the germanium. After extraction of ^{68}Ge , arsenic and selenium remain in the aqueous phase.³ This solution, therefore, represents a possible source of desirable radioisotopes of selenium and arsenic.

The irradiated RbBr pellet is dissolved in 6 M HCl and distilled into a cooled receiver containing a few milliliters of H_2O_2 . The distillate is adjusted to 8.4 M HCl and the ^{68}Ge is extracted into CCl_4 . The remaining aqueous phase contains the arsenic and selenium radioisotopes.³ In small scale testing 1 ml of saturated $\text{NH}_4\text{OH}\cdot\text{HCl}$ is added

to 10 ml of this solution to reduce selenium to the metal. The reduction step reaches 95% completion in 120 hrs. The extent of the reduction reaction is determined by the loss of ^{75}Se from the solution to the glass surface. The remaining solution is decanted, and the container is rinsed 3 times with 1.2 M HCl. Ten ml of concentrated HNO_3 is then added to the container. After 80 hrs, 75% of the original ^{75}Se is found in the concentrated HNO_3 . No arsenic radioisotopes are found in the final solution. Because a relatively old $^*\text{As} - ^*\text{Se}$ solution was used for small scale testing, no ^{72}Se was present.

Work continues on optimizing conditions to maximize $^*\text{Se}$ recovery and on the design of a $^{72}\text{Se} \rightarrow ^{72}\text{As}$ generator.

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F. Irradiation and Separation Methods for ^{67}Cu

(J. W. Barnes, K. E. Thomas, G. E. Bentley, P. M. Grant, and D. A. Miller*)

Copper is an important element in biochemistry. As a radioisotopic tracer of copper in metabolic studies, ^{64}Cu ($t_{1/2} = 12.71$ h) is generally employed because it is easily produced from stable ^{63}Cu by the (n,γ) reaction, or in a state of high isotopic purity by the $^{64}\text{Zn}(n,p)^{64}\text{Cu}$ reaction. However, in many studies its usefulness is severely limited by its short half life. Copper-67 has a half life of 61.9 hr^1 and prominent gamma photons of 93 and 185 keV. In the past, ^{67}Cu has been produced from enriched ^{67}Zn by the (n,p) reaction. The low

reaction cross section of 0.82 mb^2 coupled with the cost of the enriched ^{67}Zn target material and loss of the target due to the competing (n,γ) reaction have resulted in a high price for the reactor-produced ^{67}Cu . Because of this, we have studied alternative methods of producing ^{67}Cu .

RbBr was the initial target selected for investigation for ^{67}Cu production and a chemical separation procedure for copper was successfully developed. However, the experience gained from high-level irradiations revealed that many krypton radionuclides were produced that either had to be trapped or allowed to decay before chemical processing. We decided to switch to a ZnO target. The chemical procedure consists of dissolving the target in concentrated HCl, adding stable palladium as carrier that is then precipitated as the sulfide. Following dissolution of the precipitate, the solution is passed through a cation column (AG50-X4) and then an anion column (AG1-X8). The copper fraction is removed with 4 M HCl. The overall chemical yield of copper is ~80% and no radioactive impurities are detected in the final product.

A 90-g target of ZnO was irradiated in the Isotope Production Facility for 63 hrs; chemical processing was completed two days after the end of bombardment resulting in the recovery of 0.7 Ci of ^{67}Cu . Two collaborative research studies, one at the University of New Mexico and the other at California State University at Fullerton, were initiated.

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G. Rare Radioisotopes for Research from Tantalum

(K. E. Thomas, M. A. Ott, T. DeBusk)

The Medical Radioisotope Program facilities at LAMPF and at the Nuclear Chemistry Building (TA-48) have been used to produce large quantities of neutron-deficient hafnium and lanthanide isotopes.

* California State University at Northridge.

Several of these isotopes are long-lived and are of great interest to the nuclear chemist and physicist.

For a period of approximately two months ending on November 18, 1980, a tantalum metal target was irradiated at the Isotope Production Facility (A-6) at LAMPF. The target was irradiated with ~750 MeV protons with an intensity of ~350 μ A. The irradiation area received $\sim 10^{22}$ protons (6×10^5 μ A-hrs) during this two-month period. (NOTE: The beam intensity was not known for each irradiated target. In a separate experiment involving five 1.9-cm-thick molybdenum targets in a row, the beam intensity decreased approximately 10 to 15% for each target the beam traversed. During the bombardment of the tantalum target, as many as five targets were upstream.) The tantalum target consisted of three slabs of the metal. Each slab weighed ~250 g for a total target weight of 770 g. The slabs measured 8 cm square and 0.32 cm thick.

Chemistry was started approximately two months after the irradiation. At that time the radiation level of the target was >500 R/hr at 1.5 m. An outline of the chemical separation procedure is shown in Fig. 71. Because the radiation level of the target exceeded the shielding capacity of the hot-cell, only one slab of tantalum was dissolved at a time. The dissolution and precipitation were performed on each slab individually. One liter of 4:1 concentrated HF:HNO₃ was used to dissolve each slab of tantalum, and 250 to 500 mg of calcium carrier (as the nitrate) were added for each precipitation. Following the final precipitation, all three precipitates were combined for the remainder of the chemistry. The precipitate was dissolved in saturated boric acid solution, and a minimum volume of concentrated HCl and then diluted to 500 mL with H₂O. The acid concentration of this final solution was 0.4 M. The solvent extraction step involved three 100-mL aliquots of 10% bis-2-ethylhexylorthophosphoric acid (HDEHP) in toluene. The lanthanides were back-extracted into two 50-mL aliquots of 10 M HCl leaving hafnium in the organic phase. The HCl containing the lanthanides was washed with 50 mL of toluene to remove residual HDEHP; this organic wash was added back to the hafnium-containing HDEHP/toluene.

Fig. 71.
Chemistry for tantalum targets.

The lanthanide solution was boiled down to ~5 mL of brown solution; 10 mL of fuming HNO₃ was added and then the solution was boiled until fuming stopped. Concentrated HCl was added and the solution was boiled to a volume of ~0.5 mL. This was diluted to ~20 mL with H₂O, and a slurry containing 1.5 mL of cation-exchange resin was added. The resin was washed with H₂O then slurried with H₂O and transferred to the top of a cation-exchange column. At this point in the procedure, the lanthanide fraction measured ~2000 R/hr at contact. The resin used was the ammonium form of Dowex 50 X 8, minus 200 mesh; the column dimensions were ~65 cm long with a diameter of 0.75 cm. Elution of the lanthanides was performed using 200 mL of pH 3.24 α -hydroxyisobutyric acid (0.52 M) followed by a gradient elution using 375 mL each of pH 3.33 and pH 4.44 α -HIB (0.52 M). The flow rate was 0.2 mL/min and samples were collected in 30-min

intervals. Individual element fractions were detected by their radiations. Overall chemical yield was estimated at >90% for hafnium (in the organic phase), ~90% for lutetium and ~60-70% for gadolinium and europium.

Listed in Table XXIV are the samples obtained from the described chemistry and the isotopes identified in each sample. The mass of each isotope is calculated from the measured radioactivity. Those isotopes with stars beside the half life are shielded. In addition to the fractions listed, it is possible to recover terbium for ^{157}Tb and ^{158}Tb , dysprosium for ^{154}Dy ; and holmium for ^{163}Ho . The dysprosium is contaminated with ^{88}Y , which is a reaction product of contamination in the target material.

Nuclides that are being used or are planned for use in research are the following: $^{178\text{m}2}\text{Hf}$ and ^{150}Eu for nuclear structure studies; ^{172}Hf and ^{168}Tm for targets for neutron cross-section measurements; isotopically pure targets of ^{163}Ho , ^{154}Dy , ^{146}Gd , ^{148}Gd , ^{150}Gd , and ^{146}Sm for nuclear reaction studies; and ^{158}Tb for determination of its half-life.

XIV. THEORETICAL CHEMISTRY

A. Collision-Induced Dissociation in $\text{Ar} + \text{H}_2$ Collisions as a Function of the Rotation State of H_2 (N. C. Blais and D. G. Truhlar, University of Minnesota)

Two classes of approximation schemes appear in the literature that describe the dissociation of diatomic molecules during collisions with atoms. In one, attention is centered on the vibrational quantum number v of the diatom, and the rotational quantum number J is assumed fixed, or more realistically, the results are assumed to represent an average over a canonical distribution of J to be summed over final J' . On the other hand, in the rotational model, attention is centered on J , and v is assumed fixed, or is averaged and summed. The first is the more popular model,¹ but it is argued² that the latter rotational level master equation allows for more reasonable and accurate solutions.

TABLE XXIV
AMOUNTS OF NUCLIDES AT $t_0 = 11/18/80$

Isotope	$t_{1/2}$	Curies	mg
^{172}Hf	1.87yr	6.7	6.0
^{175}Hf	70day	58	5.4
$^{179\text{m}2}\text{Hf}$	25day	8.5	0.3
$^{178\text{m}2}\text{Hf}$	31yr	(estimated)	0.4
^{173}Lu	1.37yr	10.	6.6
^{174}Lu	3.3yr	0.11	0.16
$^{174\text{m}}\text{Lu}$	142day*	0.19	0.04
$^{177\text{m}}\text{-}^{177}\text{Lu}$	161d(6.7day)	0.047	0.01
^{169}Yb	32day	28.	1.2
^{170}Tm	129day*	0.04	0.01
^{168}Tm	93day	0.38	0.05
^{167}Tm	9.3day	15.0	0.17
^{146}Gd	48day	2.4	0.13
^{148}Gd	75yr	0.009	0.28
^{150}Gd	$2 \times 10^6 \text{yr}$		
^{151}Gd	120day	1.5	0.21
^{153}Gd	242day	0.9	0.25
^{147}Eu	24day	1.81	0.049
^{148}Eu	55day	0.084	5.1×10^{-3}
^{149}Eu	93day	2.25	0.24
^{150}Eu	36yr	2.1×10^{-4}	3.1×10^{-3}
^{145}Sm	340day	0.33	0.12
^{146}Sm	$7 \times 10^7 \text{yr}$		
^{143}Pm	265day	0.10	0.03
^{144}Pm	363day*	2.4×10^{-3}	9.5×10^{-4}
^{139}Ce	138day	0.032	4.7×10^{-3}

One interesting and controversial aspect of diatomic dissociation is the temperature dependence of the observed rate constants attributed to temperature-dependent activation energies. These activation energies are less than the dissociation energies and decrease with increasing temperature.

Using the rotational framework, a simple collision model has been proposed³ that accounts for the general temperature characteristics of dissociation. As summarized by Pritchard,³ in the following excerpt, where D_0 is the ground-state dissociation energy, J is the rotational quantum number, and $U_{\max}(J)$ is the height of the centrifugal barrier: "The physical reason for this behavior is fairly simple: [i] we have insisted [in the model] that a molecule in state J must have an energy $D_0 + U_{\max}(J)$ before it can dissociate,... and [ii] we have also insisted [on] a Boltzmann distribution of rotational states; thus as we raise the temperature, more energy to dissociate - which means that the rate of dissociation does not increase with T as rapidly as it would if the critical energy had remained constant at D_0 ." Pritchard³ recognized that this collisional model is only part of the complete description because the nonequilibrium effects¹ are important.

We describe here our tests of assumption [i], namely that the energy of activation for state-selected dissociation is equal to the energy required to surmount the centrifugal barrier. We calculated rate constants by the quasi-classical trajectory (QCT) method. The potential energy surface and techniques used for the calculations are explained elsewhere.⁴ For the calculations in Ref. 4, the temperature of all thermal distributions was taken as 4500 K, and all thermal averaging was performed by the Monte Carlo method with unbiased sampling.

Figure 72 shows the results of our classically exact calculations of the activation energy for $\text{Ar} + \text{H}_2$. We compare these energies to those of the rotation barrier model:

$$\langle E_b(v,J) \rangle_v = \langle -E_{\text{int}}(v,J) \rangle_v + U_{\max}(J) .$$

We find that almost as good a fit to our data is gained from the simple model, which relates the

Fig. 72.

Energy of activation for collisions leading to completely dissociative states (crosses) or to both completely dissociative states and dissociative-like quasibound states (circles) as compared to the average dissociation energy $\langle -E_{\text{int}}(v,J) \rangle_v$, lower curve, or to the average centrifugal barrier height to dissociation $\langle E_b(v,J) \rangle_v$, upper curve, as functions of initial H_2 rotational quantum number J for $\text{Ar} + \text{H}_2$ collisions with a translation-vibrational temperature of 4500 K.

activation energy to the average dissociation energy, $\langle -E_{\text{int}}(v,J) \rangle_v$.

We have shown that the assumption that the energy of activation for a given J level is equal to the average centrifugal barrier height for dissociation is a poor one. We attribute this to the fact that the centrifugal barrier is a two-body concept involving the internal angular momentum of the H_2 pair and that it has no meaning during the critical portion of the three-body trajectories under consideration. In connection with this argument, we find that the internal angular momentum of the H_2 pair is not even approximately conserved during dissociative collisions.

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B. Quasiclassical Trajectory Calculation of the State-Specified Differential Cross Sections and Opacity Functions for F + H₂ → HF(v') + H (N. C. Blais and D. G. Truhlar, University of Minnesota)

The only chemical reaction for which there is experimental observation or possible observation of quantum mechanical resonance effects is F + H₂ → HF + H.¹ The experimental evidence for the resonance is the shift of the differential cross section, $d\sigma/d\Omega$ for the $v' = 2$ product vibrational level from backwards peaked to having a substantial sideways peak as the relative translational energy is increased from 0.09 to 0.14 eV. The same quantity, $d\sigma/d\Omega$ for $v' = 1$ and 3 remains backward peaked under the same conditions.

The resonance is also shown in the results of quantal calculations of the opacity function, the probability for reaction as a function of impact parameter or initial orbital angular momentum.

The function is calculated for all reactions leading to each final v' state, and the function shows, for $v' = 2$ only, a pronounced peak. It can also be observed directly by examining $d\sigma/d\Omega$ calculated quantum mechanically. Such calculations have been made but the approximations involved are serious.

The important question to be resolved in interpreting the above results is whether the shift in $d\sigma/d\Omega$ for $v' = 2$ is a resonance effect. Because a resonance effect is a quantum mechanical interference effect, we would not expect to see the resonance in a quasiclassical trajectory (QCT) calculation. In the present paper we report QCT calculations designed to answer the question: is the sideways shift of $d\sigma/d\Omega$ for $v' = 2$ also present in classical calculations or is it a quantal effect? We also ask a similar question for the peak in the $v' = 2$ opacity function obtained in quantal calculations. Our calculations are based on the same potential energy surface used in the quantal calculations. The initial conditions for the present study are $E_{\text{rel}} = 0.233$ eV and the ground vibrational-rotational state. Final vibration levels are assigned by the histogram method using good action variables,² and differential cross sections are computed by the Legendre moment method.³

Figure 73 shows the calculated values of $d\sigma/d\Omega$ for each v' . For this figure we use six Legendre moments ($n = 0-5$). The results are qualitatively similar if we use more moments or use the more popular method of sorting into angular bins, but those procedures show more statistical noise. The main conclusion from the figure is that, even at $E_{\text{rel}} = 0.233$ eV, $d\sigma/d\Omega$ is still backward peaked for all three v' .

Figure 74 shows the opacity functions and compares them to those calculated quantum mechanically. The QCT opacity function for $v' = 1$ does show a maximum for nonzero l , but within the statistical error bars, those for $v' = 2$ and 3 are monotonically decreasing functions of l . The biggest disagreement in shape, as compared to the quantum calculations, occurs for $v' = 2$. Another way to compare the opacity functions is in terms of the mean value of l for reactive collisions leading to each final vibrational state.

Fig. 73.

The differential scattering cross section, $d\sigma/d\Omega$ for final product states v' . Dash-dot line is $v' = 1$, solid line is $v' = 2$, and dotted line is $v' = 3$. All have been normalized to $v' = 2$ by multiplying $v' = 1$ by 3.88 and $v' = 3$ by 1.53. Six Legendre moments were used to calculate $d\sigma/d\Omega$.

Our conclusion is that the trajectory calculations show neither the sideways shift of $d\sigma/d\Omega$ nor a big shift to larger ℓ in the opacity function for the $v' = 2$ vibrational level of HF resulting from the $F + H_2$ reaction. Thus, both these effects seem to be quantal effects. This supports, or at least does not contradict, the resonance interpretation of these features.

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Fig. 74.

The opacity function for each final product vibrational state, i.e., the probability that a product is formed in state v' at the indicated initial orbital angular momentum. The histograms are the trajectory results and the curves are quantum calculations.

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C. State-to-State Cross Sections for Vibrational-Rotational-Translational Energy Transfer in Ar-H₂ Collisions (N. C. Blais and D. G. Truhlar, University of Minnesota)

Quasiclassical trajectory calculations have been widely employed to study energy transfer and reactive collisions. However, there have been very few studies by this technique of state-to-state cross sections or rate constants involving very highly excited states, e.g., states with internal energies of at least a third of the dissociation energy. Yet this is a regime where classical mechanics should provide useful information and where more accurate quantum mechanical calculations are prohibitively difficult. In this article we present state-to-state cross sections for rotational and vibrational energy transfer from five initial states of H₂ in collisions with Ar atoms; the internal excitation energies ($E_{vj}-E_{00}$) of four of these initial states are in the range 2.022-2.667 eV as compared to a dissociation energy (D_0) of 4.477 eV, and the internal excitation energy of the other state is 0.299 eV. For the four highly excited states, the collisions are energetic enough to transfer five or more quanta of vibrational energy and ten or more quanta of rotational energy.

The potential-energy surface used for the present calculations is the one we created by combining the Kolos-Wolniewicz H₂ potential, the Wagner-Das-Wahl ArH potential, the nonpairwise dispersion term of Bell and Kingston, the LeRoy-van Kranendonk Ar-H₂ van der Waals potential, and extensively modified statistical calculations of the short-range Ar-H₂ potential. This is called the full potential in Ref. 1, which contains additional details and references.

The computational procedures for the trajectories are also the same as described in Ref. 1. The initial translational energy was fixed to yield a total energy of $E_{\text{tot}} = 1.0$ eV, where E_{tot} is measured with respect to three free atoms. The data are sufficiently precise to provide quantitative transition cross sections for energy transfer from the initial v states to all of the observed final $v'J'$ states. For the purposes of this article, the data are best represented by contour diagrams of the cross sections, plotted over all of

the product states, Figs. 75 to 78. There is a little noise in these figures due to the statistical error of the Monte Carlo sampling process, but all the global structure is statistically significant. The first characteristic of the figures is the large number of final states that have nonzero classical-mechanical cross sections for transitions from the highly excited initial states. Moreover, the figures show that the cross section for large, multiple quantum transitions is not negligible by comparison to single quantum jumps. This is consistent to results we found earlier for hydrogen atom collisions with H₂. There are 30 final states that have nonzero cross sections for (0,6), 57 for (0,18), 86 for (2,18), 122 for (4,6), and 142 for (6,0). It is of course possible that even more nonzero cross sections would be found if we computed even larger samples of trajectories. The smallest-value contour in the plots is 0.003 Å², and the area enclosed by this contour is a reasonably well converged measure of the size of the final-state space populated by classical mechanics.

Figure 74 for the low energy state shows a predominantly vertical pattern, dominated by pure rotational-translational energy transfer, but Figs. 76 to 79 for the highly excited states all show prominent diagonal structure associated with mixed vibrational-rotational-translational energy transfer. The contours for the two $J = 18$ states are almost completely diagonal, which is consistent with the large $\sigma_{\text{VRT}}/\sigma_{\text{inel}}$ fractions for these states. The contours for the (4,6) and (6,0) states show a combination of vertical and diagonal characteristics, which is consistent with large values of both σ_{RT} and σ_{VRT} for these cases.

Our trajectory calculations show that, even at a high fixed total energy, not only the quantitative cross sections but also the pattern of energy transfer, e.g., predominantly rotational-translational or predominantly vibrational-rotational-translational, depends on the way that the energy is initially distributed in the various degrees of freedom. Cross sections for transitions from highly excited initial states show extensive compensation of vibrational and rotational energy transfer. The state-to-state cross sections are not easily fit by exponentials and power law.

Fig. 75.

Fig. 76.

Fig. 77.

Fig. 78.

Fig. 79.

Figs. 75-79.

Contour plots of energy transfer cross sections for transitions from the indicated initial state of H_2 , $v=0, J=6$, to the final state $v'J'$ indicated by the ordinate and the abscissa. The contour values are indicated in the legend with the largest value closest to the $v'J'$ state equal to vJ and diminishing monotonically to other, more distant, states.

Fig. 76. Same as Fig. 75 but with $v=0, J=18$.

Fig. 77. Same as Fig. 75 but with $v=2, J=18$.

Fig. 78. Same as Fig. 75 but with $v=4, J=6$.

Fig. 79. Same as Fig. 75 but with $v=6, J=0$.

indicating that there is a large amount of information contained in the full set of cross sections.

D. Dynamic Calculation of the Temperature Dependence of the Activation Energy for a Chemical Prediction from 444 to 2400 K (N. C. Blais and D. G. Truhlar, University of Minnesota)

It is unusual for the temperature dependence of a chemical reaction rate to be measured over a temperature range of 2000 K or more. Yet for many applications, such as combustion, it is necessary to estimate reaction rates at very high temperatures, even though measurements may exist only at temperatures much closer to room temperature. The most common method has been to assume a linear Arrhenius plot ($\ln k(T)$ vs $1/T$), i.e., a temperature-independent activation energy. Recent experimental results, however, have shown many deviations from linear Arrhenius behavior.¹ This is a situation where theoretical guidance can be very helpful. Transition state theory (TST) often indicates a significant temperature dependence in the activation energy, but transition state theory may suffer from errors due to trajectories that recross the transition-state dividing surface.

In this report, we present a direct calculation of the temperature dependence of the activation energy of the exchange reaction $H + H_2 \rightarrow H_2 + H$ from three-dimensional trajectory calculation employing an accurate potential energy surface. The results are compared to a transition state theory² prediction and to available experimental results.

The activation energy $E_a(T)$ is defined as the slope of the Arrhenius plot at temperature T . For an equilibrium distribution of reactant states, it is given by the Tolman relation³

$$E_a(T) = \langle\langle E_{rel} \rangle\rangle + \langle\langle E_{int} \rangle\rangle \quad (1)$$

where $\langle\langle \dots \rangle\rangle$ denotes the average value for reactive events minus the average value for all pairs of reagents in the vessel, E_{rel} is relative translational energy, and E_{int} is internal energy. For the trajectory calculations, $\langle\langle E_{rel} \rangle\rangle$ and $\langle\langle E_{int} \rangle\rangle$ were calculated by standard techniques as explained elsewhere; in particular, initial

relative translational energies were selected by importance sampling and other degrees of freedom were initialized by unweighted Monte Carlo sampling. The potential energy surface used for the trajectory calculations was an analytic functional representation of the accurate *ab initio* calculations of Liu and Siegbahn.⁴

The theoretical results are compared to each other and to the available experimental results^{5,6} in Table XXV. All three calculations predict a large increase (5 to 7 kcal/mol) in $E_a(T)$ when the temperature is raised from 444 K to 2400 K. Thus, the large increase in the activation energy predicted by TST is confirmed by full dynamical calculations. The experimental values do not extend up to 2400 K, but they do show evidence that $E_a(T)$ increases with T at temperatures up to about 500 K.⁵

It is instructive to rewrite (1) as

$$E_a(T) = \langle E_{tot} \rangle_{\text{reactions}} - \langle E_{int} \rangle_{\text{reagents}} - \langle E_{rel} \rangle_{\text{reagents}} \quad (2)$$

where E_{tot} is the total energy and the single brackets denote averages over all reactions or over all pairs of reagents in the vessel. For the present article, we place the zero of energy at ground-state stationary reagents. The reason that

TABLE XXV
ENERGIES OF ACTIVATION (*kcal/mol)
FOR $H + H_2 \rightarrow H_2 + H$

T(K)	Trajectories	TST	TST/Q	Experiment
200	---	9.12	5.36	---
300	---	9.07	6.78	4.3, ^b 4.8 ^c
444	7.9 ± 0.2 ^a	9.12	7.63	8.1, ^b 7.5 ^c
875	8.7 ± 0.2	9.99	9.24	(8.3) ^c
1500	---	11.96	11.52	---
2400	13.9 ± 2.3	14.81	14.54	---

^aError estimate is one standard deviation statistical error due to sampling of initial trajectory conditions.

^bRef. 5.

^cRef. 6; value in parentheses is extrapolated.

^dTransition state theory with tunneling corrected

$\langle E_{\text{tot}} \rangle$ reactions increases more rapidly with temperature than does $\langle E_{\text{tot}} \rangle$ collisions is complex, but as Table XXVI shows, both the collision energies and the internal states of H_2 are responsible. The increase of the collision energy component of E_a contributes about half of the increase in E_a . As is well known, this is because of the detailed nature of the excitation function for reaction with collision energy, i.e., how the probability of reaction increases with increasing collision energy. But Table XXVI shows that $\langle E_{\text{int}} \rangle$ also contributes significantly to the increase in E_a , but with a very different temperature dependence. In fact, at the lower temperatures, it appears that the lower internal states that are populated inhibit the reaction slightly, since $\langle E_{\text{int}} \rangle$ is negative. The increase in E_a occurs primarily at much higher temperatures. Of course, both of these averages, $\langle E_{\text{rel}} \rangle$ and $\langle E_{\text{int}} \rangle$ are interrelated. Nonetheless, when analyzed by other means, such as looking at E_a for given internal states, the same conclusion is reached: The temperature dependence for both E_{int} and E_{rel} contribute significantly.

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TABLE XXVI
COMPONENTS OF THE ACTIVATION ENERGY (kcal/mol)
AS COMPUTED BY TRAJECTORY CALCULATIONS

T(K)	E_{rel}	E_{int}	E_a
444	8.1	-0.2	7.9
875	8.9	-0.2	8.7
1400	11.5	2.4	13.9

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E. Reactions of van der Waals Molecules: The Rare Gases (D. L. Thompson and L. M. Raff)

Traditionally, there has been a great deal of interest in the properties of van der Waals bonding primarily because of its importance in determining the bulk properties of solids, liquids, and gases. Currently, however, considerable effort is being devoted to obtaining an understanding of the kinetics of reactions involving the breaking and formation of these weak, nonchemical bonds. It has become apparent that van der Waals molecules play important roles in a wide variety of dynamical processes, such as energy transfer, reaction, and condensation. For example, the formation of long-lived complexes due to van der Waals forces appears to be the explanation for the observed enhancement of the rate of the self-relaxation of vibrationally excited hydrogen halides at low temperatures.¹ Also, there are many cases where van der Waals dimers are important in thermolecular reaction mechanisms, a striking example being the six-center reactions of halogens studied in crossed molecular beams first by King, Dixon, and Herschbach.² Herschbach and coworkers^{2,3} showed that the same sort of information can be obtained for the reactive and inelastic scattering in the weakly bound systems as has been obtained in ordinary chemical systems. They studied the reactive and nonreactive scattering of $\text{X} + (\text{Cl}_2)_2$, where $\text{X} = \text{Xe}, \text{Br}_2$, and HI . (Where reactive and nonreactive are used with

reference to van der Waals bonding. Herschbach and coworkers also studied reactions involving the breaking and formation of both chemical and van der Waals bonding.) The van der Waals chemistry observed in the molecular beam experiments of $\text{Br}_2 + (\text{Cl}_2)_2$, for example, includes energy transfer to give internally excited $(\text{Cl}_2)_2^*$, collision induced dissociation with the diatomic products $\text{Br}_2 + 2\text{Cl}_2$, and exchange of van der Waals bonds to yield $\text{Br}_2\text{Cl}_2 + \text{Cl}_2$.

Condensation depends on van der Waals bonding and gross features of the kinetics are usually considered in theoretical treatments, but the details are often not explicitly considered. This is primarily due to the lack of information rather than to lack of its importance. Accurate nucleation (clustering) theory must account for the kinetic behavior if it is to correctly describe condensation, especially in the initial stages. The collision of a rare gas atom with a rare gas dimer is the simplest monomer-cluster collision. Monomer-cluster collisions probably provide the dominant pathway in the initial stage of homogeneous formation of a liquid from a vapor. It is important that these simple collisions involving weak van der Waals forces be understood as a basis for the development of a better knowledge of the much more complex dynamics of collisions involving larger clusters. We have carried out extensive dynamics and statistical studies of rare gas atom-dimer ($\text{Rg} + \text{Rg}_2$) reactions. Atom-exchange and dissociation have been studied in $\text{Ar} + \text{Ar}_2$, $\text{Ar} + \text{ArKr}$, $\text{Kr} + \text{NeAr}$, $\text{Kr} + \text{Ar}_2$, and $\text{Xe} + \text{Ar}_2$; and collisional dissociation has been studied for the pure $\text{Rg} + \text{Rg}_2$ systems, where $\text{Rg} = \text{Ne}, \text{Ar}, \text{Kr}, \text{and Xe}$.

Rare gas dimers are weakly bound with dissociation energies generally over two orders of magnitude smaller than normal chemical bonds. Consequently, rotationally metastable dimers make non-negligible contributions to the total concentration of dimers, which in both equilibrium and non-equilibrium (such as beams) systems can be relatively large. Because of the shallowness of the dimer potential well, the effect of the rotational barrier is not negligible as it is for most chemically bound systems. Thus, the reaction products are divided into three categories as illustrated in Fig. 80. The product dimer is counted as stable

Fig. 80.

Illustration of the effective potential for a relatively small value of angular momentum. The various regions are labelled S ("stable"), M (metastable), and D (dissociation) to indicate how products were defined.

(S) if the total internal energy is less than that of two separated atoms, metastable (M) if the energy is greater than zero but less than the rotational barrier height (E_b), and dissociated (D) otherwise. Figure 80 shows the cross sections for atom exchange in $\text{Ar} + \text{Ar}_2$ collisions as a function of the relative translational energy. The values of the cross section for the formation of Ar_2 exchange products with total internal energy less than the potential energy of two separated atoms are shown as solid squares. The cross section for the formation of rotationally metastable Ar_2^* from $\text{Ar} + \text{Ar}_2$ is shown by the triangles. The classical threshold for Ar_2^* formation is approximately $E_{\text{rel}} = 0.25$ kcal/mole, which is about equal to the Ar_2 well depth (0.28 kcal/mole) as would be expected (reactant zero-point energy is 0.0436 kcal/mole). The cross section as a function of E_{rel} rapidly rises to a peak at about 0.4 kcal/mole and then very gradually diminishes as E_{rel} increases.

At the peak, the cross section for metastable Ar_2^* is about 50% that for "stable" Ar_2 (where "stable" refers to products with energy below the dissociation limit for nonrotating Ar_2). As the relative translational energy increases, the cross sections for the two categories of products approach one another and become approximately equal at energies greater than 0.65 kcal/mole.

The results in Fig. 81 illustrate the importance of rotationally metastable products for experimental conditions that normally would involve energies higher than 0.65 kcal/mole. Stogryn and Hirschfelder⁴ computed lifetimes of metastably bound Ar_2 for the Lennard-Jones (6-12) potential. They conclude that at atmospheric pressure and ordinary temperatures most metastable Ar_2^* do not decay before undergoing a collision. For homogeneous nucleation in a supersaturated vapor this would mean that metastable dimers would be important. However, the lifetimes of some states are sufficiently short that under conditions such as might exist in beam experiments (which can require lifetimes $>10^{-5}$ s for detection) tunneling could be a factor. And, as our trajectory results show, the metastable products are formed as readily as the stable ones at the higher energies.

Fig. 81.

Cross sections as a function of relative translational energy for $\text{Ar} + \text{Ar}_2$ atom exchange. The points at a given energy were computed from 1000 trajectories. (The curves are not fits to the points; they are drawn to illustrate the general behavior of the points.)

For states with energy near E_b , the lifetimes are effectively infinite. If it is assumed that the Ar_2^* lifetime must exceed 10^{-5} s to allow detection as a bound product in a crossed-beam experiment, WKB tunnelling calculations predict that 49% of the Ar_2^* formed by exchange will satisfy this requirement. Consequently, the importance of such metastable states in beam measurements is clear. In nucleation experiments, where the pressures are much higher than in beam experiments, metastable species may play an even greater role.

Some of the details of the mechanisms for reactions involving the exchange of van der Waals bonds have been investigated for $\text{Ar} + \text{ArKr}$ and $\text{Kr} + \text{NeAr}$. Atom-exchange and dissociation cross sections were computed for $\text{Kr} + \text{NeAr}$ as a function of initial relative translational energy, and angular scattering and product energy distributions were computed. The results indicate that mechanistic, as well as statistical, factors are of major importance in the determination of the exchange reaction dynamics. Light-atom abstraction is found to occur by a stripping mechanism, whereas abstraction of the heavier atom involves complex formation and rebound scattering. The mechanism for light-atom abstraction in some systems is found to be energy-dependent with the low-energy stripping mechanism becoming more like that for heavy-atom abstraction as the collision energy increases. When this occurs, the mechanisms become nearly identical, and the computed branching ratio therefore comes into accord with statistical predictions.

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F. Energy Transfer in Collisions of Highly Excited Diatomic Molecules (Donald L. Thompson)

Recent experimental studies of rotational lasing have provided evidence that energy transfer is at least partly responsible for the rotational-state population inversions. The initial step in the mechanism that leads to lasing is the production of an inverted vibrational-state population, possibly with some nascent rotational inversion, in the product molecule of a chemical reaction. An inverted rotational population is then produced by rapid vibration-rotation (V-R) energy transfer. As the system cascades down the vibrational ladder, it climbs the rotational ladder; thus giving an inverted J-state distribution in the lower states.

We have carried out a series of quasiclassical trajectory studies of the energy transfer in $\text{He} + \text{H}_2$, $\text{Ar} + \text{HCl}$, $\text{Ar} + \text{HF}$, and $\text{Ar} + \text{OH}$. The energy transfer in systems with both high vibrational and rotational energies had received little attention, from both theorists and experimentalists before this work. State-to-state cross sections have been computed as a function of the initial vibrational and rotational states, and the initial relative translational energy. The same qualitative behavior occurs in all the systems studied. The important features of the mechanism for relaxation of highly excited diatomic molecules colliding with rare gas atoms are illustrated (Fig. 82) by the state-to-state cross sections in a.u.^2 for the processes $\text{Ar} + \text{HCl}$ ($v_i = 2$, $J_i = 30 \rightarrow v_f J_f$) at 0.5 eV collision energy. There are upward shifts in the rotational state for the downward vibrational transitions and downward shifts for upward vibrational state changes. Similar results were obtained for the other systems studied.

Fig. 82.

State-to-state cross sections for $v_i = 2$, $J_i = 30 \rightarrow v_f, J_f$ as a function of v_f and J_f at 0.5 eV initial relative translational energy in $\text{Ar} + \text{HCl}$ collisions.

The locations of the peaks in the distributions of final rotational states in the final vibrational states display a near linear dependence on the final vibrational quantum number, as illustrated for the case of $\text{Ar} + \text{HF}$ in Fig. 83. In Fig. 83, the rotational quantum number for the peaks J_f^{max} in the final rotational state distributions are plotted against the final vibrational state v_f for $J_i = 30$ and $v_i = 0, 2, 4$ and 6. The behavior of J_f^{max} is essentially independent of both v_i and J_i .

The major conclusion of these studies is that relaxation from high v, J states may lead to inverted rotational populations in the lower vibrational states. Thus this work adds support to the energy transfer pumping mechanisms in pure rotational lasers.

Fig. 83.

Plots of the final rotational quantum number associated with the largest state-to-state ($V_i, J_i \rightarrow v_f, J_f$) cross section in the various v_f for $J_i = 30$, $v_i = 0, 2, 4$, and 6 at 0.5eV initial relative translational energy in $\text{Ar} + \text{HF}$ collisions.

G. Theoretical Studies of Surface Diffusion (J. D. Doll and H. K. McDowell, Visiting Staff Member)

Surface diffusion is an important elementary process in surface chemistry. In spite of this importance and in spite of a decade of detailed experimental studies, surface diffusion is poorly understood theoretically. For example, at present, we do not clearly understand the effects of surface geometry and composition on the diffusion process.

Recently, we have undertaken theoretical studies of surface diffusion to explore the ability of modern dynamical methods to describe such processes. Self diffusion on metals was chosen for initial

work because extensive surface diffusion constant data from field ion microscope studies already exist. Although we realized the overly simplistic nature of such an approach, we began our studies by assuming that the microscopic interactions could be approximated by simple pair potentials chosen to fit bulk thermodynamic properties (e.g., heat capacity, sublimation enthalpies, thermal expansion coefficient, etc.). These potentials were used without modification in (classical) molecular dynamics studies of surface diffusion.

The results of these surface diffusion studies are encouraging. We find that such pair potentials extracted from bulk thermodynamic data yield quantitative estimates of the surface diffusion constant and its temperature dependence for various systems. For example, we find this to be true in small activation energy systems (fcc(111)), in large activation energy systems (bcc(110)), and preliminary calculations indicate that it is true for channeled crystalline faces (bcc(211)). That such simple pair potentials derived from bulk data can accurately model such microscopic detail in surface diffusion is surprising.

XV. UNCLASSIFIED WEAPONS RESEARCH

A. Structures of Organic Explosives: Refinement of the Structures of Ammonium and Potassium

Picrates (R. R. Ryan, A. C. Larson, H. H. Cady (WX-2), and R. N. Rogers (WX-2))

It has been observed that the isostructural explosives ammonium picrate (AP) and potassium picrate (KP) are markedly different in their sensitivity to detonation by impact. The reason for this difference in behavior is not understood and we have carried out an extremely accurate determination of the structures in order to ascertain whether chemically significant differences can be detected between these two compounds.

Both compounds crystallize in the space group $Ibca$ with the following cell parameters, AP: $a = 13.480(3)$, $b = 19.793(6)$, $c = 7.130(1)$ Å and KP: $a = 13.331(2)$, $b = 19.120(4)$ and $c = 7.135(2)$ Å. Intensity data were collected for a hemisphere of data to $2\theta \leq 70^\circ$ giving four independent measurements

for each reflection. Refinements were carried out using isotropic thermal parameters for all non-hydrogen atoms (isotropic thermal parameters were used for hydrogen) and neutral atom scattering factors. The scattering factors were modified by multipole terms to the octopole level, a procedure that allows determination of the charge on each nonhydrogen atom and its deviations from a spherical charge distribution.

Interatomic distance and atomic charges are listed in Table XXVI and correspond to the labeling scheme shown in Fig. 84.

Inspection of the interatomic distances reveal small but perhaps chemically significant differences between the two structures especially in C-O and N-O distances. That is, in AP the ammonium ion is hydrogen bonded to O1, which is not involved in the potassium coordination sphere in KP; the C1-O1 distance is ca. 0.01 Å longer in AP. Similarly, O2 and O4 are involved in the K^+ coordination sphere, but not hydrogen bonded by NH_4^+ . These two N-O distances are ca. 0.01 Å longer in the potassium salt. Oxygen atom O3 is not involved in the cation coordination sphere for either salt and the corresponding N-O3 distances are identical in both compounds. Clearly, there exist significant differences between the materials and it is at least interesting that the more sensitive material (KP) contains slightly elongated N-O bonds. Whether or not these

Fig. 84.

ORTEP projection of the picrate ion in ammonium and potassium picrate. The unlabeled atoms are related to the labeled atoms by a two-fold axis through O1, C1, C4 and N1.

differences signal incipient reaction pathways for reactions which lead to detonation must await similar studies on many compounds of varying sensitivity and studies to see if these differences are magnified at elevated temperatures and pressure.

The atomic charges that are a side product of our studies are chemically reasonable and may prove to be of value in joint studies with WX-2 and with Jim Holder of the Naval Surface Weapons Center on the prediction of crystal density through molecular packing analysis. It has been found that coulombic terms are essential in these studies in defining the pair-wise potential functions that give the correct minimum energy structures. These quantities can be determined more accurately by careful x-ray (and neutron) diffraction methods than they can be estimated from theoretical calculations.

B. Raman Studies of High Explosives (B. I. Swanson)

As part of a laboratory-wide program to clarify the fundamental physics and chemistry of energetic materials,¹ a Raman study of organic high explosives (HE's) has been initiated. The bulk of

TABLE XXVI
DISTANCES AND ATOMIC CHARGES IN THE PICRATE ION

	K^+	NH_4^+	Charge
N1-O4	1.230(3) Å	1.219(3) Å	N1 +0.190
N1-C4	1.438(4)	1.440(3)	O4 -0.112
C4-C3	1.393(2)	1.387(2)	C4 -0.133
C3-H	0.992(15)	0.932(15)	C3 -0.055
C3-C2	1.373(3)	1.377(2)	C2 -0.157
C2-N2	1.459(3)	1.462(2)	N2 +0.105
N2-O3	1.232(3)	1.230(3)	O3 -0.143
N2-O2	1.233(3)	1.223(3)	O2 -0.098
C2-C1	1.458(2)	1.452(2)	C1 +0.024
C1-O1	1.244(3)	1.255(3)	O1 -0.156

FY 1981 has been devoted to setting up a new computer-controlled laser Raman facility with sufficient sensitivity to allow the study of microcrystals at extreme pressures (1 bar to 100 kbar). The overall objectives are to help develop a microscopic level understanding of the detonation process and clarify what determines the shock sensitivity of HE's. The approach here is to to characterize the molecular vibrations of sensitive and insensitive HE's and to map the response of both phonon and molecular vibrations to the extreme pressure and temperature condition relevant for shock initiation. Raman spectra of a small (ca. 80 μm on edge) crystal of pentaerythritol tetranitrate (PETN) have been obtained to 50 kbar using the new instrument; representative spectra are shown in Fig. 85. The spectra exhibit excellent signal-to-noise demonstrating that accurate estimates of frequencies, lineshapes, and relative intensities as a function of pressure are quite

feasible. One notable observation is that both the symmetric and asymmetric C-H stretching modes undergo significant frequency increases (57 and 71 cm^{-1} , respectively) in going from 1 bar to 50 kbar. Earlier time resolved measurements^{2,3} of PETN subjected to a 60 kbar shock showed no change in the frequency of these same modes. Our results show conclusively that both groups carrying out time-resolved measurements were, in fact, observing PETN at low pressures and not within the shock wave.

The spectra also show evidence for substantial relative intensity changes and variable frequency shifts with increasing pressure. The strong mode dependence of the frequency shifts do not correlate with absolute frequency showing that conventional analysis using mode Grüneisen parameters is inadequate. It is likely that pressure induced coupling are responsible for the intensity and frequency changes. Indeed, it is possible that the intensity change observed for C-H stretching modes in the

Fig. 85.
Raman spectrum of PETN.

time resolved studies arises from shock-induced structural changes in the PETN crystal.

Finally, significant lineshape changes have also been observed as a function of pressure as is consistent with dynamic coupling between optic and phonon modes. Further work, including pressure dependent studies of isotopically labeled systems, is underway to further clarify these unusual frequency, intensity, and lineshape changes.

The Study of Insensitive HE's

Picrate salts exhibit vastly different shock initiation properties;⁴ ammonium picrate is quite insensitive whereas metal picrates are shock sensitive. The most striking comparison is that of ammonia and potassium picrate, which are isostructural. In an effort to clarify what structural differences, if any, occur for these materials, Raman spectra have been obtained for both salts at 10 and 300 K. The largest difference in the Raman spectra of ammonia and potassium picrate is in the phonon region where the relative intensities of the modes are quite different. Of the internal modes, the N-O stretches are most perturbed as is consistent with strong $K^+ \cdots O_2N$ intermolecular bonding and the concomitant mixing of K^+ translation with $-NO_2$ stretching. Surprisingly, the various NH_4^+ deformation and particularly the torsional modes were not clearly discernible in the spectra of ammonium picrate. Further Raman and inelastic neutron scattering studies of isotopically labeled and mixed $K-NH_4^+$ salts are underway to further clarify the mode coupling in the picrates.

The Raman spectra of several isotopic species of triamino trinitro benzene TATB ($-^{15}NO_2$, $-^{15}NH_2$, perdeutero, and several partially deuterated samples) have been studied. Comparison of the normal, deuterated, and $-^{15}NO_2$ isotopic species shows evidence for substantial mode coupling between $-NH_2$, C-N, and $-NO_2$ motions. Mixing of this type is consistent with the strong $NH \cdots ON$ hydrogen bonding known to be present in TATB and is indicative of strong coupling of the $-NH_2$ and $-NO_2$ internal modes to the phonon bath. Spectra observed for several partially deuterated samples show striking changes indicative of H,D scrambling and long range interactions.

TATB is known to undergo UV-visible photolysis in the solid state to produce a green material with stable free radicals. The production of free radicals has been postulated⁵ as an important primary step in shock detonation and the identification of the photolysis products in HE's such as TATB is of great interest. Unfortunately, it has been extremely difficult to obtain any structural information on the photolysis reaction in TATB. In a recent experiment employing our new laser Raman facility, we have been able to rule out simple species such as NO_2 and N_2O . Note that several attempts were made to perform the photolysis experiment using the old Cary 82 Raman system; in each case no new features were observed. This current result demonstrates the utility of the more sensitive new Raman facility. Considerably more IR and Raman work is necessary to characterize the molecular and phonon modes and the photolysis reactions in TATB.

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C. Measurement of 14-MeV Neutron Cross Sections
⁸⁸Zr and ⁸⁸Y (R. J. Prestwood and K. W. Thomas,
D. R. Nethaway* and N. L. Smith*)

As part of our continuing program in CNC-11 of measuring fast neutron (~14 MeV) cross sections on radionuclides, we have measured the (n,2n) and (n,np) cross sections for 14.8-MeV neutrons on ⁸⁸Zr and the (n,2n) cross section for 14.2 MeV neutrons on ⁸⁸Y. The primary purpose of measurements such as these is to provide a rigorous test of complex nuclear model cross section calculations. A relative wealth of experimental data exists for stable targets but is almost completely lacking for unstable targets. The calculation codes receive a more meaningful test when their results can be compared with measurements for a number of target isotopes for a given element. These model calculations play a major role in our current weapons test diagnostics, and these experimental measurements are of considerable value to our diagnostics program.

The half lives of ⁸⁸Zr and ⁸⁸Y are 82.6 d and 106.6 d, respectively. The yields of reactions on short-lived targets such as these are difficult to measure because the intense target radioactivity interferes with the measurement of the radioactive product nuclides. It is generally necessary to physically separate the product from the target by means of an isotope separator, for example, or to chemically separate the daughter nuclide of the product. The latter technique was used for these experiments. Several separations as a function of time were made of the product daughter nuclide, ^{87m}Sr, from the yttrium and zirconium fractions of the ⁸⁸Zr target and from the ⁸⁸Y target itself.

The target material was produced by bombardment of molybdenum targets with ~750 MeV protons at the Isotope Production Facility at LAMPF. The ⁸⁸Zr was produced as a byproduct because the primary purpose of the molybdenum irradiation was to produce ⁸²Sr for the medical isotopes program of CNC-3. The ⁸⁸Y target material was obtained as the decay product from the original ⁸⁸Zr target material. In both experiments the radioactive target material was first purified from its daughter nuclides, aliquoted, and then coprecipitated with Tm(OH)₃ to

produce the final target. This cleanup was performed within 24 hours of the start of the bombardment. The target material was placed in a quartz tube for the irradiation. The ⁸⁸Zr target was 141 mCi and the ⁸⁸Y was 40 mCi. The ¹⁶⁹Tm(n,2n)-¹⁶⁸Tm reaction acted as an internal monitor for the neutron fluence. A cross section of 1.995 b was used for this reaction, representing the average of the LLNL (1.98) and Los Alamos (2.01) measurements at 14.1 to 14.8 MeV.

The neutron irradiations were carried out at the Lawrence Livermore National Laboratory ICT facility. This facility provides an intense source of 14-MeV neutrons by the bombardment of a rapidly rotating tritium target with 400-keV deuterons. The 14-MeV neutron source strength in these experiments was about 2×10^{12} n/s giving a neutron fluence of about 4×10^{15} n/cm² for the ⁸⁸Zr irradiation, placed in the 0° line (14.8 MeV), and 5×10^{14} n/cm² for the ⁸⁸Y irradiation, situated at 83.6° to the deuteron beam line (14.2 MeV).

Following the irradiations, the appropriate chemical separations of zirconium, yttrium, and strontium were made. By making several milkings of the ^{87m}Sr daughter from the parent fractions, it was possible to measure the ⁸⁷Y isomer ratio. For the ⁸⁸Zr experiments this ratio refers to the population of levels following the (n,np) and (n,pn) reactions and following the prompt gamma-ray cascade and for the ⁸⁸Y experiments refers to the population of levels following the (n,2n) reaction and following the prompt gamma-ray cascade (see Fig. 86). After the milking experiments, a cation-exchange column using α-hydroxyisobutyric acid was used to separate the thulium neutron flux monitor from the yttrium fraction.

The cross section results were calculated with the aid of a computer program that follows the nuclear reactions occurring during the irradiation and also follows the growth and decay of each of the relevant nuclides. The timing of the ^{87m}Sr milkings turned out to be quite important. Early milkings were necessary to get the yield for ^{87m}Y, yet enough time had to be allowed for the ^{87m}Sr daughter to grow in. Later milkings gave the results for the ground state ⁸⁷Y production. It was important to clean up the zirconium and yttrium fractions immediately after the

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Fig. 86.
Decay scheme of ^{87}Zr , $^{87\text{m}}\text{Y}$, and $^{87\text{m}}\text{Sr}$.

irradiations from any ^{87}Sr that was produced by direct reactions during the bombardment. Otherwise, this "extra" ^{87}Sr would invalidate the early milking results.

The results for these experiments are shown in Table XXVII. A note should be added here about the neutron energy of the ^{88}Y experiment. We intended to irradiate the ^{88}Y at 90° to the beam, which would have given 14.1 MeV neutrons. During the irradiation, however, the target sagged a bit in its holder (approximately 3 mm). This effectively put the target at an angle of 83.6° . This shift was detected by analyzing a series of nickel foils that had been placed at various known angles from the deuteron beam, in addition to a nickel foil placed at the tip of the quartz tube holding the ^{88}Y target. A plot of $^{58}\text{Co}/^{57}\text{Ni}$ measured for each nickel foil vs angle from deuteron beam showed that the ^{88}Y target was at 83.6° and not at the 90° originally intended. This resulted in a neutron energy of 14.19 MeV rather than 14.10 MeV.

The cross section values obtained are consistent with calculations performed both at LLNL and at

LANL. However, refinements will be necessary in the codes used at both laboratories to fit all of the data obtained more closely. This work is currently in progress.

TABLE XXVII
RESULTS FOR THE ^{88}Zr AND ^{88}Y NEUTRON IRRADIATIONS

A. ^{88}Zr , neutron energy = 14.8 MeV		
$\sigma(n,2n)$	=	$471 \pm 24 \text{ mb}$
$\sigma(n,np)$	=	$259 \pm 26 \text{ mb}$
$^{87\text{m}}\text{Y}/^{87\text{g}}\text{Y Total}^a$	=	0.90 ± 0.09
B. ^{88}Y , neutron energy = 14.19 MeV		
$\sigma(n,2n)$	=	$1145.6 \pm 57 \text{ mb}$
$^{87\text{m}}\text{Y}/^{87\text{g}}\text{Y Total}$	=	$0.70_4 \pm 0.05$

^aCorrected for the decay of ^{87}Zr .

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- Edward A. Walters and Normand C. Blais, "Molecular Beam Photoionization of (H₂S)_n, n=1-7," J. Chem. Phys.
- Presentations
- John E. Adams and J. D. Doll, "The Effect of a Precursor State on Adsorption/Desorption Dynamics," Texas Conference on Theoretical Approaches to Chemical Dynamics, University of Texas, Austin, March 1981.
- John E. Adams, "Kinetics of Thermal Desorption," Department of Chemistry, Ohio State University, Columbus, OH, February 1981; Department of Chemistry, University of Missouri-Columbia, Columbia, MO, January 1981; Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, January 1981.
- *L. M. Babcock, "A Flowing Afterglow Study of Ion Molecule Reactions of SF₆ and SF₄," Washington University, St. Louis, MO, January 1981; University of Louisville, Louisville, Kentucky, February 1981.
- *L. M. Babcock, "Ion Molecule Reactions of SF₄ and SF₆," University of Colorado, Boulder, Colorado, February 1981.
- *L. M. Babcock, "A Study of Gas Phase Reactions of Hypervalent Sulfur Fluorides," Middle Tennessee State University, Murfreesboro, Tennessee, March 1981.

*Invited talk

L. M. Babcock, "Negative Ion Molecule Reactions of Sulfur Tetrafluoride," ACS Meeting, Atlanta, Georgia, March 1981.

*L. M. Babcock, "Gas Phase Reactions of Hypervalent Sulfur Fluorides," University of Maryland, Baltimore County, March 1981.

*L. M. Babcock, "Ion-Molecule Reactions of the Sulfur Fluorides SF_4 and SF_6 ," University of Colorado, Colorado Springs, Colorado, March 1981.

*L. M. Babcock, "Ion-Molecule Reactions of the Hypervalent Compounds SF_4 and SF_6 ," University of Alabama, University, Alabama, April 1981.

L. M. Babcock, "Negative Ion Molecule Reactions of BF_3 and BCl_3 ," 182nd National ACS Meeting, New York, New York, August 1981.

*Normand C. Blais, "Quenching of Electronic Excitation by Diatomic Molecules," Harvey Mudd College, March 1981. In memory of V. Rojansky who died in March 1981.

*N. C. Blais and D. G. Truhlar, "Energy Transfer, Reaction, and Dissociation as a Function of Initial State for $\text{H} + \text{H}_2$ on an Accurate *Ab Initio* Potential Energy Surface," Second Chemical Congress of North American Continent, Las Vegas, Nevada, August 1980.

David S. Bomse, Jon B. Cross, and James J. Valentini, "Dynamics of Infrared Dissociation of van der Waals Molecules," 182nd National ACS Meeting, New York, New York, August 1981.

D. A. Cremers and R. A. Keller, "Quantitative Measurement of Solute Absorption by Optical Nulling Techniques," Los Alamos Conference on Optics '81, April 1981.

D. A. Cremers and R. A. Keller, "Optical Nulling for Trace Analysis Based on the Thermooptic Effect and an Interferometer," Conference on Lasers and Electro-Optics, Washington, D. C., June 1981.

D. A. Cremers and R. A. Keller, "Measurement of Weak Optical Absorptions by Thermally Induced Laser Pulsing," Conference on Lasers and Electro-Optics, Washington, D. C., June 1981.

J. B. Cross and J. J. Valentini, "High Repetition Rate Pulsed Nozzle Beam Source," 182nd American Chemical Society National Meeting, New York, New York, August 1981.

J. B. Cross and J. J. Valentini, "High Repetition Rate Pulsed Nozzle Beam Source," Gordon Conference on Dynamics of Gas-Surface Interactions, September 1981.

J. B. Cross and J. J. Valentini, "Dynamics of Infrared Photodissociation of van der Waals Molecules," presented at the Symposium on Interactions Between Light and Matter at the 182nd American Chemical Society National Meeting, New York, New York, August 1981.

*J. D. Doll, "Dynamics of Surface Processes," Department of Physics, University of Nevada, Reno. Chemistry Division, Argonne National Laboratory; Department of Chemistry, University of Illinois; Department of Chemistry, Northwestern University; Conference on Chemical Dynamics, University of Texas; Gordon Conference on Molecular Energy Transfer; Sandia National Laboratories, Albuquerque.

*J. D. Doll, "Stochastic Dynamics: Theory and Applications," Department of Physics, University of Nevada, Reno, Nevada, November 1980.

N. J. Dovichi, "Applications of Lasers to Gas Phase Absorption, Fluorescence, and Ionization Analysis," 1981 Utah Workshop--Lasers in Chemistry, Park City, Utah, September 1981.

C. E. Holley, "Geothermal Energy from Hot Dry Rock," Annual Meeting of the Southwestern and Rocky Mountain Division, AAAS, Greeley, Colorado, April 1981.

*invited paper

*Invited paper

*Charles E. Holley, "Chemistry and the Los Alamos Hot Dry Rock Geothermal Power Project," Physical Sciences Department, New Mexico Highlands University, Las Vegas, New Mexico, November 1980.

*R. A. Keller, "The Ultrasensitive Analysis Project," Rio Grande Society of Applied Spectroscopy, Santa Fe, New Mexico, December 1980.

R. A. Keller, E. F. Zalewski, R. Engleman, Jr., and C. T. Apel, "New Applications of the Optogalvanic Effect to Analytical Spectroscopy," Los Alamos Conference on Optics '81, April 1981.

*R. A. Keller, D. S. Bomse, and D. A. Cremers, "Concepts in Analytical Chemistry," Conference on Lasers and Electro-Optics, Washington, D. C., June 1981.

B. A. Palmer, R. A. Keller, and R. Engleman, Jr., "Uranium Wavelength Standards for Calibration of Spectrographs and Lasers," Annual meeting of the Optical Society of America, October 1980.

E. F. Zalewski, R. A. Keller, C. T. Apel, and R. Engleman, Jr., "The Optogalvanic Effect as an Atom Specific Detector for: I. Intracavity Atomic Absorption, II. Non Emission Sources," Pittsburgh Conference on Analytical Chemistry, March 1981.

D. S. Moore, David S. Bomse, and James J. Valentini, "Raman Spectroscopic Measurement of Collision-Free Internal State Distributions of Photofragments," Gordon Conference on Molecular Energy Transfer, Wolfeboro, New Hampshire, June 1981.

D. S. Moore, David S. Bomse, and James J. Valentini, "Raman Spectroscopic Measurement of Collision-Free Internal State Distributions of Photofragments," 82nd American Chemical Society National Meeting, New York, New York, August 1981.

*D. S. Moore, "Applications of Coherent Raman Spectroscopy to the Study of Gas Phase Chemical Dynamics," 1981 Utah Workshop--Lasers in Chemistry, Park City, Utah, September 1981.

N. S. Nogar, "Infrared Laser Induced Chemistry," Northern Iowa University*, March 6-7, 1980; Northeast Missouri State University*, April 4, 1980; Northwest Missouri State University*, April 18, 1980; University of New Mexico*, April 17, 1981.

N. S. Nogar, "Competitive Processes in the Infrared Laser Induced Chemistry of CH_2CClF , Chaired session, "Dynamics and Spectroscopy of Molecular Ions," Midwest Regional ACS Meeting, November 5-8, 1980, Lincoln, Nebraska.

N. S. Nogar, "Pressure and Power Dependence in the Infrared Laser Photolysis of 1-Chloro-1-Fluorethylene," SPIE, April 4-10, 1981, Santa Fe, New Mexico.

G. E. Streit, "The Electron Affinity of Sulfur Hexafluoride by Flowing Afterglow Techniques," at 182nd National American Chemical Society Meeting, New York, New York, August 1981.

*D. L. Thompson, "Formation and Decay of Quasi-bound Clusters of Argon Atoms," presented at the Reaction Dynamics Seminar Series, Department of Chemistry, University of California-Berkeley, October 1980.

*D. L. Thompson, "Dynamics Studies of Some Chemistry of van der Waals Molecules," presented as a Departmental Seminar, Department of Chemistry, University of Arkansas, Fayetteville, May 1981.

James J. Valentini, D. S. Moore, and David S. Bomse, "Coherent Anti-Stokes Raman Spectroscopy of Molecular Photofragments," Fifty International Conference on Laser Spectroscopy, Jasper, Alberta, Canada, June 1981.

*Invited paper

*Invited paper

James J. Valentini, D. S. Moore, and David S. Bomse, "Coherent Anti-Stokes Raman Spectroscopy of Molecular Photofragments," Gordon Conference on the Dynamics of Molecular Collisions, Plymouth, New Hampshire, July 1981.

James J. Valentini, Peter Esherick, and Adelbert Owyong, "Use of a Free-Expansion Jet in Ultra-High Resolution Stimulated Raman Spectroscopy," Conference on Optics '81, Santa Fe, New Mexico, April 1981.

CNC-3

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P. L. Horlock, J. C. Clark, S. W. Goodier, J. W. Barnes, G. E. Bentley, P. M. Grant, and H. A. O'Brien, "The Preparation of a Rubidium-82 Radionuclide Generator," J. Radioanal. Chem. 64, 257-265 (1981).

J. A. Katzenellenbogen, S. G. Senderoff, K. D. McElvany, H. A. O'Brien, Jr., and M. J. Welch, "^{16α}-[⁷⁷Br] Bromoestradiol-17β: A High Specific Activity, Gamma-Emitting Tracer with Uptake in Rat Uterus and Induced Mammary Tumors," J. Nucl. Med. 22 (1), 42-47 (1981).

K. D. McElvany, J. W. Barnes, and M. J. Welch, "Characterization of Bromine-77-Labeled Proteins Prepared Using Myeloperoxidase," Int. J. Appl. Radiat. Isotop. 31, 679-688 (1980).

K. D. McElvany, M. J. Welch, J. A. Katzenellenbogen, S. G. Senderoff, G. E. Bentley, and P. M. Grant, "Scope and Limitations of a Rapid Radiobromination Technique," Int. J. Appl. Radiat. Isotope. 32, 411-416 (1981).

J. K. Mazaitis, B. E. Francis, W. C. Eckelman, R. E. Gibson, R. C. Reba, J. W. Barnes, G. E. Bentley, P. M. Grant, and H. A. O'Brien, Jr., "No-Carrier-Added Bromination of Estrogens with Chloramine-T and Na ⁷⁷Br", J. Label. Compd. biopharm. XVIII (7), 1033-1038 (1981).

H. W. Moore and D. S. Wilbur, "Cyanoketenes: Mechanism of tert-Butylcyanoketene Cycloaddition to Aldo- and Keto-ketenes," J. Org. Chem. 45, 4483-4491 (1980).

F. J. Steinkruger and F. S. Rowland, "Bond Dissociation Energies of C-H Bonds in Several Haloethylenes as Estimated from the Recoil Tritium Abstraction Reaction," J. Phys. Chem. 85 (2), 136-140 (1981).

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P. M. Grant and D. A. Miller, "Considerations of Carrier (continued)," J. Nucl. Med.

P. M. Grant, D. A. Miller, J. S. Gilmore, and H. A. O'Brien, Jr., "Medium-Energy Spallation Cross Sections, 1. RbBr Irradiation with 800-MeV Protons," Int. J. Appl. Radiat. Isotop.

D. A. Miller, P. M. Grant, J. W. Barnes, G. E. Bentley, and H. A. O'Brien, "Research Scale Experimentation on the Production and Purification of Spallogenic ⁶⁸Ge at Los Alamos for Nuclear Medicine Applications", Pergamon Press.

R. D. Neirinckx, J. Kronange, G. P. Gennaro, M. D. Loberg, H. A. O'Brien, Jr., J. W. Barnes, G. E. Bentley, and P. M. Grant, "Evaluation of Inorganic Adsorbents for the Rubidium-82 Generator. I. Hydrated SnO₂", J. Nucl. Med.

H. A. O'Brien, Jr., and P. M. Grant, "Biomedical Positron Generators", Pergamon Press.

D. S. Wilbur and K. W. Anderson, "Bromine Chloride from N-Chlorosuccinimide Oxidation of Bromide Ion. Electrophilic Addition Reactions in Protic and Aprotic Solvents," J. Org. Chem.

D. S. Wilbur, G. E. Bentley, and H. A. O'Brien, Jr., "A Rapid Synthesis of A-Ring Bromine-77-Labeled Estrogens with High Specific Activity," J. Label. Compds. Radiopharm.

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G. K. Bayhurst, G. E. Bentley, "The Effect of HF on the Analysis of Al, Ba, Ca, Mg, and Sr in the Presence of Silicon," 1981 Pittsburg Conference and Exposition on Analytical Chemistry and Applied Spectroscopy March 9-13, 1981, Atlantic City, New Jersey.

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W. J. McKenna, R. M. Allan, P. L. Horlock, J. C. Clark, P. M. Grant, H. A. O'Brien, C. M. Oakley, J. F. Goodwin, and A. P. Selwyn, "Hypertrophic Cardiomyopathy: Measurement of Cation Uptake," Am. J. Card. 47, 409 (1981).

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Z. V. Svitra, G. C. Saunders, "Peroxidase Labeled Elastin: A Sensitive New Method for Detection of Elastase Activity," presented at the West Coast Connective Tissue Society Meeting held at Vancouver, B. C., March 13-16, 1981.

K. E. Thomas, M. A. Ott, T. DeBusk, "Recovery and Isolation of Curie Quantities of Hafnium and the Lanthanides from LAMPF-Irradiated Tantalum Targets," American Chemical Society Annual Meeting, New York (August 1981).

S. Vallabhajosula, S. Cochavi, S. J. Goldsmith, H. Lipszyc, and H. A. O'Brien, Jr., "Development of a ⁸²Sr/⁸²Rb Generator for Clinical Applications," J. Nucl. Med. 22, P-76 (1981).

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J. B. Wilhelmy, G. E. Bentley, K. E. Thomas, R. E. Brown, E. R. Flynn, J. Van der Peicht, L. G. Mann, G. L. Streubel, "Nuclei Far From Stability Using Exotic Targets," 4th International Conference on Nuclei Far From Stability, Helsingør, Denmark (June 1981).

CNC-4

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B. J. Krohn and L. H. Jones, "The Vibrational Transition Moment for the ν₂ Bands of ¹⁴ND₃ and ¹⁵ND₃," J. Mol. Spectrosc. 86, 16-26 (1981).

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G. J. Kubas, R. R. Ryan, and V. McCarty, "Bonding of η²-Sulfur Dioxide: Structures of Tricarbonyl-(1,10-phenanthroline)(η²-sulfur dioxide)molybdenum(0) and Dicarbonyl(2,2'-bipyridyl)bis(η²-sulfur dioxide)molybdenum(0)," Inorg. Chem. 19(10), 3003-3007 (1980).

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- B. I. Swanson and L. H. Jones, "Matrix-Molecule Interactions, Dynamics, and Exchange Phenomena in Low Temperature Matrices: SF_6 in Argon and Krypton," *J. Chem. Phys.* **74**(6), 3205-3215 (1981).
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- H. W. Clark and B. I. Swanson, "Solid State Effects in the Resonance Raman Scattering of $\text{Fe}(\text{CN})_6^{-3}$ as a Dopant in $\text{Cs}_2\text{LiCo}(\text{CN})_6$ and $\text{Cs}_2\text{NaCo}(\text{CN})_6$," *J. Chem. Phys.*
- M. P. Eastman, P. G. Eller, and G. W. Halstead, "Electron Paramagnetic Resonance and Crystal Structure Study of Bis(triphenylphosphine)iminium Hexafluorouranate(V)," *J. Inorg. Nucl. Chem.*
- P. G. Eller, and P. J. Vergamini, "Nuclear Magnetic Resonance and Chemical Studies of Uranium(V) Alkoxides," *Inorg. Chem.*
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- L. H. Jones and B. I. Swanson, "High Resolution Infrared Studies of Guest-Host Interactions and Dynamics in Low Temperature Matrices," *Proc. Third Int. Conf. on Matrix Isolation*, University of Nottingham, Nottingham, England, July 20-24, 1981.
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Presentations

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M. P. Eastman, D. Patterson, D. Bartsch, Y. Liu, P. G. Eller, "The Syntheses and EPR Spectra of Three Novel Spin Labeled Crown Ethers," 23rd Rocky Mountain Conference, Denver, Colorado, August 3-6, 1981.

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D. C. Moody and R. R. Ryan, "S-O Bond Activation in $\eta^2\text{-SO}_2$ Complexes: Novel Structure and Reactivity for $\text{Ru}(\text{CO})_2(\eta^2\text{-SO}_2\cdot\text{SO}_2)(\text{PR}_3)_2$," Spring ACS Meeting, Atlanta, Georgia, March 29-April 3, 1981.

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*R. R. Ryan, "Reactivity of Transition Metal - SO_2 Complexes," 182nd National ACS Meeting, New York, New York, August 23-28, 1981.

*B. I. Swanson, "Site Exchange Dynamics and Vibrational Dephasing in Cryogenic Matrices: An Infrared Analog to Exchange Phenomena in NMR Spectroscopy," University of Texas, El Paso, Texas, December 19, 1980.

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CNC-5

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C. J. Orth, J. S. Gilmore, J. D. Knight, C. L. Pillmore, R. H. Tschudy, and J. E. Fassett, "An Iridium Abundance Anomaly at the Palynological Cretaceous-Tertiary Boundary in Northern New Mexico," *Science*.

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R. C. Reedy, "Cosmic-Ray-Produced Stable Nuclides: Various Production Rates and Their Implications," *Proc. Twelfth Lunar and Planetary Sci. Conf.*

Presentations

D. W. Barr, "Thermonuclear Fuel Burn - Foreign and Domestic, 'Are You Sure You Can't Fool Mother Nature?'," CNC-Division Seminar, Los Alamos New Mexico, August 7, 1981.

B. P. Bayhurst, B. J. Dropesky, W. Faubel, C. J. Orth, R. J. Prestwood, and R. S. Rundberg, "A Comparison of Fission of Uranium 238 Induced by 500-MeV Protons and 350-MeV Positive Pions," 181st American Chemical Society meeting, Atlanta Georgia, March 29-April 3, 1981.

W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver, "Sorption of Am and Pu on Various Geologic Media under Reduced-Oxygen Conditions," Joint Southeast/Southwest Regional Meeting of the American Chemical Society, New Orleans, Louisiana, December 10-13, 1980.

S. J. DeVilliers, and A. J. Mitchell, "How Element Concentration and Solution-to-Solid Ratio Affect the Sorptive Behavior of Geologic Media," 181st American Chemical Society meeting, Atlanta, Georgia, March 29-April 3, 1981.

B. J. Dropesky, "Pion Single Charge Exchange Reactions," Xth European Conference on Physics and Chemistry of Complex Nuclear Reactions, Lillehammer, Norway, August 31-September 4, 1981.

W. Faubel, "Nuclear Charge and Angular-Momentum Distributions in Thermal-Neutron Fission of U-235 at Various Excitation Energies of the Fragments," Joint Southeast/Southwest Regional Meeting of the American Chemical Society, New Orleans, Louisiana, December 10-13, 1980.

G. C. Giesler, "LAMPF Nuclear Chemistry Data Acquisition System," Topical Conference on Computerized Data Acquisition in Particle and Nuclear Physics, Oak Ridge, Tennessee, May 28-30, 1981.

*J. D. Knight, "What Do Mesonic Atoms Have To Do With Chemistry?," American Chemical Society Central New Mexico Section, January 1981 Meeting, Santa Fe, New Mexico, January 16, 1981.

L.-C. Liu, "Determination of the Isotensor Potential in the Pion-Nucleus Interaction," American Physical Society Spring Meeting, Baltimore, Maryland, April 20-23, 1981.

L.-C. Liu, "Channel Coupling Effects on Angular Distributions for the Pion Double Charge Exchange Reaction $^{16}\text{O}(\pi^+, \pi^-)^{16}\text{Ne}$," 9th International Conference on High Energy Physics and Nuclear Structure (9-ICONEPANS), Versailles, France, July 6-10, 1981.

L.-C. Liu, "Pion-Nucleus Charge Exchange Reactions," Swiss Institute for Nuclear Research, July 13, 1981; University of Erlangen, West Germany, July 16, 1981; and University of Neuchatel, Switzerland, July 20, 1981.

C. J. Orth, "Evidence in New Mexico for an Extraterrestrial Event Marking the End of the Cretaceous Period," CNC-Division Seminar, Los Alamos New Mexico, May 1, 1981.

C. J. Orth, C. L. Pillmore, and R. H. Tschudy, "The Iridium Anomaly at the Palynological Cretaceous - Tertiary Boundary in the Raton Basin," U. S. Geological Survey Seminar, Denver, Colorado, May 21, 1981.

*Invited paper

C. J. Orth, J. S. Gilmore, J. D. Knight, C. L. F. Gilmore, R. H. Tschudy, and J. E. Fassett, "Iridium Anomaly at the Palynological Cretaceous - Tertiary Boundary in New Mexico," American Geophysical Union Spring Meeting, Baltimore, Maryland, May 25-29, 1981.

C. J. Orth, "The Iridium Abundance Anomaly at the Cretaceous - Tertiary Boundary in Northern New Mexico," Earth Sciences Colloquium, Los Alamos, New Mexico, June 12, 1981.

C. J. Orth, "Iridium and the Great Dying 65 Million Years Ago," Los Alamos Geological Society, Los Alamos, New Mexico, August 18, 1981.

*R. J. Prestwood, "Radiation, Can We Live With It?," 3rd Annual Meeting of the Blue River Trauma Society, British Columbia, Canada, March 7-14, 1981.

R. C. Reedy, "Extraterrestrial Studies Using Nuclear Interactions," CNC-Division Seminar, Los Alamos, New Mexico, December 5, 1980.

R. C. Reedy, "Cosmic-Ray-Produced Stable Nuclides: Various Production Rates and Their Implications," 12th Lunar and Planetary Science Conference, Houston, Texas, March 16-20, 1981.

R. C. Reedy, "Cosmic-Ray-Produced Deuterium, Carbon-13, and Nitrogen-15 in Meteorites," 44th Annual Meteoritical Society Meeting, Bern, Switzerland, August 17-21, 1981.

R. S. Rundberg, "Current Status of Crushed Rock and Whole Rock Column Studies," Waste-Rock Interactions Technology (WRIT) Annual Information Meeting, Seattle, Washington, October 13-15, 1980.

R. S. Rundberg, "Modeling of Radionuclide Transport," FY-1981 Nevada Nuclear Waste Storage Investigations Peer Review, August 24-28, 1981.

G. J. Russell, J. S. Gilmore, H. Robinson, and R. E. Prael, "Fertile-to-Fissile and Fission Measurements for Depleted Uranium Bombarded by 800-MeV Protons," Fifth Meeting of the International Collaboration on Advanced Neutron Sources (ICANS-V), Jülich, West Germany, June 22-26, 1981.

M. S. Spergel, R. C. Reedy, O. W. Lazareth, and P. W. Levy, "Cosmogenic Nuclide Production in Small Spherical Meteoroids," 12th Lunar and Planetary Science Conference, Houston, Texas, March 16-20, 1981.

M. S. Spergel, R. C. Reedy, O. W. Lazareth, and P. W. Levy, "Neutron-Capture Reactions in Meteorites," 44th Annual Meteoritical Society Meeting, Bern, Switzerland, August 17-21, 1981.

A. L. Turkevich, J. Warren, D. Boyce, T. E. Economou, H. R. Heydegger, S. Kaufman, and B. Dropesky, "Beta Measurement Technique for Radiochemical Studies of Rare Nuclear Processes," 182nd American Chemical Society meeting, New York, New York, August 23-28, 1981.

J. B. Wilhelmy, G. E. Bentley, K. E. Thomas, R. E. Brown, E. R. Flynn, J. Van der Plicht, L. G. Mann, and G. L. Struble, "Nuclei Far from Stability Using Exotic Targets," 4th International Conference on Nuclei Far from Stability, Helsingor, Denmark, June 7-13, 1981.

*Invited paper

*Invited talk.

APPENDIX B
LIST OF FACILITIES

CHEMICAL SYNTHESIS EQUIPMENT

PAR Electrochemical Equipment
Three Gas Chromatographs
Vacuum Lines, Hoods, Inert Atmosphere Boxes
for Handling Air-Sensitive Materials and
Powerful Oxidants (F_2)
High Pressure Autoclaves
High Pressure Liquid Chromatography

SPECTROSCOPIC EQUIPMENT

NMR

Varian XL-100-Fourier Transform Nuclear
Magnetic Resonance Spectrometer for ^{13}C
and Other Nuclei
EM-390 Fluorine, Proton, Phosphorus; EM-360
Proton Spectrometers; Superconducting and
Iron Core Magnets for Studies of Solids
Bruker WM-300 wide-bore spectrometer for high
resolution, multi-nuclear NMR of liquids
Bruker CXP-200 for solid state high resolution
studies

INFRARED

Perkin-Elmer 180, 283, and 683 Spectrometers
Nicolet FT-IR Spectrometer
Digilab FT-IR Far IR Spectrometer
(Cryo-Matrix Equipment)

LASER RAMAN SPECTROMETERS

Cary-81 Laser-Raman Spectrometer
SPEX plus Nicolet Data System, Spectra Physics
171 with Ar^+ , Kr^+ Lasers

ULTRAVIOLET, VISIBLE, NEAR-IR SPECTROMETERS

Hewlett-Packard 8450A uv/visible
Two Cary-14's
Moletron N_2 -pump and dye laser

X-RAY DIFFRACTION EQUIPMENT

Weissenberg, Precession and Powder Diffraction
Picker FACS-1 Single Crystal X-Ray Diffracto-
meter (Replacement being ordered)
Phillips and Picker X-ray Diffractometers
Mettler Hot-Stage for Optical Microscopy

INSTRUMENTS FOR ANALYSIS

Atomic Absorption Spectrometer (In Fume Hood)
Plasma Emission Spectrometer
X-Ray Fluorescence Spectrometer (Automatic
Read-Out and Data Analysis)
Chemical Autoanalyzer

HPLC (High Performance Liquid Chromatograph)
SP8100
Potentiostat - Coulometer
Two Dionex Anion Chromatographs
Automatic Titrator

HYDROTHERMAL LABORATORY

Circulation Loops
Rocking Vessels
Permeability Systems

INSTRUMENTATION FOR THERMOCHEMISTRY

High Temperature Solution Calorimeter
Combustion Calorimeter
Room Temperature Solution Calorimeter
Perkin-Elmer TGS-2 Thermogravimetric Balance
Differential Thermal Analysis Equipment

ROCK SAMPLE PREPARATION LABORATORY

FLUID TRANSPORT SYSTEMS

Inert Atmosphere Box - Controlled CO_2

MICROSCOPY

Scanning-Electron-Microscope (with non-
dispersive X-Ray Analyzer)
Optical: Microautoradiography

MICROORGANISMS PREPARATION FACILITY

INSTRUMENTATION FOR IN VIVO ANIMAL IMAGING

Pickar 411 Gamma Camera

INSTRUMENTATION FOR CHEMICAL KINETICS, CHEMICAL

DYNAMICS, SPECTROSCOPY AND ULTRASENSITIVE ANALYSIS

Fast-flow Tube
Crossed Molecular Beam Machine
Single Beam Machines
Stopped-flow Kinetics Apparatus for Pu Studies
Excitation Lasers uv to IR, Pulsed and cw

INSTRUMENTATION FOR THEORY

VAX-11/780 Computer

MASS SPECTROMETERS

Two Surface Thermal Ionization, Pulse-Counting
Instruments
Four Surface Thermal Ionization with Ion
Detection by Faraday Cage
One "Precision-Ratio" Gas-Source
One Gas-Source Two-Stage for "Heavy Methanes"
Two Magnetic Deflection Isotope Separators
Two-stage Mass Spectrometer
Mass Spectrometer with Multiphoton Laser Ion-
ization source

Two Cycloidal, Masses to 80
 Quadrupole with Gas Chromatograph (Masses to 1000)
 Time-of-Flight and Automated Nitrogen Isotope Ratio
 Molecular-beam Photoionization
MEASUREMENT AND HANDLING OF RADIOACTIVITY
 Automatic Beta and Gamma Counting Systems
 Alpha, Beta, and Gamma-Ray Spectrometers
 Computer Control for Data Collection and Data Reduction
 Hot Cells for High Level Gamma- and Beta-Active Materials

Facilities for Alpha-Emitting Materials
RADIOISOTOPE PRODUCTION FACILITY AT LAMPF
CRYOGENIC SEPARATION FACILITY FOR STABLE ISOTOPES OF C,O,N (ICONS)
RESEARCH REACTOR (OWR)
 Three Automated Neutron Activation Analysis Systems with On-Line Data Reduction
 Fourteen Thermal and Epithermal Rabbit Facilities
 In-Core Irradiation Facilities (Thermal flux $\approx 9 \times 10^{13}$ n/cm²s)
 Two Triple-axis Neutron Diffraction Spectrometers
 Neutron Radiography Facility
 Two Neutron Capture Gamma-Ray Facilities

APPENDIX C

DESCRIPTION OF SELECTED MAJOR DIVISIONAL FACILITIES

1. Los Alamos NMR Facilities (W. L. Earl, E. Fukushima, S. B. W. Roeder,* and W. E. Wageman)

The NMR of solids project has undergone major changes in its personnel, physical facility, equipment, and emphases during FY 1981. Bill Earl, an expert in high resolution NMR of solids, formerly at the National Bureau of Standards, has joined us as of July 1981. Bill Wageman of CNC-4, an electronic and computer specialist, has been assigned to the solid state project although he will work with all the instrumentation in the NMR Facility insofar as maintenance and troubleshooting are concerned.

We have consolidated all of the research grade NMR instrumentation, except for two analytical NMR spectrometers remaining with the rest of CNC-4 in Building 150, TA-21, as of July 1981. Thus, the solid state NMR effort is no longer physically separated from the solution high resolution NMR equipment. Most important of all, the entire NMR personnel are now under one roof and this has led to a much more effective interaction between the various NMR experts.

As for equipment, we devoted a large amount of time to the design of the optimal configuration for a wide variety of solids and liquids NMR experiments. We inspected several NMR spectrometers in

other laboratories in addition to visiting some of the firms who manufacture such instrumentation including a factory in Japan. We decided to purchase two commercial superconducting spectrometers capable of high resolution NMR in solid and liquid samples, as well as to construct our own carbon-13 machine utilizing an existing electromagnet. One of these commercial spectrometers, the Bruker CXP-200, will be capable of high resolution NMR of solids by several methods as well as of relaxation studies using complex pulse sequences. Initially, this machine will be used primarily for looking at protons and nitrogen-15, although we will expand its capabilities further to include many other nuclei. Our carbon-13 machine, currently being built, will be a low frequency spectrometer specifically designed to do high resolution NMR of solids while using an old electromagnet (with a field strength of 1.4 Tesla). Because it will utilize the cross-polarization magic-angle-spinning method, it will be ideally suited for the study of carbon-13 resonances in organic solids.

A magic-angle-spinning apparatus to spin a solid sample at speeds up to 5 kHz has been designed and constructed. It is a prototype using a cylindrical sample with air bearings symmetrically located at each end of the sample. It has achieved design speed of 300,000 rpm. After further refinement, a spinner assembly will be built for the actual NMR experiments on organic solids.

*San Diego State University

As already implied, much of the new emphasis of the solid state NMR effort is on studies of structure, molecular motion, and composition of organic solids consisting of or related to organic explosives. High resolution NMR spectroscopy of these solids will yield valuable information on the structure and composition whereas relaxation time measurements will yield information about the molecular motion in the slow regime (roughly dc to 1 MHz).

Projects performed during 1981 include:

- 1) reactivation, requiring major modifications and repairs, of an old iron-core electromagnet for high resolution NMR to be used for the carbon-13 magic-angle spinning spectrometer (Earl and Roeder);
- 2) design of a magic-angle spinner (Earl);
- 3) completion of a book on experimental NMR with an emphasis on the nuts and bolts experimental methods (Fukushima and Roeder and Fukushima);
- 4) newly designed NMR coils for better transmitter efficiency, better signal-to-noise ratio, and larger sample volume (Roeder);
- 5) change to a floppy-disk-based solid state NMR operating system from a cassette system that

has been used for the past ten years (Fukushima); and

- 6) maintenance, repair, and development of new hardware and software for NMR spectrometers in the NMR Facility (Wageman).

2. Omega West Reactor Operations (H. T. Williams, A. R. Lyle, and M. E. Bunker)

The Omega West Reactor (OWR) is operated to provide Los Alamos experimenters with an intense source of thermal and epithermal neutrons. Thermal fluxes as high as 9×10^{13} n/cm²s are available at the normal reactor power level of 8 MW. Access to the neutron flux is provided by numerous beam tubes, removable thermal column "stringers" and fourteen pneumatic "rabbit" facilities. The reactor is used for sample irradiations, external neutron-beam experiments, in-core irradiation of instrumented capsules, neutron radiography of assemblies, neutron-capture gamma-ray studies, neutron cross-section measurements, and neutron-activation assay measurements. A cross section of the reactor is shown in Fig. 87.

Fig. 87.

Horizontal cross-section view of the Omega West Reactor.

In FY 1981, 27 Los Alamos groups and 5 outside laboratories (notably Livermore) made use of the reactor. Over 69,000 samples were irradiated and approximately 2,000 experiment-hours were logged by users. Following is a partial list of the experimental programs supported by the reactor operation during the fiscal year.

Weapons

- Radiochemical diagnostics (CNC-11)
 - Tracers for radiochemical procedure development
 - Tracers for isotope-separation testing and development
 - Neutron activation analysis (NAA) of post-shot debris
 - Activation of fissile elements for interlaboratory calibrations
 - Neutron cross-section measurements
 - Miscellaneous activations for detector calibration
- Helium retention in uranium tritide (WX-5)
- Uranium and plutonium tritide structure studies (WX-5)
- Neutron radiography of weapon components (M-5)

Inertial Confinement Fusion

- Activation of microspheres for radiochemical diagnostics (P-2, LLNL)
- Neutron activation analysis of optical components (P-2)

Magnetic Fusion Energy

- Radiation damage studies (LLNL, HEDL)

Safeguards

- Spent fuel scans for development of safeguard techniques and instrumentation (Q-5)

Waste Isolation and Oklo Phenomena

- NAA for trace elements in Nevada basalts (G, CNC)
- NAA uranium assay of leachates (CNC)
- Tracers for water migration studies (CNC)
- Glassy containment (Rockwell International)

Resource Assessments

- NAA for National Uranium Resource Evaluation (G-4, CNC-5)
- NAA for strategic metals extracted from seawater (LLNL)

Geothermal and Geochemical

- Tracers for hot dry rock project (G, CNC)
- NAA characterization of Cretaceous-Paleocene boundary rock (G-2)
- NAA of basalts from potential geothermal sites (G-9)

Environmental Assessments

- NAA of mineral wastes from coal and oil shale (CMB-8)
- NAA of Los Alamos environmental samples (H-8, LS-6)
- NAA of uranium mill tailings (ALO/UMTRA)

Health and Safety

- Tracers for hot-cell chemistry development (CNC)
- NAA of urine for fissile material (H-5)
- NAA for metal aerosol evaluation (H-5)
- NAA for trace metals in health-related samples (H-5)
- Biological toxicology (LS-5, Lovelace Clinic)
- Calibration and testing of thermoluminescent detectors (H-1)

Research

- Neutron oscillation experiment; feasibility study (P-00)
- NAA for boron in meteorites (CNC-7)
- NAA for platinum-group metals study of Cretaceous-Tertiary extinction (CNC-11)
- Studies of nuclear structure via radionuclide decay (CNC-5)

3. Stable Isotopes Facilities

1. Four cryogenic distillation columns are suspended in deep holes. The longest, 700 ft, distills carbon monoxide for carbon-13 production (Fig. 88). The other columns distill nitric oxide for concurrent production of nitrogen-14, nitrogen-15, oxygen-16, oxygen-17, and oxygen-18. A test column in the fourth hole is used for research. The production facilities are operated continuously and require a set of complex control consoles for safe, automatic control. A newly installed system for reprocessing isotopically depleted

CARBON MONOXIDE DISTILLATION PLANT

ICONS TA - 46

Fig. 88.

Carbon Monoxide Distillation Plan Icons TA-46

nitric oxide by exchange with isotopically normal nitric acid also operates continuously. During FY 1981, the isotope separation plant produced 8.5 kg ^{13}C , 1.9 kg ^{15}N , and 0.2 kg ^{17}O having a combined value of \$667K.

2. Isotopic samples from the columns and other parts of the routine isotope operations are analyzed by an automated cycloidal mass spectrometer, all relevant data are magnetically stored, and a variety of displays and reports are available to the plant operators and supervisor.
3. The product gases from these columns are handled by a benchtop of process equipment for chemical conversions.
4. As a service to the outside scientific community, we have developed an automated nitrogen isotope analytical facility. Ammonium sulfate samples resulting from isotope labeling experiments are sequentially converted to nitrogen gas which is purified cryogenically and analyzed by isotope ratio mass spectrometry. This facility processes several hundred samples daily, prints out results, and stores data magnetically.

4. Mass Spectrometry Clean Room

To enlarge our array of radiochemical detector elements to diagnose thermonuclear fuel performance, we are developing sensitive mass spectrometric techniques that will permit the use of detector elements whose activation products are long-lived. These new techniques require the elimination of any particulate contamination. The latter is achieved by doing both the chemical preparation of the samples and the mass spectrometric analysis in clean rooms. A new 115-m² room was designed and constructed to house three single-stage and a newly fabricated double-stage mass spectrometer. Class 3.5 air, particle count not exceed a total of 3.5 particles per liter of a size 0.5 μm and larger, is supplied to all critical work areas. The remainder of the room is maintained at Class 350. Figure 89 shows the room with the preparation area at the left and a spectrometer at the right.

Fig. 89.
Mass Spectrometry clean room.

APPENDIX D
COMPOSITION OF ADVISORY COMMITTEES FY 1981

I. Medical Radioisotopes

Chairman:

Monte Blau, State University of New York,
Buffalo, New York, 1978-81.

Thomas F. Budinger, Lawrence Berkeley Labora-
tory, Berkeley, California, 1979-82.

Raymond E. Counsell, University of Michigan,
Ann Arbor, Michigan, 1979-82.

Allan M. Green, New England Nuclear Corpora-
tion, North Billerica, Massachusetts,
1978-81.

Paul V. Harper, Franklin McLean Memorial
Research Institute, Chicago, Illinois,
1979-82.

Thomas P. Haynie, M. D. Anderson Medical
Center, Houston, Texas, 1979-82.

David E. Kuhl, University of California, Los
Angeles, California, 1978-81.

Richard C. Reba, The George Washington Medical
Center, Washington, D. C., 1978-81.

Robert Barker, Cornell University, Ithaca, NY,
1975-81.

Harry Hogenkamp, University of Minnesota,
Minneapolis, Minnesota, 1975-81.

Kenneth Rinehart, University of Illinois,
Urbana, Illinois, 1975-81.

Donald Jenden, UCLA, Los Angeles, California,
1975-81.

Charles Sweeley, Michigan State University,
East Lansing, Michigan, 1975-81.

III. Visiting Committee for Nuclear and Radio-
chemistry

Chairman:

Anthony Turkevich, University of Chicago,
Chicago, Illinois, 1980-81.

Chairman-Elect:

Jerome Hudis, Brookhaven National Laboratory,
Upton, New York, 1980-82.

John O. Rasmussen, University of California,
Berkeley, California, 1980-83.

Robert Vandenbosch, University of Washington,
Seattle, Washington, 1980-83.

Lawrence Wilets, University of Washington,
Seattle, Washington, 1980-82.

II. Stable Isotopes Resource Advisory Committee

Chairman:

Dennis Bier, Washington University School of
Medicine, St. Louis, Missouri, 1975-81.

APPENDIX E
DIVISIONAL SEMINARS

"Flowing Afterglow Study of Ion-molecule Reactions
of SF₆," Lucia Babcock, CNC-2, November 7, 1980.

"Extraterrestrial Studies Using Nuclear Inter-
actions," Robert Reedy, CNC-11, December 5, 1980.

"Overview of Waste Isolation Activities in CNC
Division," Bruce Erdal, CNC-7, January 9, 1980.

"Nuclear Magnetic Resonance of Polymers--An Example
of a Solid State Study," Eiichi Fukushima, CNC-4,
February 6, 1981.

"Retention and Transport of Elements in the Earth's
Crust--The OKLO Experience," David Curtis, CNC-7,
March 6, 1980.

"Dynamics of the Reaction of Nitric Oxide and
Ozone," Jim Valentini, CNC-2, April 17, 1981.

"Evidence in New Mexico for an Extraterrestrial
Event Marking the End of the Cretaceous Period,"
Charles Orth, CNC-11, May 1, 1981.

"Carbon 13 NMR as a Biochemical and Physico-chemical Probe," Bob London, CNC-4, June 5, 1981.

"Thermonuclear Fuel Burn--Foreign and Domestic 'Are You Sure You Can't Fool Mother Nature,'" (classified) Don Barr, CNC-11, August 7, 1981.

"Ultra-Sensitive Analysis of Plutonium Using Laser Spectroscopy," Dr. Norbert Trautmann, Institut für Kernchemie, Joh. Gutenberg--Universität Mainz, West Germany and "Heavy and Superheavy Element Studies at GSI," Dr. Jens Volker Kratz, GSI, September 18, 1981.

APPENDIX F

LIST OF DIVISIONAL PERSONNEL BY GROUP

CNC-DO (667-4457)

CMR Building, TA-3, R. A214

*Darleane C. Hoffman, Division Leader
*N. A. Matwiyoff, Deputy Division Leader
Margaret Plageman, Budget-Fiscal Spec.
Audrey Giger, Administrative Assistant
Joan Brown, Secretary

CNC-2 (667-4686)

CMR Building, TA-3, Wings 4 and 5

*John H. Sullivan, Group Leader
Karen Peterson, Secretary
Archuleta, Frank A.
*Blais, Normand C.
*Cross, Jon B.
*Doll, Jimmie U. (Laboratory Fellow)
Fernandez, Wilbur
Garcia, Anthony R.
*Holley, Charles E. Jr.
*Keller, Richard A.
*Newton, Thomas W.
*Nogar, Nicholas S.
*Streit, Gerald E.
*Thompson, Donald L.
*Valentini, James J.
*White, Ralph W.
*Zeltmann, Alfred H.
Bomse, David S. (JRO Fellow)

Postdoctoral Appointees

Babcock, Lucia M.
Dovich, Norman J.
Miller, Charles M.
Valone, Steven M.

*Staff Member

CNC-3 (667-4675)

Radiochemistry Building, TA-48

Target Area, LAMPF Beam Stop
*Harold A. O'Brien, Group Leader
Barbara Burress, Secretary
*Barnes, John W.
*Bentley, Glenn
Debusk, Thomas P.
Ott, Martin A.
Seurer, Franklin H.
*Steinkruger, Fred J.
*Svitra, Zita
*Thomas, Kenneth E.
*Wanek, Philip M.
*Wilbur, D. Scott

Postdoctoral Appointee

Rogers, R. Scott

CNC-4 (667-6045)

Building 3 and 150, TA-21

Building 88, TA-46

*Robert A. Penneman, Group Leader
Ruth F. Capron, Secretary
*Armstrong, Dale E.
*Asprey, Larned B.
*Earl, William
*Eller, P. Gary
Ekberg, Scott
Foltyn, Elizabeth
*Fukushima, Eiichi
*Goldblatt, Maxwell
Garcia, Michael
*Han, Chung Hwa
*Hutson, Judy
*Jarvinen, Gordon

*Staff Member

*Jones, Llewellyn H.
 *Kubas, Gregory J.
 *Larson, Allen
 Lehman, Charles A., Jr.
 *London, Robert E.
 *McInteer, Berthus B.
 Medina, Raymond
 *Mills, Thomas R.
 Montoya, Joe G.
 *Moody, David C.
 Romero, Ramon
 *Ryan, Robert R.
 Salazar, Kenneth V.
 *Swanson, Basil I.
 Schmahl, Francis
 Vandervoort, Raymond C.
 *Wageman, William E.
 *Walker, Thomas E.

Postdoctoral Appointee

Fry, Herbert
 Phillippi, Martin A.
 Unkefer, Clifford J.

CNC-5 (667-4151)

Omega Site, TA-2

*Merle E. Bunker, Group Leader
 Sarabel Berna, Secretary
 *Denton, Michael M.
 Eide, Bruce P.
 *Garcia, Sammy R.
 Gomez, Richard D.
 Kent, Alex P.
 *Lyle, Alvin R.
 *Minor, Michael M.
 *Starnner, John W.
 *Williams, Herbert T.

CNC-7 (667-4498)

Radiochemistry Building, TA-48

*Ernest A. Bryant, Group Leader
 S. Kathleen Kelly, Secretary
 Aguilar, Ruben D.
 *Alej, Mohammed
 Banar, Joseph C.
 *Bayhurst, Barbara P.
 Bayhurst, Gregory K.

*Staff Member

*Benjamin, Timothy M.
 *Binder, Irwin
 *Cappis, John H.
 *Charles, Robert W.
 *Curtis, David B.
 *Duffy, Clarence J.
 Dye, Suzann
 *Efurd, D. Wesley
 *Erdal, Bruce R.
 *Fowler, Malcolm M.
 *Frank, D. James
 *Gancarz, Alexander J.
 *Guthals, Paul R.
 Handel, Deva
 *Mason, Allen S.
 Mitchell, Lia M.
 *Mroz, Eugene J.
 *Norris, A. Edward
 *Oakley, Glenda E.
 *Ogard, Allen E.
 *Perrin, Richard E.
 Pruner, Robert E.
 Raybold, Nancy A.
 *Rokop, Donald J.
 *Sedlacek, William A.
 *Treher, Elizabeth N.
 *Vidale, Rosemary J.
 Wanek, Patsy L.
 *Wolfsberg, Kurt

Postdoctoral Appointee

Rogers, Pamela S.

CNC-11 (667-4546)

Radiochemistry Building, TA-48;

LAMPF Building, TA-53

*James E. Sattizahn, Group Leader
 Marcella Kramer, Secretary
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 *Balagna, John P.
 *Balestrini, Silvio
 *Barr, Donald W. (Laboratory Fellow)
 *Butler, Gilbert W.
 Cisneros, Michael
 Cisneros, Sandra
 *Clinton, David D.
 *Daniels, William R.

*Staff Member

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Drake, Joy
*Drotsky, Bruce J.
Elder, Patricia A.
*Ennis, Martha L.
*Gallagher, James D.
Gallegos, Carla E.
*Giesler, Gregg C.
*Gilmore, James S.
*Grisham, Genevieve F.
Hansen, Gary T.
*Helmick, Sara B.
Holmes, Lynn
Kelley, Gregory M.
*Kelley, Thomas A.
Knight, Jack H.
*Knight, Jere D. (Laboratory Fellow)
*Knight, Sylvia
*Knobloch, Gordon W.
Lark, Marjorie E.
*Lawrence, Francine
Lermuseaux, Shari
*Liepins, Leila
*Liu, Lon-Chang
Longmire, Calvin C.

*Staff Member

Longshore, Joseph S.
Lucero, Fabiola
Maestas, Sixto
Mitchell, Alan J.
Myers, Thomas A.
Oliver, Petrita Q.
*Orth, Charles J.
Paulson, Lloyd L.
*Prestwood, Rene J.
*Reedy, Robert C.
*Rundberg, Robert
*Rundberg, Virginia
Schofield, Raymond G.
Staritzky, Alice W.
Stice, Richard
Tallmadge, Lois F.
*Thomas, Kimberly W.
Thompson, Joseph
Ulibarri, Larry
*Vieira, David J.
Vigil, Janet E.
*Wilhelmy, Jerry B.

Postdoctoral Appointee

Clark, James L.

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