Heavy Element Chemistry

Portfolio Description

This activity supports research in the chemistry of the heavy elements, including actinides and some fission products. The unique molecular bonding of the heavy elements is explored using theory and experiment to elucidate electronic and molecular structures, bond strengths, and chemical reaction rates. Additional emphasis is placed on the chemical and physical properties of actinides to determine solution, interfacial, and solid-state bonding and reactivity; on determining chemical properties of the heaviest actinide and transactinide elements; and on bonding relationships among the actinides, lanthanides, and transition metals. Capital equipment funding is provided for items such as instruments used to characterize actinide materials (spectrometers, diffractometers, etc.) and equipment to handle the actinides safely in laboratories and at user facilities.

Unique Aspects

This activity represents the only source of funding for basic chemical research in the actinides and transactinides in the United States. Its major emphasis is to understand the underlying chemical and physical principles that determine the behavior of these elements. The activity is primarily based at national laboratories because of the special facilities needed in order to handle these radioactive materials safely. The education of undergraduates, graduate students, and postdoctoral researchers in radiochemistry at national laboratories and universities is an important responsibility of this activity.

Relationship to Other Programs

This activity provides the fundamental understanding of the properties of the actinides and fission product elements that support DOE missions in advanced nuclear energy, stewardship responsibilities for defense programs, and environmental clean-up. The heavy element chemistry program conducts unclassified basic research on all the actinide and transactinide elements, while applied programs (nuclear energy, environmental, stockpile stewardship) generally limit their investigations to the chemical and material properties of specific elements and systems of strategic programmatic interest. This activity is coupled to the BES Separations and Analysis activity, to actinide and fission product chemistry research in DOE’s Environmental Remediation Sciences Program, and to nuclear fuel cycle research within DOE's Office of Nuclear Energy.

Significant Accomplishments

Heavy element chemistry had its genesis in the Manhattan project. Early goals were to discover new elements and to determine their chemical and physical properties from microscale and tracer experiments. Processes for the separation of plutonium from uranium and fission products on an industrial scale were then developed. The chemistry of the elements through einsteinium (Es, atomic number 99) has been determined with small but weighable quantities. For the elements heavier than Es in the periodic table, tracer techniques and one-atom-at-a-time chemistry have been developed and carried out through element 108 to determine chemical properties. Organometallic chemistry has been enriched by discovery of many unique organoactinide compounds.

Taken together, the results from this activity have repeatedly confirmed the Seaborg hypothesis that the actinides are best represented in the periodic table as a 5f element series placed under the 4f (lanthanide) series. Interpretations of spectroscopic results have provided thermodynamic quantities such as oxidation-reduction potentials and enthalpies of reactions. Specific electronic transitions determined in this activity have proven useful to develop processes for laser isotope separation of uranium and plutonium. Magnetic measurements show the light actinide metals have delocalized 5f orbitals and resemble d-orbital transition metals, whereas the 5f electrons become localized at americium, element 95; thus the heavier actinide metals exhibit behavior similar to the rare earth metals.

Mission Relevance

This activity represents the nation's only funding for basic research in actinide and long-lived fission products, especially technicium, and is broadly relevant to the DOE mission. Knowledge of the chemical characteristics of actinide and fission-product materials under realistic conditions provides a basis for advanced fission fuel cycles. Fundamental understanding of the chemistry of these long-lived radioactive species is required to accurately predict and mitigate their transport and fate in environments associated with the storage of radioactive wastes.

Scientific Challenges

The role of 5f electrons in bond formation remains the fundamental topic in actinide chemistry and is the central focus for this program. The 5f orbitals participate in the band structure of metallic and ceramic materials that contain the light actinides. Theory and experiment show that 5f orbitals participate significantly in molecular actinide compounds, for example, compounds required for advanced nuclear energy systems. Molecular-level information on the geometry and energetics of bonding can now be obtained at the Nation's synchrotron light sources and from multi-photon laser excitation studies. These tools enable studies of actinides in the gas phase, as clusters, and at interfaces between solutions and surfaces of minerals and colloids in solution. Actinide and fission product samples must be handled in special facilities because of their radioactivity, which limits the types of experiments that can be safely conducted.

Sophisticated quantum mechanical calculations that treat spin-orbit interactions accurately need further development so that they can predict the properties of molecules that contain actinides. Development and validation of computer codes yield fundamental information about actinide species that are difficult to study experimentally, predict the electronic spectra of important species, and correlate electronic properties with molecular structure. Improved modeling of actinide transport requires understanding of the processes describing sorption on surfaces such as colloidal particles. Surface complexation models can predict the migration of radioactive species; experimental validation of the theoretical properties of models will be the key to understanding the role of the 5f electrons. This activity supports research in heavy element chemistry at universities, encouraging collaborations between university and laboratory projects. Twenty-four undergraduate students, chosen competitively from universities and colleges throughout the United States, are taught actinide chemistry and radiochemistry each summer in programs at Brookhaven National Laboratory and San Jose State University. Graduate and postdoctoral students are educated to provide personnel for the technological challenges associated with the heavy elements.

Projected Evolution

At the frontier of the periodic table, theoretical chemists predict the properties of actinides and transactinides in gaseous molecules, clusters in liquids, and solid species, using modern calculation tools such as density functional theory. Because most actinide species have partly filled 5f electron subshells and all have highly charged nuclei, both spin-orbit and relativistic effects must be included in the calculations. Sophisticated quantum mechanical calculations of actinide compounds and actinide species in environmental media are being developed. Heavy Element Chemistry research pursues advances in gas-phase chemistry that explore new reactivity patterns, providing benchmarks for theoretical calculations.

Support of research to understand the chemical bonding of elements that have 5f electrons leads to fundamental understanding of separations processes and to the design and synthesis of preorganized chelating agents for the separations of particular actinide ions. Research in bonding, reactivity, and spectroscopic properties of molecules that contain heavy elements and of actinides in environmentally relevant species aids the development of ligands to sequester actinides in the environment and to remove toxic metals from the human body. Better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces, including mineral surfaces under environmentally relevant conditions, improve separations processes that are essential for advanced nuclear fuel cycles.