RARE-EARTH INFORMATION CENTER NEWS

AMES LABORATORY
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University of Munich —

RADIOCHEMISTRY GROUP

An important line of research in the study of rare-earth elements is the comparative chemistry of lanthanides and actinides. This is the major subject studied by the Radiochemistry Group at the Institute of Inorganic Chemistry, University of Munich, West Germany. This Group is headed by Dr. Fritz Weigel, Instructor of Chemistry at the University.

RADIOCHEMISTRY GROUP — In the front row from left are Dr. Volker Scherer, Anton Trinkl, Victor Wishnevsky, Petra Schilz, Dr. Fritz Weigel, Günter Hoffman and Gabriele Trinkl. In the back row from left are Alfred Rühlmann, Bernd Reichwein, Nicolaus ter Meer, Josef Hoffman, and Wolfgang Ollendorff.

In the comparative chemistry of lanthanide and actinide elements, physicochemical measurements, such as crystal structure determinations, or thermodynamic measurements play an important role for obtaining useful basic data.

Recently, a major study of promethium compounds was undertaken which resulted in the preparation of more than 30 compounds of this element. Most of these compounds were prepared for the first time. This also applies to promethium metal which was prepared for the first time in 1963. Studies of its properties were temporarily suspended because of major construction work in the radiochemistry laboratory. Work will be resumed when the laboratory is back in operation.

The crystal chemistry of promethium compounds was studied in some detail; the basic x-ray crystallographic data of about 25 compounds were obtained. These latter studies gave a clear picture of isomorphic series of compounds in which promethium is at the borderline between two series showing different structures. The major difficulty in promethium work is the high radio-activity of ^{147}Pm, which is approximately 1 Curie/mg, and requires extensive precautions.

Thermodynamic data on rare-earth chlorides and oxychlorides have been obtained by measure-

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Rare Earths In the News

EXPANDS CRYSTAL PRODUCTION

Union Carbide is expanding its research and development, and production facilities for yttrium-aluminum-garnet crystals used in lasers and masers. The new facilities are being built as part of Carbide's new technical center at San Diego, Calif. The expansion was triggered by the fast pace of laser sales which are now $70 to $150 million annually in the United States.

BOOSTS Y_2O_3 CAPACITY

American Potash & Chemical Corp. has begun expansion of its West Chicago, Ill. plant for the production of yttrium oxide. When completed, the expansion will allow American Potash to boost yttrium oxide production to a total of 150,000 pounds annually.

MERGER?

Word has been received that American Potash and Chemical Corp., one of the nation's largest producers of rare earths, has reached an agreement in principle with the Kerr-McGee Corp. for a merger of the two firms.

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Staff Changes

Charla Bertrand has joined the staff of RIC replacing Mrs. Joan Smith who resigned to pursue full time graduate study at Iowa State University. Mrs. Bertrand is a 1967 graduate of Iowa State.

Effect on Zirconia

There is much current interest in zirconia-rare earth oxide systems. In a paper by Föex and Rouanet, *Compt. rend. 264C*, 947 (1967), the authors report the effect of the heavy lanthanide and yttrium oxides on the melting point and the cubic to tetragonal transformation of ZrO_2.

Addition of rare-earth oxides raise the 2710°C melting point of zirconia by as much as 100°C. The increase of the melting point is inversely proportional to the ionic size of the rare-earth element. Of the rare-earths studied Yb_2O_3 has the greatest effect and Gd_2O_3 the smallest. The composition of the maximum in the liquidus curve is also inversely proportional to the ionic size. For Yb_2O_3 the maximum is found at 25 mol % and for Gd_2O_3 between 0 and 15 mol %.

The cubic to tetragonal transformation in zirconia is lowered by 60° to 100°C by 1 mol % and 220° to 250°C by 2 mol % additions. The size of the lanthanide ion has a slight second order effect on the lowering. The optimum lowering of the transformation occurs in the middle of the lanthanide series.

Rare Earth Detects Fluoride

Electrodes have been devised to analyze univalent and divalent cations and anions, as reported in *Chem. and Engr. News, 45*, 146, (June 12, 1967) by G. A. Rechnitz.

A new Orion solid state fluoride electrode has an active membrane of crystalline lanthanum fluoride doped with europium (II), which is in contact with both internal and external solutions. The fluoride ion within the crystal transports the electrical charge and displays a unique selectivity for the ion with some interference from OH^- ion. The europium lowers electrical resistance to (5-10) x 10^4 ohms to facilitate ionic charge transport.

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AMES LABORATORY—

Ceramic Engineering Group

CERAMIC GROUP — In the front row from left are Wayne Calderwood, Assoc.; Cecil Finch, Prin Tech.; Peter Held and Jon Schieltz, both Grad. Assts,; and Dr. David Wilder, Group Leader. In the back row from left are C. D. Wirkus, Assoc.; Denzil Stacy and Keith Johnstone, both Grad. Assts.; and Michael Berard, Assoc. Engr.

The research activities of Ceramic Engineering Group I are centered on the refractory ceramic oxides of proven and potential value to the nuclear program of the Atomic Energy Commission. The research effort is divided into two major parts. The first is concerned with processing of ceramic oxides and the relations of processing to properties; the second is concerned with the measurement of thermal, mechanical, and the electrical properties at useful elevated temperatures.

Sintering studies on Y_2O_3 have involved powder characterization and analysis of sintering kinetics. A new technique to observe the progress of sintering at low shrinkages has been developed utilizing resonance measurements.

Viscous sintering has been studied in low melting arsenic-selenium-sulfur glasses with good structural correlation.

As another part of the study of processing, diffusion rates have been measured in Y_2O_3 and several of the refractory rare-earth oxides. This work has been performed on both single crystals and polycrystalline specimens, employing tracers and a weight gain method. The latter method depends on the availability of sub-stoichiometric oxides which can be readily developed in this group of refractory compounds. Good agreement between the isotope tracer measurements and the weight gain method has been obtained.

Property determinations have included measurements of elastic constants by resonance, and thermal expansion and emissivity. The expansion work is done by conventional dilatometry and includes measurements of Y_2O_3 and the refractory rare-earth oxides. The emissivity studies of the rare-earths including UO_2 are with arc-image techniques, using hi-speed photo sensing. Some heat capacity measurements have also been made.

Several glasses have been studied with attention to the position and co-ordination of a foreign ion. Uranium in silicate glasses has been evaluated by absorption in the infrared and visible. Gadolinium in silicate glasses is presently being studied by magnetic resonance techniques.

The electrical conductivity of Y_2O_3 in both the stoichiometric and sub-stoichiometric oxide is being studied at high temperature to gain insight into the transition from one state to the other.

In 1885, C. F. Auer von Welsbach discovered that praseodymium is one of the two major components of didymium.

The name *praseodymium* is derived from the Greek words *prasios* and *didymos*, meaning green twin.

RADIOCHEMISTRY GROUP

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ment of the equilibrium constant. K_p, of the vapor phase hydrolysis reaction:

$$RCl_3 + H_2O \rightleftharpoons ROCl + 2\ HCl$$

at various temperatures. From the dependence of log K_p vs 1/T, values of ΔG°_T, ΔH_T and ΔS°_T may be derived, and the heats of formation of the oxyhalides may be calculated. In Munich, the reaction has been studied for R=Nd, Pm, Dy, Ho, Er, Tm, and Y. The particularly difficult measurement on the promethium system yielded the first thermodynamic data on this element.

Other studies of the group involve precision single crystal x-ray work on rare-earth oxalates. Data thus obtained were useful in indexing the powder patterns of some of the rarer members; promethium (III)-oxalate, and americium(III)-oxalate.

Studies of mixed oxide systems consisting of an actinide compound (UO_2, U_3O_8, NpO_2, PuO_2), and a lanthanide component (oxides of Eu, Tb, Dy, Ho, Tm) gave useful crystallographic information on parts of the phase diagrams of these systems. These findings may be important in the design of high temperature nuclear reactors employing ceramic fuels which contain a burnable poison.

Vapor pressure measurements on lanthanide and actinide halides have been started and are to be extended to most elements for a systematic study of high temperature thermodynamics.

Future plans of the group include determination of precision x-ray data from single crystals, measurements of thermodynamic data (heats of formation, vapor pressures, molten salt phase diagrams), and magnetic susceptibility measurements.

Most of the studies are carried out with the aim of collecting basic scientific data which might, but not necessarily must, have technological significance.

OUTLOOK

Despite lower color television sales so far this year with a corresponding lower-than-expected demand for phosphors, rare-earth producers remain in an expansionist mood reports *Chem. and Engr. News* 45, (25), 46 (1967).

The major U.S. producers have been busy securing long-term sources and are making substantial progress toward enlarging rare-earth markets apart from the phosphors.

From this strengthened position the rare-earth industry is working toward the day when more non-television applications can be found for the europium-yttrium oxides and markets for the other rare earths can be opened. The activity during the past three years has given the industry the opportunity and incentive to build a more secure raw material position and a more solid economic base.

Rare-Earth Industry

The Rare Earth Industry, R. J. Callow, Pergamon Press, London, 1966, 84p., $2.00 soft cover, $3.50 hard cover, is one of a series of monographs on the chemical industry prepared as teaching manuals for college seniors.

This comprehensive book briefly covers the spectrum of the rare-earth industry from its development with the advent of the "mantle" to its recent products and their uses. Topics covered include rare-earth sources, their recovery from ores and the separation of the individual elements. Thorium, because of its close association with rare-earth ore, is considered as part of the industry.

DETECTS FLUORIDE

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The electrode responds to F^- concentrations down to 10^{-6}M. The useful pH range of the electrode for fluoride ion measurements is limited by the formation of hydrogen fluoride in the acidic region and by hydroxide ion in the alkaline region.

Magnetic Behavior Of Rare Earths

The literature on the magnetic behavior of materials which appeared in 1965 has been summarized in *Magnetism and Magnetic Materials: 1966 Digest*, edited by C. W. Haas and H. S. Jarrett and published by Academic Press. A chapter by R. J. Joenk deals exclusively with the rare-earth metals and alloys.

Nine other chapters also contain useful information related to the rare earths. They deal with magnetic structures, nonmetals, electron spin resonance, preparation and structure of magnetic materials, nuclear magnetism, resonance and relaxation phenomena, magnetoelasticity, optical properties, and thermal and transport properties

MEETINGS

7TH RARE-EARTH CONFERENCE

The Seventh Rare-Earth Research Conference will be held Oct. 13-16, 1968 at the Hotel Del Coronado, San Diego, Calif., according to J. F. Nachman, Solar, San Diego, Calif. 92112, conference chairman. Details of conference arrangements will be published as they become available from the conference committee.

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Europium Oxide Switching Properties

The quasistatic and dynamic switching properties of EuO are discussed by K. Y. Ahn and M. W. Shafer, *J. Appl. Phys. 38*, 1197 (1967).

Samples were prepared by pressing EuO into toroidal cores and firing at various temperatures to obtain different grain sizes. Quasistatic measurements were performed in the range 4.2° to 70°K at 105 cps. The hysteresis loops formed were not square.

Ahn and Shafer observed that the coercivity and magnetization decreased slowly with increasing temperature but decreased rapidly near the ferromagnetic Curie temperature.

From the breaks in the switching curves they concluded that more than one switching mechanism was present. For the low-field region the flux reversal was assumed to be caused by domain-wall motion while in the high-field region it was thought to be caused by non-uniform motion.

Because of it's large switching coefficients EuO cannot compete with ferrites as computer storage elements. However, owing to its high resistivity, non-square hysteresis loops, and large magnetization, Eu may have many low temperature applications.

RARE EARTHS IN THE NEWS

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MAY POWER HEART PUMP

Critically ill heart patients will benefit if efforts to perfect a radioisotope-powered heart-pump engine are successful. Possible power sources for the proposed heart-pump engine are ^{147}Pm, ^{171}Tm, and ^{238}Pu. Aerojet-General Corp., Donald W. Douglas Laboratories, Thermo Electron Engineering Corp., and Westinghouse Astronuclear Laboratory have contracted with the U.S. Atomic Energy Commission to develop the device.

COMPLEXES

A useful review of various aspects of the rare-earth complexes is now available in *Complexes of the Rare Earths* by S. P. Sinha (Pergamon Press, New York, 1966).

The first half of the book discusses stabilities of the complexes and is divided into the following categories:

1. Coordination through the nitrogen of the donor molecule.
2. Coordination through the oxygen of the donor molecule.
3. Coordination through both the oxygen and nitrogen of the donor molecule.
4. Coordination through atoms other than nitrogen and oxygen.

Topics considered in the second half of the review are the spectral characteristics, luminescence in chelates, and laser applicability of the rare earths. In addition, the actinides are briefly reviewed with respect to spectra and stability of a few of their complexes. The price of the book is $7.50.

Gagarinite, named after the world's first astronaut Yu. A. Gagarin, is a sodium-calcium-rare-earth fluorite ($NaCaRF_6$) discovered in Russia in 1958.

Reports, Brochures, Booklets

RARE EARTHS 1965

The events concerning rare-earth developments in 1965 are summarized by J. G. Parker in "Rare-Earth Minerals and Metals, 1965", a chapter from *Bureau of Mines Minerals Yearbook*. He reports that for the first time industrial consumption of all rare-earth materials exceeded 4000 tons of equivalent RE oxides. Europium and yttrium oxides for color television phosphors were sold at rates four and five times greater, respectively, than in 1964.

Uses for RE compounds were 39% for television and electronics, 20% for mischmetal, 15% for polishing powders, 5% for petroleum catalysts, and 5% for cored carbon arcs. Parker mentions several specific and interesting uses of different RE compounds. Also, he reviews new price quotations, exports and imports, and lists the number of short tons of monazite produced from 1961 to 1965 by ten leading countries. Also covered are several aspects of rare-earth research and technology.

This publication may be obtained for $0.10 from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

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