

The importance of the work of the scientists to the ultimate control of tuberculosis was emphasized in greetings extended by James E. Perkins (managing director of the National Tuberculosis Association). "Diagnostic specificity," he said, "depends to a major extent upon the availability and use of pure, specific antigens. With further progress in research in the sphere of antigens we will be in a position to determine more nearly precisely the interrelationships of genera and species of mycobacteria, be more certain in our diagnostic procedures, more nearly accurate in our prognoses, determine better the extent of the tuberculosis problem at a given time in a given area, measure more accurately subsequent progress in the reduction of tuberculous infection, and improve our efficiency in our control procedures, particularly with regard to determining more accurately candidates for secondary chemoprophylaxis."

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Protactinium Chemistry

Although protactinium was discovered 50 years ago, it remains one of the least studied elements in the periodic system. Now, under the joint stimulus of thorium reactor programs and the British isolation of more than a hundred grams of the element, protactinium chemistry is being actively investigated in a dozen laboratories throughout the world. These recent activities were the subject of a two-day symposium on the chemistry of protactinium held at Gatlinburg, Tennessee, (25-26 April) under the sponsorship of the Oak Ridge National Laboratory. The papers presented covered a wide range of activities, including solution and solid state chemistry, adsorption behavior (Kirby, Mound Laboratory), and applications to the dating of ocean bottom sediments (Rona, Oak Ridge Institute of Nuclear Studies).

In the processing of thorium reactor fuels, the isolation and recovery of protactinium have been an unsolved prob-

lem. This becomes particularly important in homogeneous thorium breeder reactors where continuous removal of protactinium from fuel or blanket solution is desirable in order to minimize parasitic neutron captures by Pa^{233} . A promising new scheme for protactinium isolation, that involves the adsorption of protactinium from acid nitrate solutions on columns of silica gel or unfired, pulverized Vycor glass, was reported (Moore and Rainey, Oak Ridge National Laboratory); it features simplicity of application and good decontamination factors from the major fission products. The required low concentration of protactinium in breeder-blanket solutions can also be maintained by a coprecipitation of protactinium as a peroxide that also includes a small fraction of the thorium content (McDuffie and co-workers, Oak Ridge National Laboratory). Of course, all these methods require that protactinium be sufficiently stable against precipitation or adsorption in the acid thorium nitrate solution for a long enough time to allow side-stream removal. That this condition can be met in a reactor environment has not been demonstrated, but laboratory-scale experiments by Barton and co-workers (Oak Ridge National Laboratory) in pressurized systems indicate a sufficient stability up to at least 160°C , provided that the acid concentration is high enough.

Similar problems in the molten-salt reactors received attention in a paper by Shaffer and co-workers (Oak Ridge National Laboratory), who reported the successful precipitation of protactinium from a molten $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ system by the addition of a few weight percent of solid beryllium or thorium oxide.

Investigations of the fundamental chemistry of protactinium were reported from laboratories in the United States, England, France, and Germany. The study of ionic species by two-phase equilibrium techniques continues to be a popular though difficult approach. The complexities introduced by the well-known tendency to protactinium species to hydrolyze and polymerize were discussed by Hardy (Harwell) in the nitric acid-tributyl phosphate system. Paper chromatographic evidence for the existence of at least two species in the organic phase was presented together with evidence for equilibria between monomers and inextractable polymers of various degrees of aggregation in the aqueous phase. The polymerization of protactinium in sulfuric

acid solution was discussed by Campbell (Oak Ridge National Laboratory) who reported on solvent extraction by amines. The hydrochloric acid system was examined by Scherff and Herrmann (Mainz) by diisobutylcarbinol extraction with careful attention to the distribution of all components and the activity coefficients involved. Their study included some analytical work on the organic phase. Hydrolytic and solvent extraction behavior in dilute perchloric acid systems was also examined by extraction with the chelating agent, thenoyl-trifluoroacetone, as reported by Muxart (Paris).

Another approach to the problems of ionic species in solution based on spectroscopic studies is gaining favor. Preliminary Raman spectra of K_2PaF_7 (whose preparation seems not to be so simple as once thought) were obtained in an extension of techniques successfully applied to the niobium and tantalum complex fluorides (Keller, Oak Ridge National Laboratory) and work on the ultraviolet absorption spectra is continuing. It still seems fair to state, however, that no ionic species of protactinium in aqueous solution has been positively characterized.

Considerable progress in the preparation of solid compounds of protactinium has been made recently, though not without some surprises. The dry preparation of the tetra- and pentavalent fluorides has been further investigated (Stein, Argonne). The pentafluoride seems not to be as volatile as previously reported, and the oxyfluoride prepared either from oxidation of PaF_4 or hydrolysis of PaF_5 has the composition $\text{Pa}_2\text{O}_2\text{F}_6$.

The peroxides precipitated from various mineral acids have been studied (Bouissieres and co-workers, Paris) and informal discussions revealed other studies in progress on the protactinium oxides (at Harwell), sulfates (at Harwell and Mound), and complex fluorides (at Cambridge and Oak Ridge National Laboratory).

While it is too soon to say that any real understanding of the chemistry of protactinium has been achieved, the stimulation of this conference should do much toward increasing the interest in this little understood element.

The proceedings of the symposium will be published by the Technical Information Division (USAEC).

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