

## CHEMISTRY OF THE HEAVY ELEMENTS

RECENT work on the chemistry of the heavy elements formed one main topic of a symposium, organised by the Chemistry Division of the Atomic Energy Research Establishment, Harwell, on behalf of the Chemical Society, and held at Rhodes House, Oxford, during March 28–30. The discovery of the transuranic elements, neptunium, plutonium, americium and curium, has demonstrated that a new transition series, like that of the rare earth elements, arising from the filling of  $5f$ -electron levels, commences at some stage subsequent to actinium (atomic number 89). Any attempt to trace the chemical relationships between these heavy elements, and the elements standing above them in the Periodic Table, shows how fragmentary and inexact is the existing knowledge even of the chemistry of uranium and thorium, although the former was discovered by Klaproth in 1789 and the latter by Berzelius in 1828.

The first session of the symposium was devoted to the elements other than uranium. Dr. R. E. Connick (Radiation Laboratory, University of California) gave a review of the chemistry of the transuranic elements. These display a clear similarity among themselves, as is shown by the existence in solutions of the  $M^{4+}$  cations of all elements from uranium to americium, of  $M^{3+}$  cations from uranium to curium, and of the oxyocations  $MO_2^+$ ,  $MO_2^{2+}$  for the quinquevalent and hexavalent states of uranium, neptunium and plutonium. Curium is invariably trivalent, americium most stable in its trivalent state; and these elements are separable only with difficulty from the rare earth elements—most readily by ion-exchange methods like the separation of the rare earths themselves. The similarity between rare earth and transuranic elements extends to their narrow-banded absorption spectra in solutions. In particular, the resemblance between the absorption spectra of  $Ga^{3+}$  and  $Cm^{3+}$  suggests that in the latter the electronic group  $5f^7$  is present. As was pointed out by Dr. A. G. Maddock (Cambridge) in the subsequent discussion, this would imply that the  $5f$ -series virtually commences after actinium ( $Z = 89$ ), even although the crossing-over of the  $6d$ - and  $5f$ -levels may occur only at some higher atomic number. The variable valency of the first members of the series points to a much weaker screening of  $5f$ -levels than of the  $4f$ -levels of the rare earth elements.

Dr. M. Haissinsky (Institut du Radium, Paris), in a paper on "The Position of the Cis- and Transuranic Elements in the Periodic System", argued that classifications and terminology applied to the heavy elements must conform to the known chemical relationships of the elements. Thorium is the perfect homologue of zirconium and hafnium, uranium that of molybdenum and tungsten, as is confirmed by the new contributions to the chemistry of thorium and uranium presented later to the symposium. To classify these elements, and protoactinium, with actinium in an 'actinide' series, as exemplifying any 'horizontal' relationship, is not logical. There is such a horizontal relationship between uranium, neptunium and plutonium, in their highest valence states, and if this relationship cannot be extended to americium and curium, the reason may, in part, be in our insufficient chemical knowledge of these elements. This point was, indeed, cogent: participants in the discussion were agreed that the study of transuranic

elements on a radio-tracer scale in solution, or by ultramicrochemical methods, is at best incomplete, and provides no substitute for the methods of classical inorganic chemistry.

Contributions to the chemistry of thorium and protoactinium followed this discussion. Mr. R. W. M. d'Eye (Harwell) described work showing the existence of compounds of the hitherto unknown bivalent and trivalent states of thorium. Two iodides,  $ThI_2$  and  $ThI_3$ , have been characterized analytically and by X-rays, and have been shown to resemble in every respect the corresponding compounds of zirconium, but to have no resemblance to the cerous salts. The evidence suggests that in the  $Th^{2+}$  and  $Th^{3+}$  cations, the unutilized valence electrons are disposed in  $6d$ -orbitals; if so, the occupation of  $5f$ -orbitals cannot begin before protoactinium.

Since it was stated that in the  $U^{4+}$  ion two electrons are in  $5f$ -orbitals, the chemistry of protoactinium assumes considerable interest. Dr. A. G. Maddock and Mr. G. F. Miles discussed the tracer chemistry of protoactinium solutions. The important result obtained was the demonstration that, except in the most acid solutions (for example, 6 *N* hydrochloric acid), protoactinium solutions are hydrolysed to radiocolloids. Coprecipitation is therefore not selective and affords no evidence for isomorphism of protoactinium compounds with those of tantalum, zirconium or other elements. There is no evidence for the formation of soluble protoactinates, analogous to the tantalates, nor—in tracer solutions at least—for the reducibility of quinquevalent protoactinium to any lower valence state. Only in stable complex salts—for example, with citrate, fluoride or cupferron—can protoactinium be brought into true solution. The cupferron complex is soluble in organic solvents, and, in conjunction with coprecipitation of protoactinium on manganese dioxide, should afford a convenient means of isolating protoactinium in macroscopic quantities.

M. Haissinsky and G. Bouissère, working on a microchemical, as distinct from a tracer, scale, reported that protoactinium can be reduced from the quinquevalent to a lower state. Coprecipitation with lanthanum, and separability from zirconium, suggest that  $Pa^{3+}$  is formed thereby, the  $Pa^{3+}/Pa^{4+}$  potential being not very different from the  $Cr^{2+}/Cr^{3+}$  potential.

Subsequent discussion emphasized the need for much more study of the chemistry of protoactinium. Prof. O. Hahn (Göttingen), in discussing the original isolation of protoactinium in his institute in Berlin, pointed out that one well-crystallized compound,  $K_2PaF_7$ , at least, and probably the oxide  $Pa_2O_5$ , as well, has been definitely characterized. Dr. Maddock recalled an American statement that protoactinium oxide has the fluorite structure. In the view of the reporter, even if this is confirmed, it does not necessarily imply, in the absence of chemical evidence, that the oxide is  $PaO_2$ . The chemistry of the heavier transition elements provides numerous instances of oxides with defect structures, so that formulae based on X-ray data only must be treated with reserve.

The second session of the symposium was devoted to the complex chemistry of uranyl solutions. Mr. J. Sutton (Harwell) discussed the constitution of uranyl perchlorate solutions, as evidenced by cryoscopic measurements, *pH* measurements, conductivities and absorption spectra. In such solutions, the cations  $U_2O_5^{2+}$  and  $U_3O_8^{2+}$  are successively formed by condensation reactions; further hydrolysis can be interpreted as involving hydroxo-complexes  $[U_3O_8.OH]^+$ ,

[ $U_3O_8(OH)_2$ ] (in metastable solution) and ultimately the anionic complex [ $U_3O_8(OH)_3$ ]<sup>-</sup>. Mr. T. V. Arden (Teddington) and Mr. F. W. Cornish (Exeter) confirmed this general mechanism of hydrolysis, but gave evidence for the formation of still more condensed poly-cations, for example,  $U_4O_{11}^{2+}$ , in solutions of uranyl nitrate, chloride and sulphate. Dr. R. H. Betts and Miss R. K. Michels (National Research Council, Canada) described measurements on ionization equilibria in uranyl nitrate and uranyl sulphate. Precise absorption spectrophotometry makes it possible to determine the extent of ion-pair formation, and the formulae of the species concerned can be deduced from the equilibrium data. Measurements of this kind require a knowledge of activity data for concentrated and multi-component solutions. An ingenious method of calculating such data was described by J. F. Duncan, E. Glueckauf, H. A. C. McKay and A. R. Mathieson (Harwell); the uranyl ion activity can be compared directly with that of pure uranyl nitrate solutions by means of liquid-liquid partition equilibria, and the activity of the second electrolyte in a mixture can be compared with that of the uranyl ion by an ion-exchange method. The solubility of uranyl nitrate hexahydrate in ethers and ketone solvents has long been known. Mr. A. R. Mathieson has isolated molecular compounds  $UO_2(NO_3)_2 \cdot 3H_2O \cdot K$  ( $K$  = acetone or other ketone molecule) from such solutions, and shown their existence in solution.

In a further session of general chemistry, Dr. F. G. Mann and Mr. J. A. C. Allison (Cambridge) described complex compounds of uranium tetrachloride with tertiary alkyl phosphines, [ $UCl_4(R_3P)_2$ ], analogous to those formed by  $SnCl_4$ . A paper on the lower oxides of uranium, by Mr. K. B. Alberman (Harwell), revealed a complex system comparable with that of the oxides of molybdenum and tungsten. Oxidation of uranium oxide,  $UO_2$ , proceeds at quite low temperatures, apparently by a diffusion-controlled process. A non-stoichiometric oxide phase is thereby formed, with cubic symmetry up to the composition  $UO_{2.2}$ , becoming tetragonal with increased oxygen content up to the level  $UO_{2.3}$ , at which oxidation ceases. These oxides are unstable above 250°, and split up into two-phase mixtures of  $UO_2$  proper, a well-defined intermediate phase with composition close to  $UO_{2.20}$ , and the previously known  $U_3O_8$  or  $U_2O_5$  phase. Dr. H. A. Wilhelm (Iowa State College) reviewed the high-temperature phase equilibria in the uranium-carbon and thorium-carbon systems. UC, with rock-salt structure, forms solid solutions with UO and UN;  $UC_2$  appears able to incorporate carbon in excess of the ideal formula. It was pointed out in discussion that this suggests an analogy with sulphide chemistry, in the ability of pyrite-type sulphides to incorporate an excess of sulphur. The miscibility of UC and  $UC_2$  at high temperatures, or the possible existence of an intermediate phase  $U_2C_3$ , is shown by the beautiful Widmanstätten unmixing structures in materials of that composition.

The only contribution on polonium chemistry came from Dr. P. Bonet-Maury and M. Leport (Paris). The formation of hydrogen peroxide from water by the action of polonium  $\alpha$ -rays is inhibited if there is direct contact of the solution with the polonium source, and polonium has a strong specific catalytic effect on the decomposition of hydrogen peroxide. Dr. Haissinsky pointed out that true peroxides are formed only by elements with electronegativities less than that of hydrogen. The action of polonium might

be interpreted if, as an exception to the general rule, it formed a per-compound from tetravalent polonium rather than from the highest valence state. Dr. R. E. Connick (Berkeley) cited the reduction of plutonium (VI) compounds, with destruction of hydrogen peroxide, as an analogy:  $Pu(VI) \xrightarrow{H_2O_2} Pu(V) \rightarrow Pu(VI) + Pu(IV)$ : Pu (IV) is then either converted to peroxide or reduced to Pu (III). Dr. Maddock, however, inquired whether the chemical effects of the recoiling polonium atoms were not of some possible importance.

Analytical aspects of the subject were dealt with in two papers. Dr. R. B. Jacobi (Harwell) described improved techniques for the determination of radon and radium in natural waters. Mr. T. V. Arden, Dr. F. H. Burstall and Dr. R. P. Linstead (Chemical Research Laboratory, Teddington) gave an account of a new and highly selective method for the detection and determination of small amounts of uranium, based on their use of paper chromatography. When an organic solvent is allowed to diffuse over a strip of filter paper, or a column of pulp, impregnated with a dilute nitric acid solution of the sample, the high solubility of uranium in the solvent makes this element move with the advancing front of solvent, so that the appropriate section of paper can be 'developed' to reveal uranium, or isolated, ashed and subjected to quantitative micro-analysis. The movement of most other elements is relatively small, and the method is useful in the analysis of low-grade minerals and similar materials. J. S. ANDERSON

## OBITUARIES

### Prof. Felix d'Herelle

THE death in Paris on February 22 has been announced of Prof. Felix d'Herelle, best known for his monumental work on bacteriophage.

Felix d'Herelle was born at Montreal, Canada, in 1873, of French-Canadian parentage, and though he retained throughout life his British nationality, of which he was always proud, he gave to his acquaintances the impression of being rather more French than British in temperament and outlook. Educated at the Lycée Louis le Grand, Paris, he took his baccalauréat in 1888, after which he returned to his native Canada to take up the study of medicine and to graduate M.D. at Montreal. During 1901-7 he was professor of bacteriology at Guatemala, to become bacteriologist to the Mexican Government during 1908-9. In 1909 he joined the staff of the Pasteur Institute, Paris, as assistant, to be promoted later to *chef de laboratoire* (1914-21). During these years his services were much in demand to go on special missions, at the request of various foreign Governments. Thus he visited the Argentine (1911-13), Turkey (1914), Tunis (1915) and Indo-China (1921). Then he went to the University of Leyden as visiting professor during 1922-23. In 1924 he was appointed to the International Quarantine Council, Egypt, as director of laboratory service, with a laboratory at Alexandria. Here he remained until 1926, when he went to India on a special mission at the request of the British Government. In 1928 he was appointed professor of protobiology at Yale University, from which post he retired in 1933 to found the Laboratoire du Bacteriophage, Paris. Between 1934 and 1936 he was entrusted by the Government of the