It may also be seen from Fig. 22 that E_{br} is higher for polar polymers than for non-polar ones. For example, comparison of curves *4* and *7* shows that the introduction of 8% of chlorine into polyethylene increases E_{br} to practically twice the value at low temperatures, although at higher temperatures the difference is no longer found.

Fig. 23 shows E_{br} for PE_{HP} as a function of temperature, as determined by a number of workers [42,44-6]. It may be seen from the figure that the values of E_{br} for quenched and slowly cooled samples are the same, i.e. the reduction of the degree of crystallinity from 60% to 50% by quenching has no effect on the breakdown voltage. However, comparison of the variation of the degree of crystallinity and the breakdown voltage with temperature shows that these two relationships are similar, which suggests that a considerable change in the degree of crystallinity would change E_{br}.

It is interesting that, as may be seen in Fig. 23, the values of E_{br} obtained at a frequency of 3.3×10^9 c/s and with direct current fall on the same curve.

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NEW STUDIES ON THE CHEMISTRY OF PROTOACTINIUM

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INTRODUCTION

The existence of an element occupying the position between thorium and uranium in the Periodic System was pre-

dicted in 1871–1872 by Mendeleev[1,2], who described the chief chemical properties of the element and suggested for it the name "eka-tantalum". Protoactinium was discovered in 1918 and in the following 40 years considerable progress has been made in the study of the chemistry of this rare element*; nevertheless, protoactinium can still justifiably be regarded as one of the least studied elements. In the words of Katz and Seaborg[4], protoactinium at present enjoys "a well-deserved reputation as the most capricious and elusive of the actinide elements". The recent renewal of interest in protoactinium is due primarily to the production of large quantities of Pa^{233} during the production of U^{233} by neutron bombardment of natural thorium, and also to the continuing argument regarding the position of the start of the actinide family.

There are a number of review articles on the chemistry of protoactinium[4-12]; the most recent, by Haissinsky and Bouissieres[13], covers papers published up to the end of 1957. The present paper deals chiefly with work published during the period 1957–1958.

ISOLATION OF PROTOACTINIUM FROM NATURALLY OCCURRING SOURCES

A large proportion of the information on the chemistry of protoactinium has been obtained in the course of its isolation from naturally occurring sources, chiefly the waste residues from the production of radium or uranium. At present, the only raw material used for the isolation of protoactinium is the waste material obtained during the isolation of uranium from uranium ores, and the nature and protoactinium content of the raw material are determined by the methods used to isolate the uranium and by the uranium content of the original ore. Protoactinium is isolated, as a rule, from the waste products from the treatment of rich uranium ores and concentrates containing up to 60% U_3O_8. When radioactive equilibrium is established, 1% uranium in the ore corresponds to a protoactinium content of 3.1 mg/ton.

The behaviour of protoactinium during the isolation of the uranium depends on the type of ore, and on the nature and concentration of the acid used in the leaching process. If nitric acid alone is used, approximately half of the protoactinium present in the ore goes into solution[14,15]. During extraction by sulphuric acid or a mixture of sulphuric and nitric acids, the quantity of protoactinium dissolved increases; increase in the proportion of sulphuric acid in the mixture and a high total acidity favour the transfer of protoactinium to the solution[16,17]. Increase in the phosphorus content of the ore hinders the dissolution of protoactinium[17]. The behaviour of protoactinium during the isolation of uranium is also influenced by the presence in the ore of natural protoactinium carriers — zirconium, titanium, tantalum, and niobium.

The nature of the raw material chiefly used for the isolation of protoactinium has changed with the methods used for isolating uranium. The acid–soda method for the treatment of uranium ores was chiefly used in the initial years of the development of the atomic industry, and the protoactinium was concentrated in the so-called "carbonate residue" precipitated when the acidic solution containing the uranium was treated with excess sodium carbonate. The "carbonate residue" contained ~65% of the protoactinium in the original ore; its Pa^{231} content amount to 300–350 mg/ton.[3] The isolation of protoactinium from this type of raw material is described by Thompson and coworkers, and others[18,19]. With the development of extraction methods for the isolation of uranium, it became possible to extract protoactinium directly from the waste solutions left after the removal of uranium[20,21]. These solutions contain up to 50 mg of Pa^{231} per m^3. The protoactinium-rich precipitate obtained from these solutions at low acidity contains 100–300 mg Pa/ton and is a convenient starting material for the isolation of protoactinium[22]. The starting material of highest protoactinium content is the so-called "ethereal sludge" described below.

Since the protoactinium content of the raw material is extremely low, the first stage in the isolation is the concentration of the protoactinium into a small volume, using either extraction or precipitation methods. Extraction methods are normally used when the starting material for the isolation of the protoactinium is a solution. Extraction from nitric acid solution by tributyl phosphate is unsuitable for concentration purposes; since the efficiency is low. For example, Peppard and coworkers[21] could extract only 5–35% of protoactinium with tributyl phosphate for a 20-fold decrease in volume.

Acid esters of phosphoric acid are exceptionally powerful extracting agents for protoactinium[23,24] and their use for the extraction of protoactinium and thorium-230 (ionium) from the nitric acid solutions obtained after removal of uranium by tributyl phosphate has been described by Shevchenko and coworkers[15]. The original solution containing up to 10 mg/m^3 Pa^{231} is treated with one-twentieth of its volume of a 15% solution of a mixture of mono- and diisopentyl phosphoric acids in isopentyl acetate. The extract is washed with dilute nitric acid to remove part of the impurities extracted into the original phase, chiefly trivalent iron, after which the protoactinium is re-extracted with saturated ammonium carbonate solution. The iron remaining in the original phase after washing is also re-extracted, with the formation of soluble carbonato complexes[25]. Iron and other heavy metals are removed by precipitating their sulphides directly from the carbonate solution. The black precipitate obtained when the extract is treated with ammonium sulphide contains almost no protoactinium, which is kept in solution by the excess ammonium carbonate. (An analogous method for separating heavy metals is used in the purification of thorium[26]. The purification of protoactinium from heavy metals by precipitation of their sulphides from tartrate solution has also been decribed[27]). The ammonium carbonate is decomposed by heating and a concentrate containing up to 0.01% of protoactinium is precipitated from the filtrate. The concentrate also contains Zr, Ti, Sc, U, Th, and up to 1% of thorium-230 (ionium) from the original raw material. Approximately 85% of the original Pa and 80% of the original Th^{230} are present in the concentrate, which contains no α-emitters other than the isotopes of thorium, protoactinium, and uranium. The radiochemical purification of protoactinium thus involves merely its separation from Th^{230}, and this can be done in the usual way, for example, by treating the concentrate with dilute hydrofluoric acid and carrying out a double precipitation of thorium fluoride from the filtrate. This yields radiochemically pure Pa^{231} specimens with the α-particle energy spectrum characteristic of this isotope (Fig. 1). No attempt appears to have been made to extract Pa^{231} from such dilute solutions.

The most highly developed method is that used for the isolation of protoactinium from the ethereal sludge from the

* In 1950 the total quantitity of pure protoactinium in all the laboratories in the world amounted to only about 2 g[3].

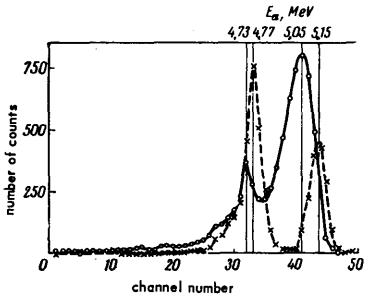


Fig. 1. α-Radiation spectrum of protoactinium-231. O — Pa^{231}; × — Np^{237} + Pu^{239}.

uranium plant at Springfield, England[17], where rich ore concentrates containing 60–70% U_3O_8 [28] are leached with a mixture of sulphuric and nitric acids, and up to 95% of the protoactinium accompanies the uranium into solution. Uranium peroxide $UO_4 . 2H_2O$ is precipitated from the resultant solution at pH 2, and carries down most of the protoactinium. The precipitate is dissolved in nitric acid and the solution extracted with ether. The dissolution is carried out at very low acidity and the resultant sludge, containing ~25% of the protoactinium present in the original raw material, is most convenient for the isolation of the element. Considerable quantities of uranium, iron, silicic acid, barium, zirconium, lead, and other impurities are also present. The protoactinium content of the sludge may amount to 3.7 g/ton, which is more than 10 times the quantity present in the carbonate residues.

The scheme illustrated in Fig. 2 has been suggested for the preliminary concentration of protoactinium, which is isolated from hydrofluoric acid solution by making use of its tendency to concentrate in the black deposit formed on sheets of aluminium metal placed in the solution. It is not yet clear whether separation of the protoactinium results from hydrolysis or from reduction to the tetravalent state.

The protoactinium is extracted from the resultant hydrochloric acid solution with two 25 litre portions of diisobutyl ketone. The combined extracts are washed with 25 litres of 8 *N* HCl and the protoactinium is re-extracted with two 2.5 litre portions of 8 *N* HCl containing HF; 2 moles $AlCl_3$ per mole HF are then added to the re-extract, and the extraction cycle is repeated: in this way, 100 kg of sludge yields 0.5 litre of a solution containing 77% of the protoactinium in the original sludge. Further purification of the protoactinium can be achieved in various ways. Good results are obtained by precipitating the protoactinium from sulphuric acid solution with hydrogen peroxide, dissolving the precipitate in 2 *N* HF, and precipitating the sparingly soluble potassium heptafluoroprotoactinate, K_2PaF_7. The Pa_2O_5 obtained in this way contains less than 1.5% of impurities, and about 1 g of Pa^{231} has been isolated by the method.

A more economical scheme has been suggested for the simultaneous isolation of uranium and protoactinium from large quantities of etheral sludge[29]. The sludge is treated in the cold with 4 *N* HNO_3 + 0.1 *N* HF; more than 95% of the protoactinium and about 99% of the uranium goes into solution. The uranium is extracted completely from the solution by 20% tributyl phosphate solution. Attempts to separate protoactinium from the purified solution by normal ion-exchange, extraction, and precipitation methods have not given good results, but it has been found that the addition of aluminium chloride, in the cold, to the purified solution gives rapid and reproducible precipitation of 85–95% of the protoactinium. It is assumed that the precipitate is formed as a result of hydrolysis and the precipitation of insoluble phosphates after the fluoride ion has been bound in a fluoroaluminate complex. This mechanism does not, however, explain why the precipitation of protoactinium is less complete when aluminium nitrate is added to the solution. Silicic acid, aluminium, and phosphorus are removed from the resultant precipitate by treating twice with concentrated caustic soda solution and washing thoroughly. The residue, which contains chiefly iron and zirconium, is dissolved in hydrochloric acid. If removal of the phosphate is incomplete, zirconium phosphate is formed during the dissolution and carries down considerable quantities of protoactinium.

Attempts to use ion-exchange methods for the further purification of protoactinium have proved unsuccessful, due to the very low capacity of the resin for Pa (~ 50 μg/g resin) in the presence of large quantities of zirconium, which leads to poor separation from this element. Further purification and concentration of protoactinium is therefore carried out by the diisobutyl ketone extraction described above. The factor for purification from Fe and Zr is over 1000, and the solution volume is reduced by a factor of 50 in 1 cycle. When the solution is left to stand, part of the protoactinium is hydrolysed, and the extraction is less satisfactory. To restore the extractability of the protoactinium, the solution is treated, before extraction, with a small quantity of HF, which is then bound with a 5-fold excess of $AlCl_3$. The hydrolysed solutions show a sharp maximum in the ultra-violet range of the absorption spectrum, at λ = 260 mμ.[30]

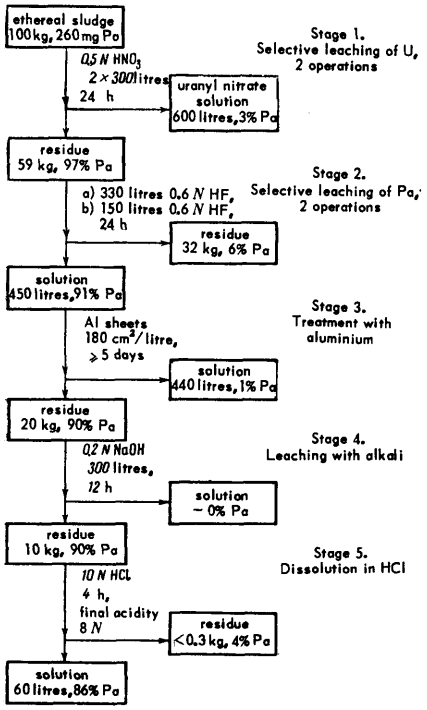


Fig. 2. Preliminary concentration of protoactinium-231[17].

The final purification of protoactinium involves 8 extraction cycles with diisobutyl ketone, adsorption from 8 *N* HCl on an anion exchange column, which is then washed with 7 *N* HCl, elution with 7 *N* HCl + 0.5 *N* HF, and precipitation of K_2PaF_7. The yield of protoactinium during the operations of the final purification is 68%.

At present the Springfield plant has ~ 50 tons of ethereal sludge, from which more than 100 g of protoactinium can be isolated[31].

The behaviour of protoactinium during the treatment of Madagascar uranothorianite ores containing ~ 40 mg/ton of protoactinium has been studied by Bouissieres and coworkers[32]. On treatment with boiling concentrated nitric acid, 65–75% of the protoactinium remains in the insoluble residue. Isolation of protoactinium from this material requires a double fusion with sodium bisulphate, which is difficult on a large scale.

ARTIFICIAL PREPARATION OF PROTOACTINIUM-231

Work on the chemistry of protoactinium is hindered by the low availability of the element. It is therefore necessary to examine briefly methods for the artificial preparation of Pa^{231}, although this subject is not directly related to the chemistry of protoactinium.

One method is by the irradiation of thorium-230 with slow neutrons, when the following reaction occurs:

$$Th^{230}(n, \gamma)Th^{231} \xrightarrow[23.5\ h]{\beta} Pa^{231}.$$

Seaborg considers that this method is more convenient than the difficult isolation of protoactinium-231 from natural sources[4,33,34]. It should be remembered, however, that the irradiated Th^{230} specimens have a high activity due to Pa^{233} and fission products. The isotopes, Pa^{233}, U^{233}, and fission products are produced as a result of the unavoidable presence of thorium-232 in the specimens.

The irradiation of Th^{230} also leads to the secondary reaction:

$$Pa^{231}(n, \gamma)\, Pa^{232} \xrightarrow[1.32\ days]{\beta} U^{232}.$$

The thermal-neutron capture cross-sections for these reactions are 50 [35] and 293 [36] barns respectively, so that on prolonged or very intense irradiation, a considerable fraction of the Th^{230} is converted to U^{232}. Our calculations show that for a flux density of 5×10^{13} neutrons $cm^{-2}sec^{-1}$ and irradiation time 10 months, 5.2% of the original Th^{230} may undergo conversion to Pa^{231}, the yield of U^{232} under these conditions being 1.1%. The maximum possible conversion of Th^{230} to protoactinium (11.8%) requires almost 5 years at the above flux density, and in the process 19.1% of the Th^{230} is converted to U^{232}.

Since the equilibrium thorium-230 content of uranium ores is more than 50 times greater than their protoactinium-231 content, this method may become important in the future, particularly since the thorium-230 enrichment of production wastes is often greater than the protoactinium enrichment. Methods for isolating thorium-230 from uranium ore residues are fairly well developed[15,21,29,37-39]. Peppard and coworkers have obtained about 66 g of thorium-230 by one of these methods[40].

Another method for the artificial preparation of protoactinium-231 is by irradiating thorium-232 with fast neutrons. At neutron energies above 6.35 MeV, the nuclear reaction is

$$Th^{232}(n, 2n)Th^{231} \xrightarrow[1.07\ days]{\beta} Pa^{231},$$

first discovered by Japanese workers in 1938[41].

Recently, as a result of the extensive use of thorium for the artificial preparation of U^{233}, it has become possible to isolate considerable quantities of protoactinium-231 from the waste products obtained after treatment of the irradiated thorium. The effective cross-section of the reaction of Th^{232} $(n, 2n)$ on irradiation with thermal neutrons depends on the relative quantity of fast neutrons in the total neutron flux and is usually 0.002–0.013 barn[42]. Calculation shows that for an integral flux of 10^{21} neutrons cm^{-2}, which corresponds approximately to irradiation with a flux of 10^{14} neutrons $cm^{-2}sec^{-1}$ for 100 days, the Pa^{231} content of the irradiated thorium amounts to 1.6–10.4 g ton^{-1}. When 1 ton of thorium is irradiated under these conditions, ~ 6 kg of thorium is converted to uranium-233, so that the yield of Pa^{231} relative to U^{233} is 0.03–0.17%. In the majority of methods used at present for treating the irradiated thorium, the Pa^{233} is isolated for the subsequent removal of the U^{233} which accumulates in it.[43] The product remaining after removal of the U^{233} should contain considerable quantities of comparatively pure Pa^{231}. It has been suggested that U^{233} will be the chief nuclear fuel of the future, so that the residue from its production may in time become an important source of Pa^{231}.

METHODS FOR DETERMINING PROTOACTINIUM

The isolation of protoactinium from natural sources and artificial products is hindered by the difficulties encountered in the quantitative determination of the element in the presence of large quantities of foreign α-emitters and macro-impurities.

For the radiochemical purification of protoactinium after separation from macro-impurities, it is convenient to coprecipitate the element with zirconium α-hydroxyphenylacetate, as proposed by Starik and coworkers[44,45]. Other useful analytical methods include extraction from hydrochloric acid solution by diisopropyl ketone and coprecipitation from HF solution with $BaZrF_6$ and BaF_2.[46] It is desirable in all cases to determine simultaneously the chemical yield of Pa^{231} by adding beforehand a known quantity of Pa^{233} to the weighed test specimen. The necessity to determine the chemical yield complicates the procedure and means that isotopic equilibrium between the different chemical forms of protoactinium must be reached.

The γ-spectrometric method for the determination of protoactinium[47], based on measurement of the activity in the Pa^{231} γ-radiation peak at an energy of ~ 300 keV, appears more promising. Foreign radio-elements do not give sharp peaks in this energy range, and after removal of Pa^{231} by treatment with hydrofluoric acid, it is easy to introduce an appropriate correction for these elements. The method makes it possible to determine reliably approximately 1.5 μg of protoactinium-231 in a 5 g sample, with an error of 1–3%. Barnett[48] has used γ-activity measurement at 300 keV for the relative determination of Pa^{231} in the absence of foreign γ-emitters.

Protoactinium-231 can be identified, and its radiochemical purity checked, using multi-channel α-analysers with

sufficiently high resolution, to record the energy spectrum of the α-particles emitted by the specimen (Fig. 1). The radiochemical purity of Pa^{231} can also be characterised fairly fully from the shape of the γ-spectrum[48].

Protoactinium-231 in natural radioactive formations in which radioactive equilibrium has been disturbed can be determined by an indirect method based on measurement of the α-activity of the daughter Th^{227}.[49] This method is of course unsuitable for the determination of Pa^{231} in materials after chemical treatment.

A recent study of the colour reactions of protoactinium with various organic ragents indicates the possibility of applying colorimetric methods to the determination of small quantities of protoactinium and for purity control[30].

Methods for the determination of Pa^{233} have been dealt with in a number of papers[50,51].

EXTRACTION OF PROTOACTINIUM BY ORGANIC SOLVENTS

Like its neighbours in the Periodic System, thorium and uranium, protoactinium is readily extracted from aqueous solutions by many organic solvents, and the use of extraction for the isolation of protoactinium from natural sources and for its subsequent purification have been described above.

The purity of the solvent is of particular importance in the extraction of protoactinium (as it is in the extraction of small or tracer quantities of other elements), since the distribution of protoactinium between the phases may be altered considerably by the presence of impurities. Thus the presence of organic peroxides in esters hinders the extraction of protoactinium from hydrochloric acid solutions[52], and extraction of the element from weakly acidic solutions by commercial tributyl phosphate is due entirely to the presence of the mono- and dibutyl phosphates[23,52]. A synergic effect is observed in the extraction of protoactinium from hydrochloric acid solutions by diisopropyl ketone–diisopropyl carbinol mixtures, i.e. there is an increase in the extracting power of the mixture compared with that of its components[52]. To avoid the adsorption of protoactinium which takes place on glass, work with the element is often carried out in polyethylene vessels, which must be treated several times before use with organic solvents to remove impurities in the polyethylene, which might otherwise be leached out gradually by the solvent and influence the extraction process[53].

Protoactinium exhibits a number of features during its extraction by organic solvents, which are not shown to the same extent by other elements. It is capable of changing from an extractable state to a non-extractable form even in 6–8 M HCl.[52] When stored in polyethylene vessels at room temperature, solutions containing protoactinium-231 can remain unchanged for several weeks, but once started, the conversion proceeds very rapidly and is complete in 1–2 days: subsequent prolonged heating with concentrated hydrochloric acid does not restore the extractability completely. Data on the extraction of partly "aged" hydrochloric acid solutions can be explained on the assumption that protoactinium exists in solution in only two forms, one of which is normally extractable while the other cannot be extracted at all. The extractable form may be a single complex or several complexes which reach equilibrium rapidly with one another. Only a normally extractable and a completely non-extractable form of protoactinium are detected in nitric acid solutions during extraction with tributyl phosphate[53]. The conversion to the non-extractable hydrolysed form in hydrochloric acid solutions is accompanied by a change in the absorption spectrum of the protoactinium[29,30]. The hydrolytic processes develop more slowly in polyethylene than in glass vessels. Protoactinium retains its ability to undergo conversion to a non-extractable colloidal form even in the organic extracts.

Best results are obtained with diisopropyl ketone in the extraction from hydrochloric acid solutions[46], but its low availability has justified the use and study of less effective extracting agents. Goble and Maddock[52] have studied the effect of the HCl concentration in the equilibrium aqueous phase on the extraction of protoactinium by the following organic solvents: diisopropyl carbinol, benzonitrile, chlorobenzene, tributyl phosphate, β,β'-dichlorodiethyl ether, nitrobenzene, *o*-nitrotoluene, *o*-nitroanisole, and a 5% solution of tributylamine in benzene. Chlorobenzene has almost no extracting action on protoactinium. The plot of the protoactinium extraction with tributyl phosphate vs. HCl concentration is a gently sloping curve, indicating its low selectivity. Nevertheless, in combination with re-extraction by a mixture of HCl + HF, extraction from hydrochloric acid solutions by tributyl phosphate has been used successfully for the separation of thorium, uranium, and protoactinium[54,55].

The ketones cyclohexanone, mesityl oxide, diethyl ketone, acetophenone, methyl n-hexyl ketone and diisobutyl ketone have been studied in more detail. For all ketones except cyclohexanone, which is completely miscible with moderately concentrated hydrochloric acid, the dependence of the distribution constant E on the mean activity of the acid, like the dependence of E on $[H^+]$ at $[Cl^-] = 5$ M and of E on $[Cl^-]$ at $[HCl] = 3$ M, is given, in logarithmic coordinates, by a family of parallel straight lines, which indicates that the mechanism of the extraction of protoactinium is the same for all these ketones. Extractable protoactinium compounds are formed at HCl concentration 3–10 M, and appear to be anionic chloro complexes. This is confirmed by the adsorption of protoactinium by anion exchange resins in this HCl concentration range. Aliphatic ketones also extract protoactinium from nitric acid solutions[56].

The extraction of protoactinium from HCl + H_2SO_4 mixtures by diisobutyl ketone has also been studied. At a constant 8 M HCl concentration , the addition of a small quantity of H_2SO_4 sharply reduces the extractability of protoactinium (from 99% to 3%), but with further increase in the H_2SO_4 concentration the extractability increases considerably. At lower HCl concentrations almost no improvement in extractability takes place with increase in the H_2SO_4 concentration. Protoactinium is extracted to a slight extent by ketones from sulphuric acid solutions, but even in 12 *N* H_2SO_4 an equal volume of diisobutyl ketone extracts only 9% of protoactinium.

Equal volumes of pentyl acetate or diisopropyl ketone extract 7% and 16% of protoactinium respectively from 1 M HCl solution 3 M with respect to ammonium thiocyanate.

Unlike tantalum and niobium, protoactinium is not extracted by methyl isobutyl ketone, even from 15 M HF.

Goble and Maddock[52] have put forward an interesting suggestion regarding the nature of the protoactinium compounds extracted from hydrochloric acid solutions. They showed that the extracting power of a solvent is directly related to its basic nature, which is in accordance with an oxonium extraction mechanism. They chose as a measure

of the basic nature the values of K_B from Gordy and Stanford[57], and the extracting power was characterised by the concentration of acid required for 50% extraction of protoactinium. The plot of the relationship between these quantities, on logarithmic coordinates, is linear, and the most basic extracting agents (cyclohexanone, mesityl oxide) extract 50% of protoactinium from weakly acidic solutions. The dependence on the basicity, together with certain other data, indicate that the solvent is associated with the cationic part of the extractable ion pair, which may be either a hydrated solvonium ion $SH^+ . aq . S$ or a solvated oxonium ion $H_3O^+ . S . aq$. This extraction mechanism shoud lead to a correlation between the extracting power of different solvents relative to different metals. Fig. 3, taken from Goble and Maddock's paper[52], shows the relationship between the distribution constants of gold and protoactinium for extraction from 8 M HCl by different solvents. For the same cationic part of the extractable ion pair, for example, in the extraction by tributylamine solutions, the extraction of protoactinium increases with increase in the dielectric constant of the solvent. Since water has the highest dielectric constant, the only ions which can be extracted are large anions whose transfer to the organic phase is accompanied by a considerable gain of energy as a result of the decrease in the work of formation of the cavity occupied by the ion.

As a rule, the extractability of protoactinium decreases with increase in its concentration*. Thus for extraction with nitrobenzene, the Pa^{231} distribution constant for an initial concentration 10^{-5} M is smaller by a factor of 30 than that found for Pa^{233} under the same conditions at an initial concentration $4-6 \times 10^{-10}$ M. For β,β'-dichlorodiethyl ether the ratio is close to 10, and for diisopropyl ketone close to 1. The increase in the distribution constant at low protoactinium concentrations is shown more clearly when the dielectric constant of the solvent is high, and can be related to the dissociation of the extractable ion pair in the organic phase. The introduction into the organic phase of a strong acid such as trifluoroacetic acid suppresses the dissociation and decreases the protoactinium distribution constant.

Moore[58] gives data for the extraction of Pa^{233} from hydrochloric acid solutions by a 5% solution of methyl di-n-octylamine in xylene. The protoactinium is extracted almost completely even from 6 M hydrochloric acid, whereas under the same conditions, only 1.2% of zirconium is extracted. Thorium does not form anionic chloro complexes and is therefore not extracted by amines. Separation from thorium and zirconium can also be achieved with more readily available amines, such as triisooctylamine. Small quantities of phosphoric acid, which prevent the extraction of protoactinium by most organic solvents, do not interfere in the extraction by a 5% solution of methyl di-n-octylamine in trichloroethylene[50].

Nikolaev and coworkers[59] have described the extraction of protoactinium salicylate by acetone in the presence of calcium chloride, which facilitates separation into layers: Zr, Th, U(VI), and Pu(IV) are also extracted. The method is suitable for the separation of protoactinium from trivalent elements, particularly the rare-earth elements.

The extraction of protoactinium from nitric acid solutions has been studied in most detail by Hardy, Scargill, and Fletcher[53], who found that when benzene solutions of tri-n-octylamine are used, the dependence of E on the HNO_3 concentration, over a wide range of the latter, corresponds to the adsorption of protoactinium by the anion-exchange resin Deacidite FF. At constant HNO_3 concentration, the protoactinium distribution constant is approximately proportional to the amine concentration in the organic phase (to the power 1), which indicates the formation, in the aqueous phase, of an anionic nitrato complex with charge -1.

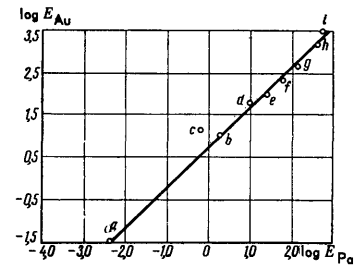


Fig. 3. Relation between distribution constants of protoactinium and gold for extraction by various organic solvents from 8 N HCl[52]. Pa^{233} concentration 5×10^{-10} M: *a*) chlorobenzene; *b*) diisopropyl ether; *c*) dibutyl phthalate; *d*) nitrobenzene; *e*) pentyl acetate; *f*) β,β'-dichlorodiethyl ether; *g*) benzaldehyde; *h*) tributyl phosphate; *i*) acetophenone.

Part of the protoactinium in nitric acid solutions, as in hydrochloric acid solutions is present in a non-extractable form. Hardy and others determined the amount of non-extractable form by the following method, first suggested by Martin[60]. If C_o and C_a are the concentrations of metal in the organic and aqueous phases respectively, and C_n the concentration of the non-extractable form, the average distribution constant of the extractable form D will be

$$D = \frac{C_o}{C_a - C_n},$$

so that

$$C_o = DC_a - DC_n .$$

Thus, if we determine the distribution of metal between the phases at different phase-volume ratios and plot C_o vs. C_a, the intercept on the C_o axis will give the value of C_n. Moreover, if equilibrium between the different complexes making up the extractable form is established rapidly, i.e. if the time taken is small compared with the time for which the phases are mixed, the plot of C_o vs. C_a will be a straight line with slope D. If this condition does not apply, the curve will be convex towards the C_o axis. In the extraction of Pa^{231} from 10^{-5} M solution in 6 M HNO_3 by a 30% solution of tributyl phosphate in kerosene, the proportion of the non-extractable form varies between 5% and 20% for different solutions. The plot of C_o vs. C_a is linear, indicating that equilibrium is established rapidly between the various nitrato-protoactinium complexes. The value of D varied from 2.2 to 3.0 in different experiments. The addition of small quantities of HF (10^{-3}–10^{-4} M) decreases D sharply, but has almost no effect on the value of C_n.

The protoactinium distribution constant for extraction by tributyl phosphate solutions is approximately proportional to the square of the tributyl phosphate concentration in the

* Earlier experimental data, which indicated the higher extractability of macro-quantities of Pa^{231}, [46] have been shown to be erroneous.

organic phase. At moderate ionic strengths, maintained by adding $NaNO_3$, the protoactinium distribution constant is apparently independent of the acidity. At higher ionic strength, the relationship between the two is complex, showing a minimum value, and is analogous to the corresponding relationship for the adsorption of protoactinium by cation-exchange resins. The distribution constant also ininceases with increase in the nitrate ion concentration. Hardy and others suggest that protoactinium is extracted by tributyl phosphate as $Pa(OH)_2 . (NO_3)_3 . 2TBP$, but it is doubtful if tributyl phosphate can extract the hydroxo form. According to Gresky[61], the extractable form is $Pa(NO_3)_5 . 3TBP$.

The extraction of protoactinium by mono- and dibutylphosphoric acids was first described by Fudge and Woodhead[23], and the extraction of Pa^{233} by various alkylphosphoric acids has been studied independently and in greater detail by Shevchenko, Mikhailov, and Zaval'skii[24]. The protoactinium distribution constants are close to 1000, even when dilute dialkylphosphate solutions are used, and this should prove useful for the concentration and purification of protoactinium, particularly since these substances can extract hydrolysed and even colloidal forms of protoactinium, which are formed in solutions of low acidity and are not extracted by other solvents*[62]. The lower monoalkylphosphates are less efficient extracting agents for protoactinium.

Mikhailov, Shevchenko, and Kolganov[63] studied the influence of the extracting agent and aqueous phase composition (at an ionic strength of 6) on the efficiency of the extraction of Pa^{233} by solutions of mono- and diisopentylphosphoric acids in isopentyl acetate. The extraction process may be represented by the equilibrium

$$Pa(OH)_n A_{3\,aq}^{-} + 2HA_{org} + H_{aq}^{+} \rightleftarrows PaA_{5\,org} + 3H_2O_{aq},$$

according to which the extracting agent HA is also the complex-forming material in the aqueous phase. With increase in the acidity, the proportion of complexes of the type $Pa((OH)_n A_m^{5-n-m}$ with smaller numbers of hydroxo groups increases slightly[64]. The nitrate ion does not take part in the extraction equilibria and protoactinium can be extracted by these compounds from solutions in any mineral acid, and even from solutions containing moderately powerful complex-forming species such as $H_2C_2O_4$.[23] According to Hardy et al.[53] the extraction of protoactinium is even improved in the presence of $H_2C_2O_4$, due to the decrease in the proportion of the non-extractable polymeric form.

Although the above equation for the extraction process describes satisfactorily the available data on the extraction of tracer quantities of Pa^{233}, the actual mechanism of the process is undoubtedly much more complex, due to the extensive dimerisation of the dialkylphosphates and polymerisation of the monoalkylphosphates in the organic phase[65-68]. Moreover, these compounds can extract partly hydrolysed forms under certain conditions, as shown by Lewis and Crabtree[69] for the extraction of trivalent iron by di-2-ethylhexylphosphoric acid.

The extraction of tetravalent protoactinium has been little studied. Bouissieres and Vernois[70] found that benzene solutions of thenoyltrifluoroacetone extract Pa(IV) as $Pa(TTA)_4$ and Pa(V) as $Pa(TTA)_5$. Protoactinium(IV) is more readily extracted from hydrochloric acid solutions by thenoyltrifluoroacetone than Pa(V), but it is not extracted at all by methyl isobutyl ketone or tributyl phosphate.

* This assertion by Carleson[62] has, however, been disputed by other authors[53].

ION EXCHANGE, ADSORPTION, AND COPRECIPITATION OF PROTOACTINIUM

Protoactinium is adsorbed by strongly basic anion exchange resins from sufficiently concentrated hydrochloric acid solutions[71-74], but all the earlier data are for Pa^{233}. Goble and Maddock[52] studied the adsorption of Pa^{231} at an initial concentration $(4-6) \times 10^{-5}$ M, on Dowex 1 resin. Comparison of their data with the corresponding data for Pa^{233} obtained by other workers[71] shows that the distribution constant for the distribution of protoactinium between resin and solution increases with decrease in the protoactinium concentration, as in the extraction processes.

The ion-exchange adsorption of protoactinium from nitric acid solutions has been insufficiently studied, but Hardy and coworkers[53,75] have recently studied the adsorbability of thorium, protoactinium, and uranium from nitric acid solutions by anion and cation exchange resins. The adsorption of Pa^{231} from 10^{-5} M solutions in nitric acid on the anion exchanger Deacidite FF increases with increase in the HNO_3 concentration up to 8 M. The adsorbability of different actinides by strongly basic anion exchangers from solutions with HNO_3 concentration greater than 4 M decreases in the series

$$Np^{IV}, Pu^{IV} > Th^{IV} > Pa^{V} > U^{VI}, Np^{VI}, Np^{V}.$$

The plot of the distribution constant vs. HNO_3 concentration passes through a minimum at 3–6 M HNO_3 in the adsorption of Pa^{231} by Zeocarb 225 cation exchange resin. A minimum is also observed in the case of thorium, but that for protoactinium is much sharper. The steeper rise on the curve after the minimum in the case of protoactinium is apparently due to an increase in the average positive charge on the cation, as a result of the partial suppression of hydrolysis at higher acidity. The positive charge on the cations containing protoactinium, found from the slope of the straight line $\log D_U$ vs. $\log[HNO_3]$, is approximately 1.6. Similar values were obtained by Japanese workers[76], who used Dowex 50 cation exchange resin to separate Th^{234} (UX_1) from Pa^{234} (UX_2). The Pa^{234}, which is adsorbed in the upper part of the column together with the Th^{234}, is separated from the latter by eluting with 1–2 M HNO_3 or 0.1–0.7% oxalic acid solution. The tendency to undergo adsorption on cation exchangers from 1 M HNO_3 decreases in the series

$$Th^{IV} > Pu^{IV} > Pu^{III} > U^{VI}, Np^{VI}, Np^{V}, Pa^{V}.$$

Protoactinium-231, which forms complexes on the addition of a 1000-fold excess of HF^-, and is not extracted by tributyl phosphate, is readily adsorbed by anion exchangers, and to lesser extent by cation exchangers.

Protoactinium-231 is also adsorbed from nitric acid solutions by finely-divided graphite. For graphite powder with specific surface 68.5 m^2/g, the distribution constant is

$$\frac{\mu g\ Pa/g\ graphite}{\mu g\ Pa/ml\ solution} = 9.0 \pm 0.5.$$

The area per protoactinium atom, for the highest value of the adsorption reached (20 μg Pa/g graphite), corresponds to that of a square of side 30 Å, so that the graphite surface is far from saturated. Protoactinium is also strongly adsorbed on freshly-precipitated silicic acid and on cellulose (filter paper). The adsorption of protoactinium on silica gel is prevented by Nb, Fe(III), and Cr(III).[77]

Starik and Skul'skii[78] found that Pa^{233} is adsorbed from nitric acid solutions on fluoroplast-4 [plastic similar to

Teflon (Ed. of Translation)] and paraffin wax, which exhibit no ion-exchange properties. It is suggested that these processes involve molecular adsorption of neutral complexes of the type $[Pa(OH)_x(NO_3)_y]^0$ present in the solution. The mechanism of adsorption of protoactinium on graphite is probably similar.

Tracer quantities of Pa^{233} are readily adsorbed from nitric acid solutions on to glass, and this can be used to achieve separation from zirconium[79,80]. Starik and coworkers[81] used data on the adsorption of protoactinium by glass at different pH values to calculate the solubility product of $Pa(OH)_5$, and obtained the value 10^{-55}. The characteristic features of the adsorption and desorption of protoactinium in contact with glass indicate that ionic forms of protoactinium predominate at pH values lower than 4–4.5.

The coprecipitation of protoactinium with manganese dioxide was used long before the introduction of ion-exchange resins, and still retains its importance[59,82-85]. Lead and tin dioxides, at the moment of formation, are also able to adsorb protoactinium[86]. The adsorption of protoactinium under these conditions can probably also be regarded as molecular[78].

Nikolaev and coworkers[59] have described the coprecipitation of protoactinium-233 with various thorium precipitates and the use of the "similar-carriers" method for separating protoactinium from thorium.

Chzhaun Ya-ui[87] studied the distribution of Pa^{233} between disalicylalethylenediamine complexes of tantalum and niobium, of general formula MCl_3R_2, and their solutions in dry carbon tetrachloride. The distribution constants D were found to remain unchanged and equal to 1.6 ± 0.1 and 1.2 ± ± 0.1 in both cases respectively. The fact that D is constant indicates that the corresponding Pa, Ta, and Nb compounds are isomorphous. Isomorphous coprecipitation of Pa^{233} was not observed with the analogous titanium compounds $TiCl_2R_2$.

A number of papers have been published on the paper chromatography of protoactinium. Vernois[88] studied the influence of HCl and HF concentrations in butanol–HF–HCl–water mixtures on the relative rate of movement of protoactinium and a number of other cations along a paper chromatogram. This method can be used, with suitable choice of conditions, to effect the following separations: Pa–Ta–Nb, Pa–Ti, Pa–Bi, Pa–Fe, and Pa–Po. The separation of zirconium from protoactinium by this method is difficult[89], and in this case better results are obtained by paper electrophoresis. Lederer[90] studied the behaviour of protoactinium and its mixtures with U(VI), U(IV), Zr, and Th in the acetone–water–HCl system. The behaviour of protoactinium is altered by the presence of macro-quantities of these elements. Goble and Maddock[52] showed that when different organic solvents are used, the R_f values decrease with decrease in the extracting power.

THE STATE OF PROTOACTINIUM IN AQUEOUS SOLUTIONS

The accumulated data, obtained by different methods, on the behaviour of protoactinium, lead to some general conclusions regarding the forms in which the element exists in aqueous solutions. Most workers[53,63,64,78] favour the view that in acid solutions (at any rate in nitric acid solutions) protoactinium is present in a variety of cationic, neutral, and anionic acido complexes of the type $[Pa(OH)_nX_m]^{5-n-m}$, and that equilibrium between these forms is established rapidly. This viewpoint explains fairly satisfactorily the behaviour of protoactinium during ion exchange, adsorption, and solvent extraction.

Welch's suggestion[91] regarding the existence of the PaO_2^+ ion, analogous to the similar ions of U, Np, Pu, and Am, is difficult to reconcile with the marked differences in the chemical properties of protoactinium and the other pentavalent actinides in aqueous solutions[92]. Protoactinium shows a greater resemblance to niobium and tantalum than to the pentavalent actinides.

Most protoactinium solutions also contain macromolecular hydrolysed forms which take almost no part in the rapid equilibrium processes in the solution. At low protoactinium concentrations and high acidity, the proportion of hydrolysed form may be small, but higher protoactinium concentrations and low acidity facilitate the hydrolytic processes, as a result of which the behaviour of protoactinium at concentrations above 10^{-4} M is usually not reproducible[53].

The present author has made an approximate calculation[93] of the first acid dissociation constant of the $Pa(H_2O)_p^{5+}$ ion from the ionic potential of the Pa(V) ion, and obtained the value $10^{3\pm1}$. This high value for K_h appears to refute Elson's suggestion[5] regarding the possible existence of hydrated Pa^{5+} ions, even in strongly acidic solutions and solutions containing no complex-forming species. This value of K_h shows reasonable agreement with the stepwise acid dissociation constants of the $[PaA_3(H_2O)_3]^{2+}$ ion calculated from data for the extraction of Pa^{233} by diisopentylphosphoric acid and HA; the values were approximately 100.29 ± 5 and 21 ± 2.[64] Tracer quantities of Pa^{233} form protoactinate ions[94] in 1 N NaOH or KOH solutions, showing the weak amphoteric properties of protoactinium.

There are no quantitative data on complex-formation by protoactinium in solution. Experiments on the extraction of Pa^{231} from nitric acid solutions by tributyl phosphate in the presence of HF have given only the relative tendency of protoactinium to form complexes with the fluoride ion[53]:

$$H^+ < Fe^{3+} < UO_2^{2+} < Al^{3+} < Th^{IV} < Pa^{V} \simeq Zr^{IV}.$$

PROTOACTINIUM AND THE ACTINIDE FAMILY

The chief point in support of Seaborg's actinide hypothesis is the presence of seven 5f-electrons in curium[95]. The exact point at which the first 5f-electron appears is of less importance, in view of the proximity of the energy levels of the 5f- and 6d-electrons in the elements immediately following actinium and the possibility of a change in the electronic structure on going from one compound to another. Actinium is thus regarded as the nominal first member of the actinide family, whose members only gradually acquire features showing similarity to actinium. Thus the undeniable, though incomplete, analogies between thorium, protoactinium, and uranium and the corresponding elements in the IVA, VA, and VIA sub-groups can, in our view, be explained on the actinide hypothesis if we are not excessively rigorous with regard to terminology. Seaborg's characterisation of trans-actinium elements as elements of the 5f-6d region has been put in more concrete form by Makarov's suggestion[96,97], confirmed by extensive crystal-chemical data, regarding the dual chemical character of the first members of the actinide family.

In practice, the chemist working with protoactinium is reminded more often of its resemblance to tantalum, niobium, and zirconium than of its place in the actinide family.

The resemblance between protoactinium, zirconium, and hafnium is an example of the diagonal relationship in the Periodic Table.

The possible existence of trivalent protoactinium has not yet been confirmed. Published data on the effect which is observed in some cases in the polarographic curves, and which may be interpreted as due to the change Pa(IV)→Pa(III), are insufficiently conclusive[4,34]. The existence of lower valency states does not prove that protoactinium belongs to the actinide family, since such states are also known for tantalum and niobium.

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THE FORMATION OF TWO LIQUID PHASES IN INORGANIC SYSTEMS

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INTRODUCTION

The phenomenon of complete or partial mutual insolubility of inorganic substances in the liquid state (formation of separate layers) is encountered in various fields, such as metallurgy, glassmaking, geology, etc. Although the mechanism of separation into two or more phases has been clarified by the concept of the possible existence of microheterogeneous liquids[1], there is still no general theory of the solubility of one substance in another, nor any theory