# *Studies in the concentration of radioactive elements*

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# "STUDIES IN THE CONCENTRATION OF RADIOACTIVE ELEMENTS"

A Thesis submitted for the degree
of Doctor of Philosophy

by

Frank Morgan

October 31st., 1949.

Abstract at end.

## OBJECTS

A. With the present expansion in the use of artificial radioactive elements, the separation, purification, and concentration of extremely minute amounts of material are rapidly becoming routine problems. The manipulation by normal chemical methods of radioactive atoms in the presence of comparatively overwhelming amounts of target material is generally impossible without dilution of the radioactive atoms by inactive atoms of the same chemical species or of comparable chemical behaviour. For many types of application of radioelements, such dilution is undesirable, and other means of extraction must be sought. These are generally more of a physico-chemical nature, such as electrolysis, complexing elution from ion-exchange resins or extraction by organic solvents. The electrolytic operation is often preferred, wherever its use is practicable, by reason of the neatness and rapidity with which a separation may be performed and the cleanness of the resultant product.

Fundamental to a study of electrochemical behaviour is the Nernst Law, $E = E_o + RT/nF \ln C$, relating the potential taken up by an electrode in a solution of its own ions to the concentration of those ions. In regions of concentration down to $10^{-8}$N, there is no doubt that the law holds and this has been frequently verified by normal electrochemical procedure. Below this rough limit of $10^{-8}$N, there is scarcely enough material to form even a monatomic layer on the electrode, and some change in the relationship might be expected to occur.

In this region, radioactive tracers have been used as a sensitive means of detection and, by their aid, measurements have been made down to the region of $10^{-12}$N. Until comparatively recently,however, only naturally radioactive elements have been available and, as will be discussed later in extenso, none of them is entirely suitable for the task. Perhaps as a result of this, experimental evidence is largely contradictory and some are inclined to affirm, some to deny, the validity of the Nernst relationship in concentrations insufficient to form monatomic layers.

It seemed that, by the use of an artificial radioactive element more amenable to experimental treatment, the matter might finally be resolved. The number of radioactive substances which may be used for this purpose is extremely limited, and radio-silver of half-life seven days is one of the few to fulfil all the conditions.

It was therefore necessary to prepare the radioelement free from all inactive silver, from irradiated uranium: this task, upon which the remainder of the work hinged, was felt to be difficult but soluble.

B. More effectively to utilise the equipmentt available, and to minimise loss of time while irradiations of target material to produce the requisite radioactive species were in progress, it was decided to carry out a parallel investigation into a smaller problem. The extraction of protactinium from its naturally-occurring sources has largely been complicated by lack of information about its chemical properties and by the vast amounts of chemically complex material which have to be treated for the recovery of even milligram quantities of the element.

Of recent years, there has become available a suitable tracer, P $a^{233}$, in large activities, by the use of which the study of the chemical behaviour of the element is enormously facilitated. The attention of the author was drawn by Mr.G.R.Martin to a paper in which the rapid transformation of $UO_3$ into $UF_4$ by heating in Freon (dichlorodifluoromethane) was described. It seemed not unlikely that the well-known volatility of the fluorides of Group V should extend to P a, and that, by ignition in Freon a separation from non-volatile fluorides might be achieved. It was decided to investigate the reaction using the tracer P $a^{233}$.

C. Before work could begin on the problems outlined above, due to the lack of apparatus and the requisite radioactive material, a request was made by the Medical Research Council for the working-up of several sources of radio-phosphorus from iron phosphide irradiated with deuterons. No suitable methods had previously been described in the literature and it was necessary to evolve a method for the separation not only of radio-phosphorus but also of the minor radioactive constituents present in the highest possible yield and purity.

Achievement of these objects :

A. After several months' work little progress had been made in the extraction of radio-silver, though a variety of different methods was tried, and it was decided to abandon the attempt. (In an Appendix, a method is described, for extraction of carrier-free $Ag^{111}$ from fission products, worked out by the author at the Atomic

Energy Research Establishment, Ministry of Supply). However, that approach to the subject which was being made concurrently, by spontaneous deposition experiments, was carried forward; localized deposition on surface imperfections and crystal boundaries was found to occur. For this, P $a^{233}$ was used. This material was also used in an investigation of the electrochemistry of P a in sulphuric solution, on which little information was available.

B. It was shown that reaction between Freon and P a is immeasurably slow in several hours at temperatures up to 580° and therefore of little use in any separation procedure. Incidental, however, to this work is a series of experiments on the solvent extraction of P a from hydrochloric solutions. This work was taken to a point where it afforded a rapid, easy, and complete, separation of P a from Th and Zr, to facilitate the preparation of sources of P a from irradiated Th.

C. By choice of suitable methods, the separation of the constituents of irradiated iron phosphide was found to be comparatively simple and the extraction entirely successful.

For the sake of clarity, each of these objects will be discussed in separate sections, with an appropriate introduction to each.

## Apparatus and Technique

### Counting apparatus :

The electronic apparatus used was bought from the Atomic Energy Research Establishment, Harwell, and consisted of :

1. A potentiometer panel fed from a Type T.1007 multichannel high-tension unit delivering 20 mA at 2000 volts positive or negative,
2. A probe unit Type T.200 embodying a single amplification stage,
3. A scale-of-100, Type T.200.

These were generally perfectly reliable, except for routine replacements such as neon lights,etc. in the scaler.

Counter-tubes were commercially available also, but, since the window was too thick (25 mgm./cm$^2$ of copper) to measure soft radiations, particularly those from Co, Mn, and Zn, two new counter tubes were prepared with mica windows.

Counter No.1 : This, except for a period of about two months, was used throughout. Dimensions are as shewn in Fig. 1. The inside surface was finished mirror-smooth

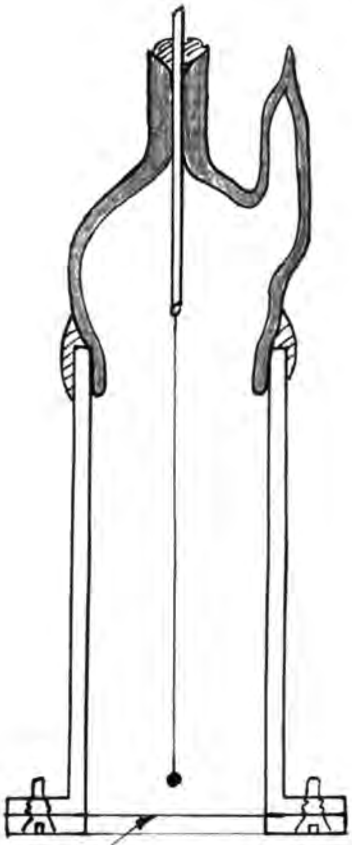

Fig. 1: Counter #1

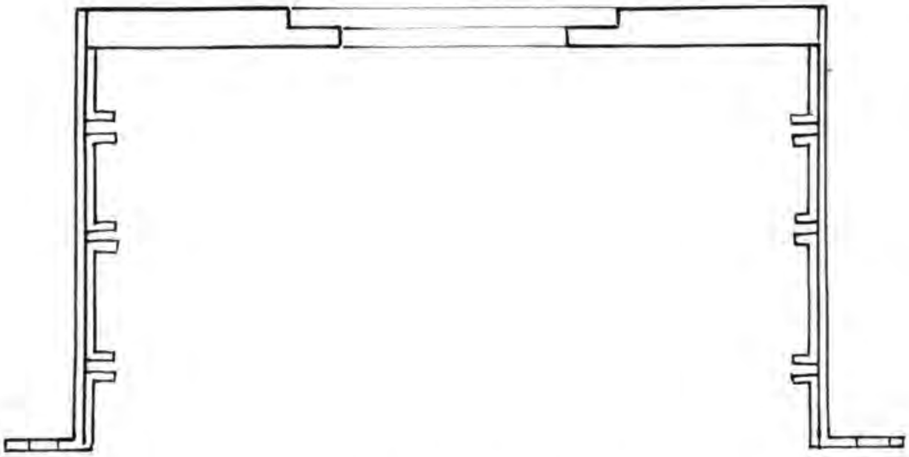

Fig. 2: Counter base

with fine emery and "Brasso" : the window was 6.4 mgm./cm$^2$ of mica. When working, this was most satisfactory, having a plateau with a slope of about 1/2%, generally from about 1460-1600 volts. Normal operating voltage was in the region of 1530 volts. The chief disadvantage was found on the two occasions when the counter had to be disassembled - once, when a leak occurred through the wax at the top, and again, when, due to operating the counter in a horizontal position, the tungsten wire bent slightly. On these occasions, centring the wire and simultaneously ensuring a good seal at the top proved rather tricky.

Counter No.2 was therefore constructed. Libby (1) gives experimental curves showing that the background of the counter is lower, the smaller the ratio diameter/length of the metal wall. The counter was therefore made with rather more favourable dimensions than No.1. The top of the metal portion was turned to fit a standard B.24 taper and the two waxed together with hot black Apiezon wax. (At the first attempt, Apiezon grease 'N' was used, but the counter was found to have an operating life of a few days only, presumably due to to imbibition of the alcohol from the filling vapour (q.v.) into the grease). The metal

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(1) Libby, Anal.Chem.,1947. 19. 2.

portion was finished on the inside by treatment with yellow ammonium sulphide - the resultant askin of CuS is supposed by some to have a beneficial effect on the counter characteristics. Dimensions are shewn in Fig. 3.

The window of this counter was 2.3 mgm/cm$^2$ of mica, and the plateau from 1420-1700 volts with little slope. The background count was generally about 8 - 10 c.p.m. lower than No.1, and the efficiency ( measured with a known weight of $U_3O_8$) 5.7% for one particular geometry. Unfortunately, at the third filling, the window imploded under vacuum; due to the fact that at that time the author was working with a strongly active source and possibly having hands slightly contaminated, it was shelved and subsequently not used again.

**Filling :** A standard mixture of 10% ethyl alcohol, 90% argon, at 10 cm.pressure, was always used.

On the few occasions when the background of the counter grew to be rather higher and decontamination was felt to be necessary, this was easily accomplished by immersing the whole counter into 8N.$HNO_3$. and washing with distilled water and acetone.

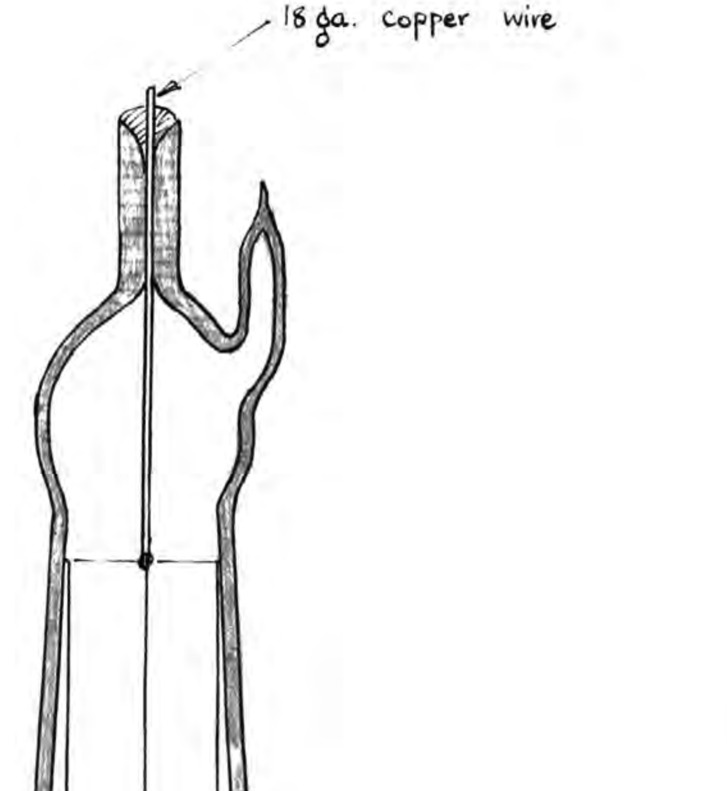

Fig. 3
Counter #2 (full scale)

_Mounting and Operation_ : Although a commercially-made assembly was obtainable to hold counter, absorbers and source in various geometries, it was felt that this arrangement was too complicated for general use, and undesirable because of a large mass of aluminium below the source and around the counter. The presence of a large mass of material below the counter can give rise to a spurious increase in the counting-rate due to back-scattering of beta-particles. (See Fig. 4 and Yaffe and Justus[2]: although comparative figures for aluminium are not available, the danger of spurious counts at low beta-energies is evident). The plates of aluminium at the side of the counter may also cause aberrations by scattering into the counter particles which otherwise would not have been intercepted by the window. While these errors are probably quite reproducible for a given geometry of source, absorber and counter, and for a given energy of particle, nevertheless it was felt that a simpler and more flexible arrangement was desirable. This consisted, see Fig. 2, of a piece of thin aluminium sheet bent to form three sides of a square, with a piece of "Perspex" bolted on to form a top :

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[2] Yaffe and Justus, 1948. Phys.Rev., 73. 1400.

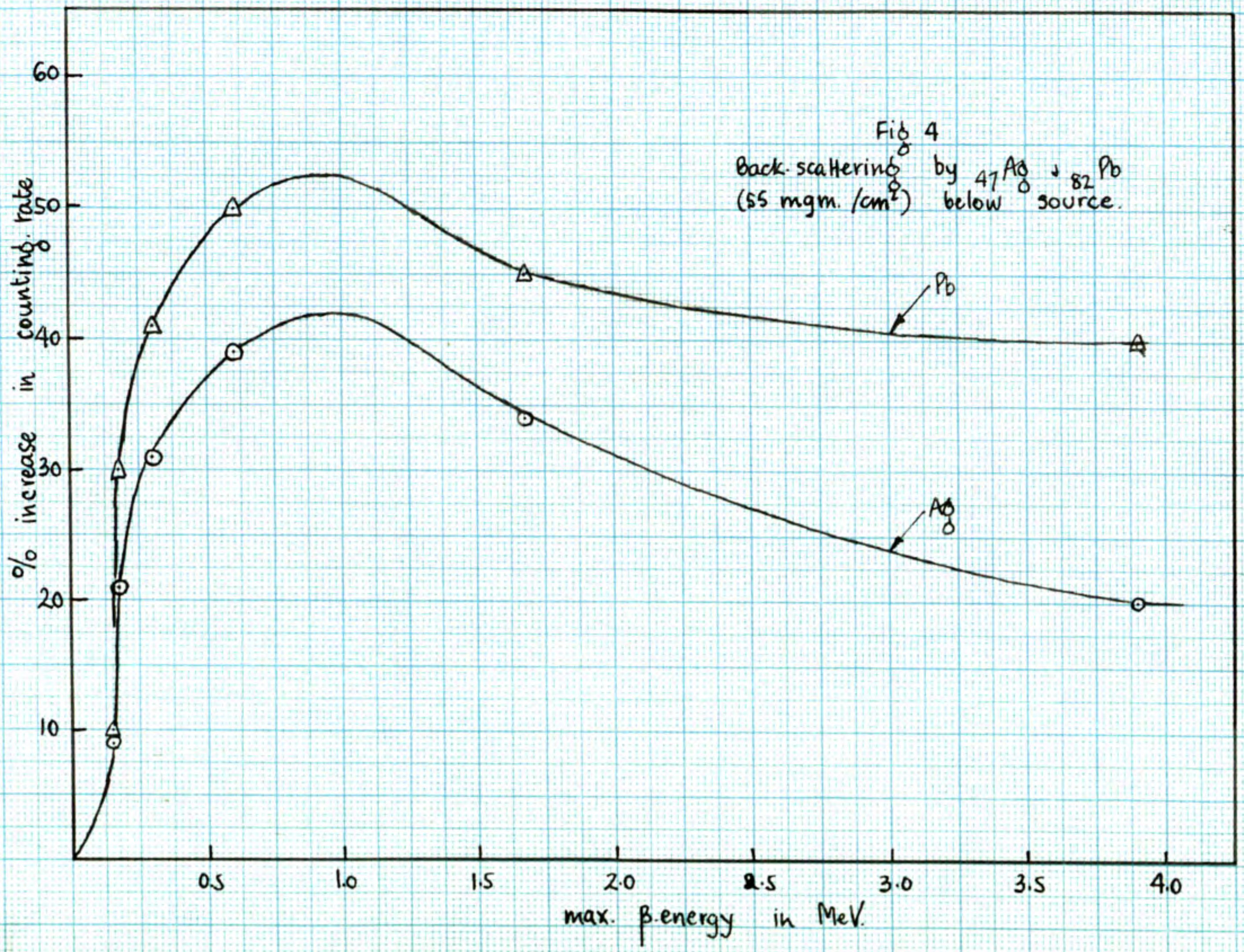


Fig 4

Back-scattering by $_{47}Ag$ + $_{82}Pb$
(55 mgm./cm²) below source.

this sheet had a central hole cut to the size of the counter window and rebated to form a seat for the counter base. Below this, strips of aluminium were bent and rivetted on to form three slots. The shelves to fit these slots were cut from 18 ga. aluminium, with a central circular hole 2" in diameter. These served both to mount sources and to hold absorbers. In use, the holder was screwed to the base of a lead "castle", the lead from the probe unit being taken out through the back.

The counter was initially calibrated by means of a thin layer of aged $U_3O_8$ of known weight, and the observed counting-rate due to $UX_2$ compared with the calculated value. On the three shelves of the holder, the efficiences were, for Counter 1 : top shelf 13.5%

middle shelf 6.3%

bottom shelf 2.7%.

Since a standard for everyday use should have a value of something in the region of 10,000 c.p.m., so that a statistical accuracy of 1% or better may be obtained in a minute or two, a subsidiary standard was prepared to give this counting-rate, consisting of a rather thick layer of aged $U_3O_8$ of unknown weight, cemented together to form a permanent source with a little diluted collodion. This was then calibrated against the primary standard.

**Absorbers :** These were made in thicknesses of from 1.56 mgm./cm$^2$ , and were mounted with "Durex" cellulose tape across the central hole in an aluminium plate. For the thinnest sheets, old dry electrolytic condensers proved to be the best source of material. As few sheets as possible were used to form a given thickness, as it was found that, e.g., one sheet of 50 mgm/cm$^2$ gave rather less absorption than five sheets of 10 mgm./cm$^2$ each : this is probably due to extra scattering in the latter.

**Sources :** These were mounted either on a small 1" disc of aluminium or (preferably) on a 1" watchglass. After drying under an infra-red lamp, they were mounted on a strip of cellulose tape gummed across the hole of an aluminium sheet.

## Chemical Manipulation :

This differs considerably from that obtaining in normal laboratory practice, since the scale of operation is generally rather small (with milligrams or so of material) and since the properties both chemical and physiological of radioactive substances necessitate special precautions being taken. It may therefore not be irrelevant to give a brief résumé of the manipulative methods used: these vary somewhat depending on the particular problem, but certain principles may be given.

*Strongly active materials* : These were always worked up into the desired form in a special room and only brought out under definite conditions : either in tracer quantities only for long-living material (say, of half-life greater than a month) or as a pure source where the half-life is reasonably short as for $P^{32}$ or $Pa^{233}$. The object of this was to avoid contamination of other rooms and apparatus. Also, with the same object in view, glassware which had been used in the treatment of strong sources was not transferred from room to room, or from preparation to preparation, without strict cleansing and checking for activity with a beta-counter.

To avoid harmful physiological effects, work was performed behind a 2" lead wall wherever the activity was greater than 5 millicuries, particularly of gamma-emitters, and always in a strong draught in a fume-cupboard. Surgical rubber gloves were worn. Nothing was placed in the mouth while work was in progress; pipettes of different capacities were used for transfer of liquids or suspensions, and were operated by means of rubber teats. Similarly, a small hand wash-bottle was operated with a squeeze-bulb.

Precautions were taken to avoid the creation of active dust: material was not allowed to contaminate the outside of containers, pipettes always being used to transfer liquids from one vessel to another. Even with tracer quantities, where pouring was occasionally resorted to, the hanging drop on the rim of the container was washed off with the vessel still in the inclined position. Any material spilled was immediately and rigorously wiped up with paper tissue and much water. To avoid the creation of spray, which might carry activity, solutions were never boiled, but steamed on a waterbath, and held partly immersed by a perforated can in the case of tubes.

Generally, both with strong sources and with tracer quantities, centrifugation was used to separate solid and liquid phases; wherever the material represented a pure source, or the total amount possessed, the space between centrifuge tube and the metal container of the spinner was filled with water to equalise pressure:

this has always prevented breakage, which otherwise occasionally occurred. Filter-paper was never used; not only does it adsorb amounts of material greater or less, depending on the conditions, but also these contaminated papers remain a health hazard until permanently destroyed. In addition, centrifugation is a much more efficient process: previous experience has shewn that a precipitate of less than 0.2 mgm. can be recovered better than 99% by 15 mins. centrifugation at 2000 r.p.m.

Separating funnels were never used: not only is it difficult to obtain a sharp separation, but also leakage around tap and stopper may be dangerous and is always undesirable. Also, if organic solvents are used, the introduction of tap-grease into the system is most unwelcome. Therefore, all separations of two liquid phases were made with transfer pipettes, which avoid these difficulties.

Before breaking off for meals, etc., when strongly active material was in use, the hands were always scrubbed and checked underneath a counter.

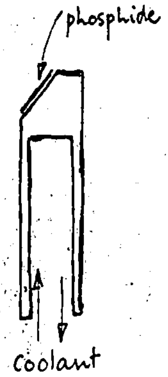
## SECTION I

### Separation of the Constituents of Iron and Copper irradiated with Deuterons.

There was a period of two or three months before work could begin on the other problems outlined, due to lack of apparatus and the requisite radioactive material. A request was made, however, by the Medical Research Council for the working-up of several sources of radio-phosphorus, prepared in the Berkeley (Calif.) and Cambridge cyclotrons.

Since the power to be dissipated in a cyclotron beam may be of the order of Kw/cm$^2$, the use of elementary phosphorus is precluded, due to danger of volatilisation and contamination of the machine. The general method of bombardment utilises therefore iron phosphide or copper phosphide, both of which are relatively non-volatile and are good thermal conductors. They have the further advantage that they may be volatilised in vacuo or soldered to a metal backing for water-cooling.

Typical of these sources is a copper probe target from the Cambridge cyclotron. The weight of iron phosphide was about 100 mgm. and was fused onto the copper probe tip in a small hydrogen furnace. The actual size of probe and deposit is shewn in Fig.5. Bombardments were with 6.7 Mev deuterons for several hours with beam currents up to 50 microamps.



The main reactions and products to be expected are the following :

| | Half-life |
|---|---|
| $\mathrm{Cu}^{63}(d,p)\,\mathrm{Cu}^{64}$ | 12.8 hrs. |
| $\mathrm{Cu}^{65}(d,p)\,\mathrm{Cu}^{66}$ | 5 mins. |
| $\mathrm{Cu}^{65}(d,2n)\,\mathrm{Zn}^{65}$ | 250 days. |
| $\mathrm{P}^{31}(d,p)\,\mathrm{P}^{32}$ | 14.3 days. |
| $\mathrm{Fe}^{56}(d,\alpha)\,\mathrm{Mn}^{54}$ | 310 days. |
| $\mathrm{Fe}^{56}(d,2n)\,\mathrm{Co}^{56}$ | 72 days. |
| $\mathrm{Fe}^{56}(d,n)\,\mathrm{Co}^{57}$ | 270 days. |

and, to a lesser extent, because of the low abundances of the target nuclei,

| | |
|---|---|
| $\mathrm{Fe}^{54}(d,\alpha)\,\mathrm{Mn}^{52}$ | 6.5 days. |
| $\mathrm{Fe}^{54}(d,p)\,\mathrm{Fe}^{55}$ | ca. 4 yrs. |
| $\mathrm{Fe}^{58}(d,p)\,\mathrm{Fe}^{59}$ | 47 days. |

The activities due to copper disappeared practically completely before treatment began, due to their short half-life and the time necessary for transport. The overwhelming proportion of the activity was due to $P^{32}$ and extraction of this was the prime objective. The result of this was two-fold: it was necessary for the separation to be completed in a short time, before the radio-phosphorus had appreciably decayed, so that the minor constituents could not be detected if some of them were to contaminate the final product. And, secondly, to separate the minor constituents from each other with certainty, it was necessary to wait several half-lives of $P^{32}$ until traces of this nuclide left behind by the extraction process had disappeared.

The only constituents present in weighable amount were the original Cu, Fe and P. The other possible elements, active Mn, Co and Zn, are present only on a sub-microscopic basis. It may be readily calculated, for example, that one microcurie of $Zn^{65}$ has a weight of about $1.5\ 10^{-10}$ gm. In most of the targets extracted, the activity due to these minor constituents was in the region of 8-10 microcuries. Generally, therefore, except for Zn present as impurity in the original copper, there is an absolutely unweighable amount of material present which behaves chemically as Zn. (For comparison, one of the most sensitive chemical tests - the turmeric thread test for boron -

has a limit of identification of $10^{-9}$ gm. [3]).

In normal chemical manipulation, particularly for precipitation reactions, there must be a reasonably large mass of material, otherwise anomalous behaviour may occur. Also at these concentrations, even in dilute acid, there may be a much larger concentration of hydroxyl ions than of the radioelement, and also traces of dissolved salts which are not of significance in normal chemical practice may have an overwhelming effect. Therefore, to stabilise the chemistry, and to facilitate chemical manipulation, small quantities of the stable naturally-occurring element (or an element chemically similar in the reactions to be studied) are added, as "carrier". The amount is generally about 5-10 mgm., though this may vary with considerations of the ultimate specific activity desired and the scale of operations.

The previously described method [4] for the separation of phosphorus from such a target involves its dissolution in aqua regia with subsequent precipitation of ammonium phosphomolybdate. This precipitate is converted to magnesium ammonium phosphate by solution in

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[3] Benedetti Pichler, "Microtechnique of Inorganic Analysis" Wiley, 1942.p.70.

[4] Wilson and Kamen, Phys.Rev., 1938.54. 1031.

ammonia and treatment with magnesia. This may be converted to sodium phosphate by treatment with the stoichiometric quantity of sodium hydroxide in the hot. The phosphate may be decanted from the residual magnesia precipitate.

This method is disadvantageous in that, though separation of the phosphorus is simple, the addition of excess ammonium molybdate for the initial precipitation makes the separation of the minor constituents difficult and no satisfactory solution has yet been described.

To avoid this procedure, a new approach was outlined by Dr.K.F.Chackett and worked out by him in collaboration with Mr.G.R.Martin and the author 4a). The initial idea was to chlorinate the whole of the target material at an elevated temperature, in the hope that the phosphorus might distil off as $PCl_5$, leaving the other constituents behind. This was tested, and chlorination found to proceed rapidly, but the separation was not clean, due to the comparatively low volatility of $PCl_5$ and the volatility of $FeCl_3$. The chlorine was therefore displaced by air, which in turn was displaced by hydrogen. Heating then reduced the compounds to the lower chlorides, when $FeCl_2$ remained behind, the $PCl_3$ being

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4a) F.A.Paneth, Quarterly Reviews, 1948. II.102.

carried forward.

A typical run carried out with Dr.Chackett may be described: The tip of the copper probe was cut off with a hacksaw to minimise the amount of inactive material - a rough check of $\beta$- and $\gamma$- activity showed that the portion to be discarded was essentially inactive. The residual tip was placed in a Pyrex tube 12 mm. i.d. and about a metre long. A slow stream of chlorine, from a $KMnO_4$ -HCl generator, was dried with conc. $H_2SO_4$ and led over the sample, which was heated with an electric tube furnace. The gases bubbled through a train of three water traps. At 350°, the reaction began and proceeded with great vigour, the mass sintering and glowing dull red. The chlorine generator was quite unable to keep pace with the demand and water began to suck back within the traps, which had to be disconnected. For future chlorinations, a cylinder of gas was held to be essential. The iron and phosphorus, as their upper chlorides, distilled a distance of 10 - 15 cm. from the reacting mass. When assimilation of chlorine was complete, the traps were re-connected and the products allowed to cool in chlorine. A stream of air, dried over sulphuric acid, was passed through. This was then displaced by hydrogen, and the furnace temperature raised to 250° - 300°. No further sublimation occurred from the sintered mass, so the furnace was gradually moved along the tube towards the traps. These quickly separated the sublimate into two fractions, a white band of shining crystals about 4 cm wide, presumably of ferrous chloride, and a colourless distillate, which was moved along as far as the traps. The tube was cut, after cooling in hydrogen, at the visible limits of deposition. The contents of the traps were combined and evaporated to a smaller bulk. The chlorination and reduction occupied rather more than an hour and a half.

Further treatment of the phosphorus distillate was felt to be necessary. The precipitate, which was unexpected, was centrifuged off and its activity measured. This was about 8% of the total. The residual solution was taken down to small bulk, when a further small precipitate came out, this was joined to the first. The total weight of these precipitates was estimated at about 2 mgm. It was found that it was soluble both in $8N.HNO_3$ and in caustic soda, and was felt to be an aluminium phosphate. The source of the aluminium is not clear - the iron phosphide used to prepare the target was later found to be not of "AnalaR" grade, but an old specimen of indeterminate history:

presumably it contained a small amount of aluminium. In view of the smallness of the proportion of total phosphorus activity associated with the precipitate, and the difficulty of conversion into free phosphoric acid on such a tiny scale, it was abandoned after identification.

In all, there were extracted from this particular target 2.2 millicuries of $P^{32}$ as phosphoric acid, which was estimated to be about 90% of the total from $\beta$-activity measurements made on the initial material.

The residues were washed together, dissolved, and taken down to dryness with conc. $HNO_3$, to ensure oxidation of cuprous and ferrous chlorides, then fumed down twice with conc. HCl to convert them completely to chlorides. This solution was allowed to stand for five months, to ensure almost complete decay of $P^{32}$ present.

## Separation of the Minor Constituents :

These consist, as we have seen, of isotopes of the chemical species Mn, Co, Fe, and Zn, in the presence of a comparatively large amount ( 5 - 10 gm.) of Cu.

Preliminary Experiments : These were made on a small aliquot (about 10%) of the total.

Removal of Iron : The most obvious starting-point is to remove iron by extraction with ether of ferric chloride. The sample was evaporated to dryness and taken up in warm 6.5N.HCl, cooled, and then extracted with equal volumes of ether (previously equilibrated by shaking with a large excess of 6.5N.HCl) until no further yellow colour due to iron could be seen in the ether layer. This generally entailed three or four extractions. Since the weight of iron was reasonably high (about 8 mgm.) the efficiency of this step was quite high and little iron could be detected in later stages. (The overall efficiency could not be determined since the initial amount present was not well-defined). These ether extracts were combined and the ferric chloride extracted into a small volume of water. The measured activity of this was always extremely low, but activities due to iron in the residual copper solution were minimised by adding 50 mgm. of ferric chloride and re-extracting. This step was repeated.

The disadvantage of the ether method for the removal of iron is that the partition coefficient for ferric chloride in ether-water mixtures is high with respect to ether only in the immediate neighbourhood of 6.5N.HCl and is small at acidities less than 5 N or greater than 7.5N.[5),6)] In an attempt to obviate this difficulty, trial experiments were made to remove ferric ion in a complex with thiocyanate by means of extraction with methyl propyl ketone. It was found that in widely different concentrations of iron and ammonium thiocyanate the iron was visually almost completely extracted with an equal volume of solvent. Unfortunately, cobalt, and, to a lesser extent , manganese are extractable also in these conditions (molybdenum also, should an ammonium phosphomolybdate precipitation be used at an earlier stage). It has been reported 6) that di-isopropyl ether is excellent for removing ferric chloride from 9N.HCl - a quantity of this solvent was ordered, but arrived too late to be of use.

Separation of Copper : The separation of copper from zinc by electrolysis is a standard analytical procedure, but it was thought that in the deposition of a large amount of copper, microamounts of Co, Mn and Zn might be occluded. Later work showed, indeed, the feasibility of

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5) Noyes,Fray, "Qualitative Analysis for the Rarer Elements", p.161.

6) Dodson et.al.,J.A.C.S.,1936.58. 2375.

a perfectly sharp separation of Cu and Zn by electrolysis, but in the meantime a chemical method of removing the copper was successful. However, to preserve continuity, we may describe the electrolytic method here.

Portions of an old copper target which had no adhering iron phosphide and therefore no activity but $Zn^{65}$ were etched with $8N.HNO_3$ to an average depth of 100 $mgm./cm^2$, or 0.1 mm; this removed over 90% of the activity (showing the very small depth of penetration of the bombarding deuterons), This solution was evaporated to dryness and taken up in 200 ml. of $0.18N.H_2SO_4$ plus a little conc. $HNO_3$. Current from a 6 v. accumulator with a few ohms resistance to give 700 mA. was passed through the solution with a rotating Pt cathode and a Pt wire anode, at 70°, until the solution was colourless, and continued thereafter for an hour. This took eleven hours in all, and the residual solution had then no colour with $H_2S$. The weight of the Cu deposit was 2.714 gm.; there was no detectable $\gamma$- activity in the deposit, whereas the residual solution was intensely active. Measurements of $\beta$ - activity showed about 200 c.p.m. on the deposit, and $10^7$ c.p.m. left in the solution. This shows the great sharpness of the separation.

The next most obvious step would be the removal of copper by sulphide precipitation from acid solution. It was felt that this procedure would be unwise, since most text-books of analytical chemistry stress the possibility of Group IV cations (including Co, Mn, and Zn) coming down to someextent in the presence of a large amount of copper sulphide; this also agrees with the comparatively small amount of evidence we possess on adsorption and coprecipitation. In fact, as will be seen presently, this objection was trivial.

It was hoped to separate out the cobalt by formation of a complex with $\alpha$-nitroso- $\beta$ -naphtol, either as a precipitate or by extraction with an organic solvent. It was found nexessary, though, to add much larger quantities of the reagent than corresponded to the 5 mgm. of Co present - presumably to complex the copper. Exactly the same type of objection was found in the extraction of Zn with dithizone. The residues from these attempts were evaporated down with nitric acid to remove organic matter, then taken up in hydrochloric acid. In crystallising cupric chloride from the solution, no great fractionation was found to occur. The use of ammonium chloride to complex the copper produced no material improvement.

At this point, precipitation of copper sulphide was resorted to. The solution was taken to dryness and the residue dissolved in 1.5 N.HCl:$H_2S$ was then passed until the copper sulphide coagulated, using a fine drawn-out tube to increase mechanical agitation. The precipitate was centrifuged off and washed twice with a few ml. of 0.2 N.HCl. A portion was transferred to a counting tray by means of acetone - it was found to be inactive.

(When pure active manganese and cobalt had been prepared, this was further investigated. Two centrifuge tubes were prepared , each containing 10 mgm. of copper as chloride dissolved in water. To one was added active manganese, to the other active cobalt, with only an infinitesimal amount of free acid - certainly insufficient to lower the pH below 4. Quantities were chosen to give 10,000 c.p.m. in the counter, through a screen of 14 mgm./$cm^2$ of aluminium, to minimise differences of source thickness, this activity being associated with 0.2 mgm. of manganese and 0.01 mgm. of cobalt respectively. $H_2S$ was passed through each to coagulation, and the precipitates washed with water twice; they were then mounted with acetone and counted through the aluminium screen. No activity above background could be detected with either, certainly less than 5 c.p.m. could have been detected in the prolonged counts made. This shows then that the 10 mgm. of copper had carried less than 0.1 microgram of manganese or 0.005 microgram of cobalt. In view of this, a projected series of experiments similar to the above, with varying conditions of acidity, etc., was not made.

The feasibility, shown by this experiment, of precipitating quantities of the order of grams of copper as sulphide from a weakly acid solution containing only milligrams of Co, Mn, and Zn, without entrainment of these, was amply confirmed in later work where no difficulty arising from such entrainment was encountered).

From the copper-free solution, containing only Mn, Co, and Zn, $H_2S$ was expelled by evaporation to dryness. From this point onwards, there are several means described by which the remaining constituents may be separated.

Separation of Mn : The method recommended by Noyes and Bray (7) for the removal of Mn without carrying of other Group IV cations, by oxidation to $MnO_2$ in conc.nitric acid solution with potassium chlorate, was found to proceed quite readily.

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7) "Qualitative Analysis for the Rarer Elements", p.197.

Separation of Co : From the residual solution, Co was precipitated with caustic soda to alkalinity, followed by a little solid sodium peroxide powder to ensure complete removal of cobalt axide and to ensure separation from Zn.

Separation of Zn : We are now left with a solution of Zn in excess caustic soda; since Zn forms very few insoluble compounds, the precipitation of the hydroxide seemed as good a method as any for removal from the large excess of sodium salts and any impurity which might have entered.

Hildebrand and Bowers 8) and Britton 9) describe potentiometric titrations of Zn in sulphate solution with caustic soda. Experiments made using known quantities of zinc chloride, and measuring the pH on a "Cambridge" pH meter proved an effective way of estimating the zinc even in low concentrations. Plots of d(pH)/dV, where V is the volume of standard NaOH used, were used to estimate discontinuities in the titration curves accurately. The volume of solution was 75 ml. (In conformity with the results of Britton, a disparity was found between quantity added and found, for high concentrations. As

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8) J.A.C.S., 1916. 38. 785.

9) J.C.S., 1925. 127. 2110.

Table I shews, however, the method is reliable for small quantities).

Table I

| | | | | |
|---|---|---|---|---|
| Mgm. Zn added : | 1.75 | 8.60 | 34.3 | 79.0 |
| Mgm. Zn found : | 1.63 | 8.60 | 34.0 | 69.2 |

The pH obtaining while $Zn(OH)_2$ was precipitating was found to rise slowly from 7 to about 8.4, as NaOH was added. For routine precipitations of Zn, it was found sufficient to approach the end-point of phenolphthalein from the acid side. Centrifugation of suspensions of $Zn^{65}$ at pH 8.3 determined in this way gave a coagulated precipitate of over 99% of the total activity present.

Having thus obtained a suitable method, the residues of six targets were worked up. It is perhaps best to describe the extraction of the most active, since the less active were combined for convenience of extraction.

Final Extraction : This target was of iron and copper bombarded in the Berkeley (Calif.) cyclotron and was by far the most active. The weight was estimated to be about 4 gm. No details of irradiation, except that deuterons were used, were available. All the target material - phosphorus being absent - was dissolved in conc.HCl with a little conc.$HNO_3$ added to hasten reaction. Then 10 mgm. each of Co, Mn and Zn were added and the mass evaporated to dryness on the waterbath.

Following the preliminary experiments outlined above, the following procedure was adopted :

1. Dissolve in 20 ml. 6.5 N.HCl and extract five times with 15 ml quantities of ether equilibrated with 6.5 N.HCl : extracts were combined and re-extracted with water, giving what we may call an "iron concentrate".

2. Precipitation of the copper as sulphide from the residual solution, diluted to 1.5N. The precipitate was washed well twice with 10 ml. of 0.1 N.HCl and the $\beta$- activity compared with that of the supernatant solution; it was found to be negligible. The precipitate was discarded, the washings being added to the main bulk of solution, which was evaporated to dryness on the waterbath.

3. Residue taken up in 10 ml conc. $HNO_3$, heated, and about 200 mgm. of powdered $KClO_3$ was added slowly. A watchglass was placed over the basin, and the whole steamed for 15 mins. The suspension was centrifuged and the precipitate of $MnO_2$ washed with 2 ml. of conc. $HNO_3$, giving a manganese concentrate.

4. The supernatant solution and wash were taken to a volume of about 1 ml. in the evaporating basin, then washed with water into a 50 ml. centrifuge conc. This was suspended in boiling water and 6N.NaOH added until precipitation occurred : 200 mgm. of sodium peroxide were added slowly, with stirring. The suspension was heated for 15 mins., centrifuged, and the precipitate washed with a little diluted precipitant. This gave a cobalt concentrate.

5. To the cooled caustic solution, phenolphthalein was added, followed by 6N.HCl dropwise until the magenta disappeared; very dilute caustic soda was then added until the pink tinge barely returned. The suspension was heated to coagulate the zinc hydroxide, which was then taken off and washed with water. The washings and supernatant liquor were almost inactive and were therefore discarded.

It is preferable to refer to these separated fractions as "concentrates", since they must inevitably contain at least traces of the other radioelements present, the quantity depending on the efficiency of the chemical separation employed. It is therefore necessary to repeat the separation process on the concentrate at least once and perhaps several times to obtain a pure radioelement. We may illustrate this with the cobalt concentrate.

This was dissolved in a little conc. $HNO_3$ and 5 mgm. of "hold-back carriers" added for the possible contaminants - in this case, only for Mn and Zn, since the activity of iron was so low (a few microcuries totally) and the weight of inactive iron so great (1550 mgm.) that any activity due to iron left in the sample would be negligible. The separation processes were repeated, beginning with the precipitation of $MnO_2$, then, from the solution, precipitating Co as the oxide.

An absorption curve of this cobalt was made, by interposing between counter and source screens of aluminium of varying weight/$cm^2$. A plot of observed count for each screen versus the weight was then made.

The separation cycle was repeated a second time, after again adding Mn and Zn. The precipitate of $MnO_2$ was washed and counted - it was found to be essentially inactive (less than $10^{-4}$ of the activity in the cobalt). The Co was precipitated, then the Zn : the Zn also was found to be inactive. Another absorption curve (shewn in Fig.6) was prepared for an aliquot of the cobalt - it was exactly superimposable on that previously obtained. These facts show that one repetition of the separation process is sufficient to obtain a reasonably good "decontamination" of the cobalt from unwanted activities. In this case, a decontamination factor of $10^4$ was held to be adequate for medical purposes: radioactively pure and chemically pure may not necessarily be concomitant[10).]

Similar cycles of decontamination were made to purify the Mn, Fe, and Zn. To give an idea of the scale of operation, we may quote the activities separated from this target, to the above degree of purity :

7.5 microcuries of $Fe^{59}$ (with 1550 mgm.inactive Fe)
142 microcuries $Co^{56}$ and $Co^{57}$ (10 mgm.Co)
8 microcuries of $Mn^{54}$ (10 mgm. Mn)
8.5 microcuries $Zn^{65}$ (10 mgm.Zn).

Absorption curves for Co, Mn and Zn are shewn in Figs. 6 and 7, respectively. In the case of Mn and Zn, the energies calculated from the Feather relationship between range in aluminium, R gm/cm$^2$, and maximum beta-energy, $E_m$ (Mev) :

$$R = 0.543\ E_m - 0.160$$

and the number of components present corresponds with published values for simple $Mn^{54}$ and $Zn^{65}$ respectively[10a)].

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10) V., e.g.Hevesy & Paneth, "Manual of Radioactivity",1938. p.203.

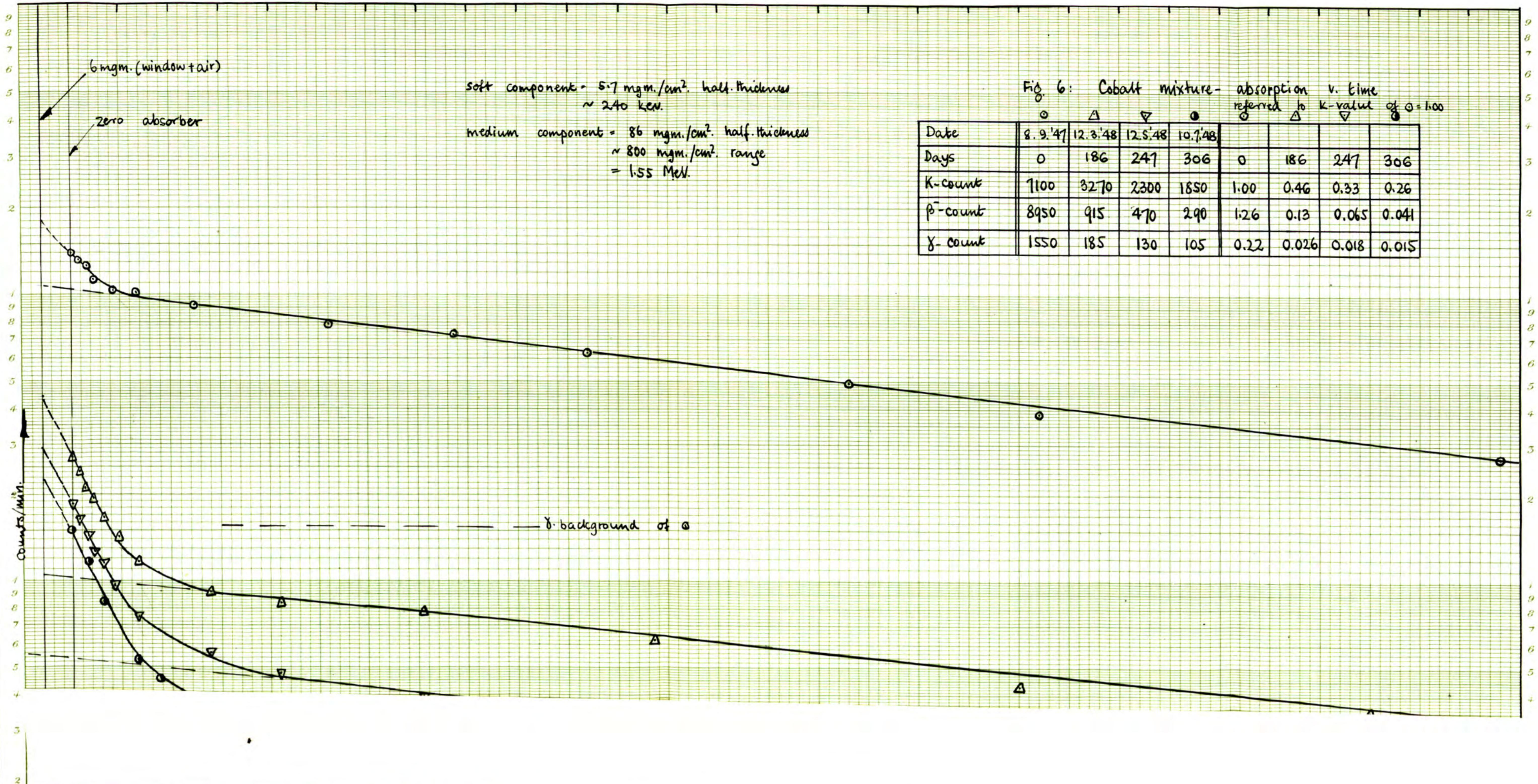
10a) Seaborg, Rev.Mod.Phys., 1944. 16. 1.

For cobalt, values were found which corresponded to $Co^{56}$ and $Co^{57}$ (half-lives of 72 days and 270 days respectively). The absorption curve of this sample was plotted at widely-separated intervals and showed a gradual change in form and in the proportions of the various components present, as the shorter-living died out. As might be expected from the very low natural abundance of $Fe^{58}$ (0.28%), there is no significant quantity of $Co^{58}$ formed by a (d,2n) reaction.

Fig 6: Cobalt mixture- absorption v. time

referred to K-value of ○ = 1.00

| | ○ | △ | ▽ | ● | ○ | △ | ▽ | ● |
|---|---|---|---|---|---|---|---|---|
| Date | 8.9.'47 | 12.3.'48 | 12.5.'48 | 10.7.'48 | | | | |
| Days | 0 | 186 | 247 | 306 | 0 | 186 | 247 | 306 |
| K-count | 7100 | 3270 | 2300 | 1850 | 1.00 | 0.46 | 0.33 | 0.26 |
| β⁻-count | 8950 | 915 | 470 | 290 | 1.26 | 0.13 | 0.065 | 0.041 |
| γ- count | 1550 | 185 | 130 | 105 | 0.22 | 0.026 | 0.018 | 0.015 |



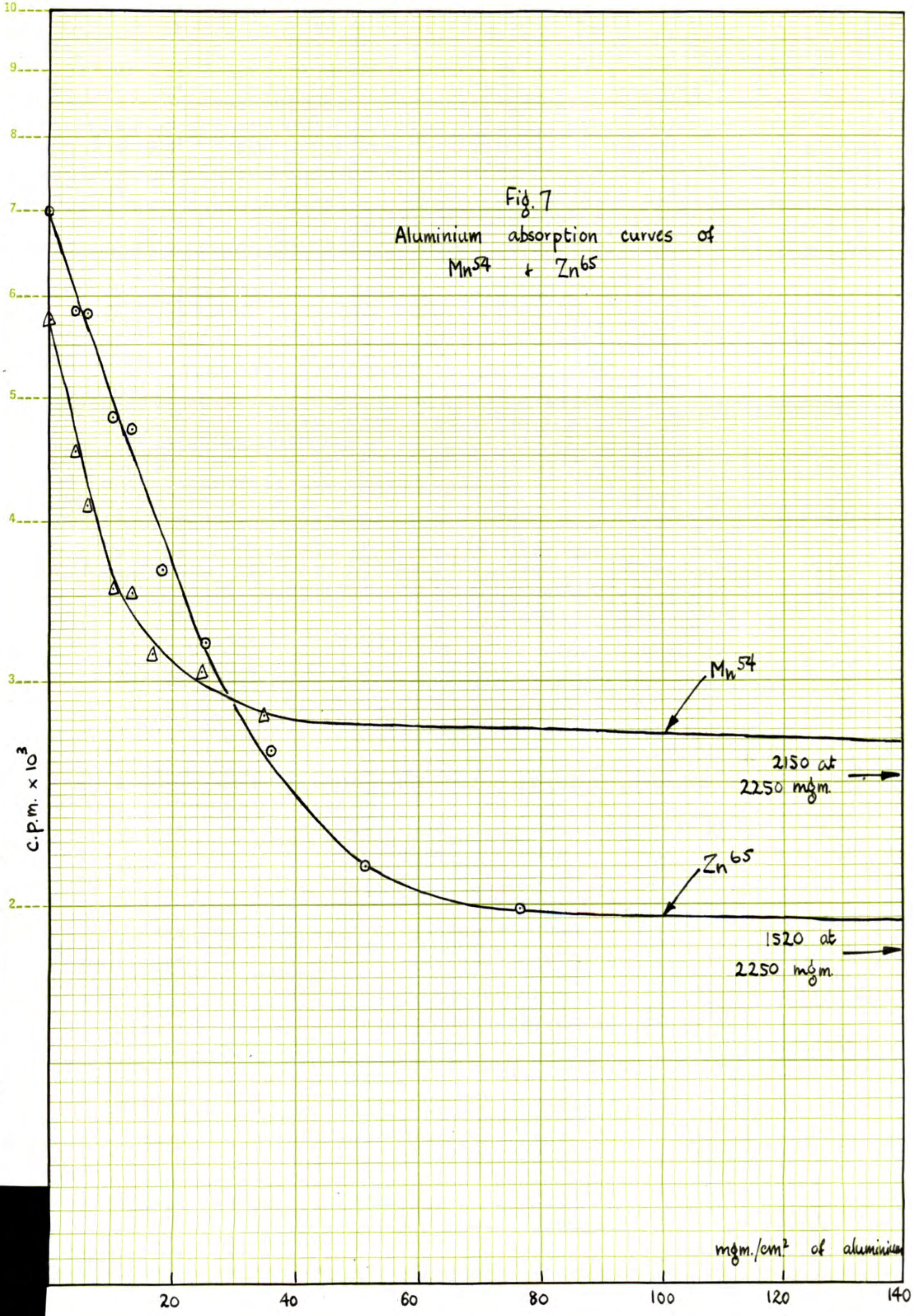


Fig. 7
Aluminium absorption curves of $Mn^{54}$ + $Zn^{65}$

## Section II

### A. The volatilisation of Protactinium in Freon.

The extraction of natural P a$^{231}$ is a tedious business, since its chief source is the final siliceous residue (Rückrückstände) of uranium extraction from pitchblende. Although the major part of the P a content of the ore concentrates here, due to the processes normally used in uranium extraction, and to the chemical inertness of P a,[p] nevertheless the absolute concentration is small.

The element can be detected only by its rather weak $\alpha$-radiation, which is largely swamped by the much more intense radiation coming from traces of Ra and of RaD-E-F left from previous treatment. Any extraction, then, is a long and complicated process involving the manipulation of many kilograms of silica to obtain a small weight of P a - the large-scale operations of v.Grosse and Agruss 11) and of Graue and Käding 12) illustrate this : the latter

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[p] Footnote : U$^{235}$ → UY$^{231}$ → P a$^{231}$ → (P a$^{231}$ half-life = 32,000y).

P a content of a ton of natural uranium is therefore (since U- 235 is 0.7% abundant)

ca. 7,000 x 32,000/7.10$^{8}$ gm. - ca.320 mgm.

11) Ind.Eng.Chem., 1935. 27. 422.

12) Angew.Chem., 1934. 47. 650.

workers treated 5.5 tons of residues to obtain 500 mgm. of product. For these reasons, Pa is still a scarce element.

However, it seemed that some concentration from these silica residues might be feasible using the well-known volatility of the fluorides of this group. Both Ta and Cb fluorides are volatile from boiling HF solution[13) ] the volatility of Cb in these conditions had previously been checked by the writer in work with radioactive $Cb^{95}$ ; it seemed likely therefore that $PaF_5$ might be similarly volatile. The use of HF on such a large scale is scarcely feasible, but in a discussion with Mr.G.R.Martin, the author's attention was drawn to a paper by Booth et al.[14)] where Freon 12 (dichlorodifluormethane) was used to transform $UO_3$ into $UF_4$ at elevated temperatures :

$$UO_3 + 2\ CCl_2F_2 \xrightarrow{400°} UF_4 + CO_2 + COCl_2 + Cl_2$$

This reaction was found to proceed rapidly and quantitatively.

It was decided therefore to attempt to volatilise Pa similarly in a stream of Freon. Fortunately, a tracer for Pa is available : $Pa^{233}$ of half-life 27.4 days and emitting mostly beta-particles, but some gammas. This

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13) Noyes and Bray, Ref.7), p.37.

14) J.A.C.S., 1946. 68. 1969.

may be conveniently prepared by neutron irradiation of Th[15] :

$$Th^{232} (n,\gamma) \; Th^{233} \xrightarrow[23 \text{ mins.}]{\beta} Pa^{233}$$

The cross-section (probability of capture per atom) of $Th^{232}$ for thermal neutrons is about $6.10^{-24}$ $cm^2$, and we may make an approximate calculation of the amount of activity to be expected in a sample of irradiated Th : this was, in both irradiations performed, about 5 gm. of thorium oxycarbonate, which does not undergo any appreciable decomposition at the temperature of about 50° attained by a sample in GLEEP (the low-energy chain-reacting pile at A.E.R.E., Harwell). The flux of thermal neutrons in this pile is approximately $10^{10}$ $/cm^2/sec.$

$$5 \text{ gm. } ThOCO_3 = 5/308 \times 6.10^{23} \text{ atoms Th.}$$

Then saturation activity of $Pa^{233}$ formed/sec.

$$= 5/308 \times 6.10^{23} \times 6.10^{-24} \times 10^{10}$$

$$= \text{about 16 millicuries.}$$

For a period of irradiation of a few days, activities of the order of a millicurie were to be expected. This was quite adequate for the proposed experiments.

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[15] Meitner, Hahn and Strassman, Z.f.Physik,1938.<u>109</u>.538.

Preliminary experiments : 10 mgm. samples of dried $Cb_2O_5$ or $Ta_2O_5$ were placed in a small porcelain boat inside a one metre length of 8 mm. Pyrex tubing, with an electrically - heated furnace surrounding the sample. Commercial Freon 12 was passed over this sample from a cylinder at the rate of 1 litre/hr., after drying with conc. $H_2SO_4$ and $P_2O_5$; the furnace temperature was gradually raised and, in all cases, a small amount of volatilisation occurred, sufficient to give a white mirror on the tube. However, even at 580° , when the Pyrex tube sagged strongly, there was no sign of complete volatilisation. On cooling, the sample was always yellowed, but weighed practically the same.

Experiments with P a : Despite the non-encouraging nature of these results, it was decided to proceed with the P a. A small siliceous residue from the extraction of P a from irradiated Th (v.p. 52 ) of estimated weight 0.5 mgm. was placed in the boat : it had an activity of about 4000 c.p.m. measured through the glass and the furnace by a standard counter -- the counter tube being clamped on a stand so that it could be swung into a standard position above the sample for measurement, and removed in the intervals, to avoid temperature changes in the characteristics. The background was kept as low as possible by means of a 1/4" thick lead shield, the whole counter being wrapped in black cloth to avoid photoelectric effects through the glass insulator.

At first, dry air was passed over the sample, while the furnace temperature was slowly raised.

| Time from start (mins.) | Temp. range °C | Count $\gamma$/min. |
|---|---|---|
| 0 | 18 | 3658 |
| 8 - 9 | 18 - 200 | 3600 |
| 20 - 21 | 200 - 295 | 3593 |
| 40 - 41 | 295 - 310 | 3531 |
| 60 - 61 | 310 | 3525 |

There is no significant change on drying, except for a small diminution probably due to mechanical removal by the air stream.

Freon was then substituted for air :

| Time from start (mins.) | Temp. range °C | Count /min. |
|---|---|---|
| 5 - 6 | 270 - 280 | 3574 |
| 15 - 16 | 280 - 300 | 3530 |
| 25 - 26 | 300 - 340 | 3618 |
| 45 - 46 | 340 - 380 | 3671 |
| 60 - 61 | 380 - 400 | 3332 |
| 75 - 76 | 400 - 530 | 3909 |
| 110 - 111 | 530 - 540 | 3739 |

Although there is some fluctuation in these figures, ascribable probably to errors in replacing the counter and/or temperature effects, there is no indication of volatilisation.

It would be expected that chlorine might have some effect, so this was substituted for Freon. At a temperature of 520°:

| | | | | |
|---|---|---|---|---|
| Time (mins.) | 20 | 30 | 36 | 47 |
| Count ($\gamma$/min) | 5209 | 5074 | 4593 | 4379 |

i.e. volatilisation apparently proceeds slowly at high temperatures in chlorine : probably attack is governed not by the volatility of the P a, but by the rate of removal of the silica substrate.

In view of these results, no further experiments were performed.

## B. Solvent Extraction of Protactinium from Hydrochloric Solution.

The extraction of $Pa^{233}$ from irradiated Th necessitated as part of the final purification an electrolytic deposition from ammonium fluoride solution in which a zirconium phosphate carrying precipitate had been dissolved. This solution was electrolysed for 15 hours with a Pt wire anode and a copper foil cathode, with 16 v. applied potential. A black skin formed on the cathode, but this dissolved with the copper in later treatment with acid; since even in ammonium fluoride alone this precipitate forms, it cannot be of zirconium or protactinium. (cf. the work of Haïssinsky and Emmanuel 16) on the electrodeposition of P a from ammonium fluotitanate solutions -- they describe two types of deposit, a black adherent skin which resembles that under discussion, and a white thick hydrous mass, low pH and agitation favouring the former). In this time, deposition of the P a was practically complete. The copper foil was dissolved in strong hydrochloric acid, the solution diluted, and a few mgm. of iron added. Ferric hydroxide was precipitated

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16) J.Chim.Phys.,1937. 34. 641.

with excess ammonia, washed well, redissolved, and reprecipitated as hydroxide. This sufficed to remove traces of Cu (no coloration with $H_2S$).

This ferric hydroxide precipitate contained still about 85% of the initial $\gamma$-activity, and was dissolved in dilute HCl. From a portion, iron was removed by extraction with methyl propyl ketone (MP K) and residual traces of solvent removed with an ether strip. Rough measurements of $\gamma$-activity showed that no P a was removed by the solvents. A second run was made with the remainder of the ferric chloride solution, this time made 6.5N in HCl, and extracted with ether. This did not remove the iron completely, so a further wash was made with MP K. This removed the iron completely, but also a large portion of the P a. It was decided to investigate this further.

The starting-material in the first series of experiments was a solution of ferric chloride containing about 3 mgm. of iron and about 100 microcuries of P a/ml. The standard procedure was to take 0.2 ml. of this solution, to add 5 ml. of acid of the required normality, and to stir vigorously with 5 ml. of the solvent for one minute. The yellow colour of the ferric chloride was removed in all cases practically entirely into the upper layer, showing that equilibrium had been attained. The layers settled out in about 15 secs.; in those cases where ammonium chloride was added, settling was slower and was hastened by a brief centrifugation. Measurements of $\gamma$-activity were made by removing the supernatant layer to a clean tube with a transfer pipette, and counting in a standard set-up. Results are shewn in Tables II, III and IV.

$Th^{4+}$ as a Salting-out agent : Since the addition of ammonium chloride seems to increase the extraction of P a, while decreasing the mutual solubility of the two layers, it was thought that the action of cations more strongly hydrated than the ammonium ion might have a greater effect. Also, since Th is in this case a necessary concomitant of the P a, an investigation of the behaviour of thorium is necessary both as regards its extraction and its salting-out power.

Preliminary experiments had shewn that a concentration of $ThCl_4$ of about 500 mgm./ml. was most favourable, since at higher concentrations there is a tendency for the volume of the organic layer to be increased at the expense of the aqueous -- probably due to salting-out of HCl : settling is also slow at high $ThCl_4$ concentrations.

A set of experiments was performed similarvto those already described, except that measurements were made by evaporation of an aliquot onto a small aluminium counting tray for measurement of betas. Mixtures of $ThCl_4$, HCl and $H_2O$ were made to give the desired normality in HCl, the tracer added in a negligibly small volume (0.1 ml.) and the whole extracted with an equal volume (5 ml.) of MPK. Settling was in all cases rapid and complete in less than a minute. Results are shewn in Table V.

## Table 11

### Extraction of $Pa^{233}$ from Hydrochloric Acid solution by Ether.

| Acidity | Aqueous layer | | | Solvent layer | | | Final vols. | | %Extraction |
|---|---|---|---|---|---|---|---|---|---|
| | Count | B.G. | Corrected | Count | B.G. | Corrected | Aq. | Solv. | |
| 2N.HCl | 1940 | 137 | 1800 | 183 | 222 | — | 6.0 | 5.0 | — |
| 4N. | 2316 | 185 | 2128 | 178 | 187 | — | 6.2 | 4.6 | — |
| 6N. | 2375 | 262 | 2110 | 223 | 209 | — | 6.8 | 3.9 | — |
| 8N. | 2428 | 189 | 2240 | 257 | 194 | 63 | 8.5 | 1.8 | 3 |

## Table III

Extraction of $Pa^{233}$ from Hydrochloric acid solution with MP K.

| Acidity | Aqueous layer |  |  | Solvent layer |  |  | Final vols. |  | % Extraction |
|---|---|---|---|---|---|---|---|---|---|
|  | Count | B.G. | Corrected | Count | B.G. | Corrected | Aq. | Solv. |  |
| 2N.HCl | 2514 | 575 | 1941 | 191 | 186 | — | 7.6 | 4.8 | — |
| 2.8N. | 1208 | 127 | 1081 | 157 | 132 | 25 | 5.2 | 4.8 | 2 |
| 3.3N. | 1140 | 147 | 993 | 145 | 134 | 11 | 5.2 | 4.8 | 1 |
| 3.7N. | 1210 | 141 | 1070 | 194 | 156 | 38 | 5.2 | 4.8 | 3 |
| 4.0N. | 2065 | 646 | 1420 | 730 | 201 | 529 | 8.4 | 4.5 | 27 |
| 4.3N. | 1014 | 143 | 870 | 399 | 124 | 275 | 5.6 | 4.6 | 24 |
| 4.6N. | 946 | 121 | 825 | 551 | 136 | 415 | 5.9 | 4.5 | 34 |
| 5.0N. | 1014 | 409 | 605 | 1237 | 181 | 1056 | 9.3 | 4.8 | 63 |
| 6.0N. | 862 | 208 | 654 | 1602 | 186 | 1416 | 11.2 | 2.5 | 69 |

## Table IV

Extraction of Protactinium by MPK from ammonium chloride - HVl solutions.

| Acidity | Ammonium chloride | Aqueous layer | | | Solvent Layer | | | Final volumes | | % Extraction | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Count | B.G. | Corrected | Count | B.G. | Corrected | Aq. | Solv. | | |
| IN | IM | 1351 | 148 | 1200 | 148 | 136 | - | no change | | - | |
| IN | 2M | 1426 | 145 | 1280 | 194 | 196 | - | " | " | - | |
| 1N | 3M | 1404 | 135 | 1270 | 188 | 148 | - | " | " | - | |
| 1N | 4M | 1515 | 149 | 1366 | 163 | 176 | - | " | " | - | |
| 3N | 1M | 1450 | 133 | 1210 | 178 | 116 | 62 | " | " | 3 | A few mgm. $NH_4Cl$ crystallises |
| 3N | 2M | 1165 | 138 | 1030 | 430 | 137 | 293 | " | " | 22 | |
| 5N | 1M | 762 | 168 | 594 | 789 | 143 | 646 | 5.5 | 4.5 | 53 | |
| 5N | 1.5M | 502 | 181 | 320 | 1032 | 149 | 783 | 5.5 | 4.5 | 74 | about 15 mgm. of $NH_4Cl$ crystallises |

## Table V

Extraction of Protactinium by MP K from thorium chloride - HCl solutions.

| Acidity | Thorium chloride | Aqueous Vol. | layer Count | Solvent Vol. | layer Count | % Extraction |
|---|---|---|---|---|---|---|
| 3.3N | 1.04M | 5.4 | 1.7 $10^{6}$ | 4.6 | 3.41 $10^{5}$ | 17 |
| 3.3N | " | 5.4 | 1.7 $10^{6}$ | 4.6 | 3.56 $10^{5}$ | 17 |
| 3.8N | " | 5.9 | 1.3 $10^{6}$ | 4.1 | 7.2 $10^{5}$ | 35 |
| 4.0N | " | 5.8 | 1.07 $10^{6}$ | 4.2 | 9.8 $10^{5}$ | 48 |
| 4.2N | " | 5.7 | 8.9 $10^{5}$ | 4.3 | 1.16 $10^{6}$ | 57 |
| 4.4N | " | 5.6 | 3.5 $10^{5}$ | 4.4 | 1.70 $10^{6}$ | 83 |
| 4.6N | " | 5.4 | 3.2 $10^{5}$ | 4.6 | 1.73 $10^{6}$ | 84 |
| 5.0N | " | 5.3 | 5.1 $10^{5}$ | 4.7 | 1.54 $10^{6}$ | 75 |

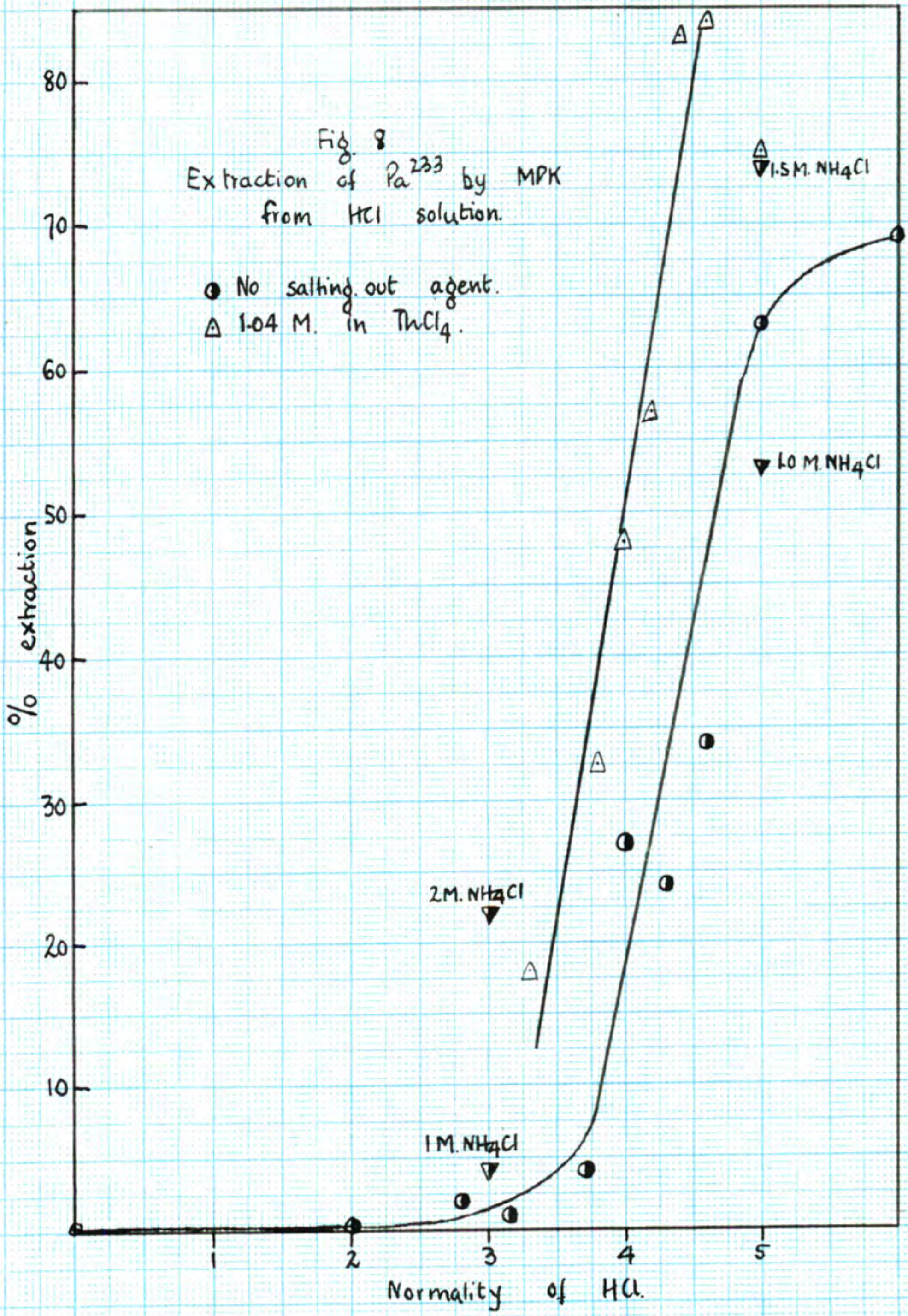

Fig. 8

Extraction of $Pa^{233}$ by MPK from HCl solution.

Solubility of $ThCl_4$: There are no published data on the solubility of $ThCl_4$ : it is extremely soluble and deliquescent. A rough check shewed that 45 gm. of damp $ThCl_4$ would dissolve in 20 ml. of water at room temperature and that, on addition of an equal volume of conc. HCl, crystallisation just occurred on standing. It would seem from this that the solubility of hydrated $ThCl_4$ in 5N.HCl is about 1 kgm./l. Since for reasons expressed in an earlier paragraph there was no intention to work with saturated solutions, no other determinations were made for the system $ThCl_4$ - HCl - $H_2O$.

Extraction of $ThCl_4$ with MP K : No separation process is, of course, feasible if Th is extracted from HCl solutions to any appreciable extent. There are few data published on the solubility of $ThCl_4$ in organic solvents. Moissen and Martinsen 17) found it to be insoluble in chloroform, turpentine, benzene and toluene, and to be soluble in rectified spirits. Baskerville 18) found that one part was soluble in 1000 parts of ether. J.M.Matthews 19) found addition complexes with methylamine and ethylamine.

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17) Comptes Rendus, 1905. 140. 1510.

18) J.A.C.S., 1901. 23. 761.

19) J.A.C.S., 1898. 20. 815.

(Rosenheim and Schilling[20) could not prepare $H_2ThCl_6$, but made the dipyridine salt, $(C_5H_5N)_2ThCl_6$, which they considered to establish the existence of the acid).

A solution 5N. in HCl and containing 510 mgm. of Th/ml. was made; 3.1 ml. were extracted with 2.9 ml. of MP K, settling being hastened by centrifugation. The solvent layer was evaporated on a tared porcelain dish. A tarry residue remained, and the mass was calcined to remove this and to convert Th salts to $ThO_2$. The extract was 25.3 mgm. of $ThO_2$, or 22.0 mgm. Th. I.e. Th is 1.3% extracted in these conditions.

The extract was counted for betas, at different times after extraction :

| Time (mins.) | 30 | 70 | 103 | 175 | 300 | 1075 |
|---|---|---|---|---|---|---|
| Count | 3420 | 2370 | 1950 | 1310 | 920 | 602 |

When plotted on semi-log.paper this resolves into two straight lines, the one constant at 600 c.p.m., the other with a slope corresponding to a half-life of 70 mins. This latter is near to the value of 60 mins. for ThC, a bismuth isotope: it would not be surprising if some extraction had occurred in these conditions, as $BiCl_3$ is known to be soluble in some lower ketones. Calculation shows that 15% of the ThC

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20) Ber., 1900. 33. 977.

is extracted, assuming Th to be in equilibrium with its decay products : as the Th used was at least 22 years old from previous chemical manipulation, this assumption is fairly safe.

Extraction of Zirconium with MP K : The behaviour of Zr. on extraction of a chloride solution with Mp K is of interest, since the methods so far used for the extraction of P a$^{231}$ have all utilised the co-precipitation of P a with zirconium phosphate; the exact mechanism of this has not been elucidated, but it is thought[21)] that not true co-precipitation but adsorption of a hydrolysed P a salt is involved. The major disadvantage of this method is that it then necessitates a long separation by fractional crystallisation or volatilisation. (There was also interest here to the author in that a stock of P a$^{231}$ would be of use in electrochemical studies later to be described).

100 mgm. of Zr. as chloride were dissolved in 25 ml. of 5N.HCl and shaken with 29 ml. of MP K. Final volumes were : aqueous, 38.5 ml; solvent, 15.5 ml. The solvent extract was shaken with an equal volume of water, and this aqueous extract made alkaline with ammonia - no

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[21)] I.Joliot-Curie, "Les Radioéléments Naturels",p.46.

precipitate could be detected even after heating for some time, and centrifugation.

There is no significant extraction of Zr. in these conditions.

<u>Re-extraction of Pa from MPK solution</u> : The solvent layers from two runs were taken - those of Table V for 4.2 and 4.4N.HCl - and each shaken with an equal volume of water. Counting shewed that less than 1% of the activity remained with the solvent and, as would be expected from previous data, re-extraction is virtually complete.

<u>Discussion</u> : Ether shows no significant extraction. In the case of methyl propyl ketone, addition of ammonium chloride has a slight effect, but not so great an effect as acidity. The effect of $ThCl_4$ in one molar concentration is to shift the sudden rise in extraction to lower acidities. In both cases, addition of salting-out agents causes a decrease in mutual solubility.

It may be significant that, in the absence of salting-out agents, the sudden increase in extraction of Pa is almost coincident with the increase in mutual solubility of the two layers, which becomes complete at about 6.5N. Also the effect of acid upon MPK[p] is to produce a light pinkish

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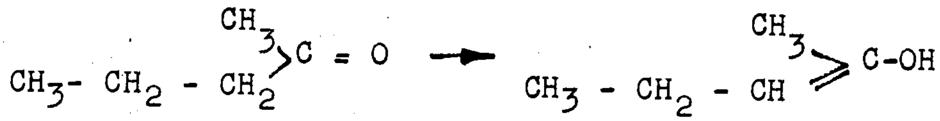
[p] Supplied by British Industrial Solvents, Hedon, Hull.

tinge in the aqueous layer. These suggest that there may be some conversion of the ketone to an enolic form, thus :



$$\begin{matrix} & CH_3 \\ CH_3-CH_2-CH_2 & \rangle C=O \end{matrix} \longrightarrow \begin{matrix} & CH_3 \\ CH_3-CH_2-CH & \gg C{-}OH \end{matrix}$$

This is rather militated against by the observations shewn later (v. p. 53 ) that in extractions of the same aqueous layer by successive volumes of MP K, there is a diminution of the organic layer only in the first ; subsequently, the volumes of the organic layers are almost unchanged, while extraction proceeds with almost the same efficiency.

In this case, it may be possible that some complex such as $H_2P\ aCl_7$ is formed at higher acid concentrations, and that it is this complex which is extracted.

A further possibility is that at low acid concentrations the P a may not be in true solution and that it attains to ionic behaviour only in strong acid. According to A.G.Maddock who applied with Miles 22) the well-known centrifugation technique to solutions of P a of varying acidity, an appreciable percentage may be centrifuged out of 3N.HCl solution but not from 6N.HCl - the values found here are in agreement with this.

It would be desirable to extend the work to other

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22) Private communication from Dr.Maddock - later presented in a paper at the Oxford meeting of the Chemical Society, April 1949.

solvents, with or without complexing agents such as sulphosalicylic acid, which is a useful complexing agent for tantalum and columbium[22a)]. In view of the current supply situation, particularly for organic solvents, this line was not pursued.

Practical Application : The remainder of a new sample of irradiated $ThOCO_3$ was dissolved in just enough 5N.HCl to give a clear neutral solution, apart from a small precipitate of siliceous appearance and about 1 mgm. bulk. This, although it contained about 5% of the total activity, was discarded. A portion of the solution was taken, containing Th equivalent to about 670 mgm. of $ThOCO_3$, in 2 ml. of solution. To this was added 2.4 ml. of conc. HCl and 0.6 ml. of water, giving a solution 4.8N in HCl and containing about 180 mgm. of hydrated $ThCl_4$/ml. This was extracted with three successive 5 ml. volumes of MP K, each solvent layer, on settling, being transferred to a clean tube. These extracts were counted totally by their gamma radiation, and the volumes measured : results are given in Table VI.

These solvent layers were combined and washed with an equal volume of water, which was found to leave less

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[22a)] Schwartz, Angew.Chem., 1934. 47. 228.

than 100 $\gamma$-cts./min. in the solvent. This aqueous extract was stripped twice with ether to remove traces of MP K which would be undesirable in the subsequent evaporation, due to tar formation with acid. On evaporation, a yellowish-white residue of estimated weight 5 - 6 mgm. was obtained, presumably of Th.

In contrast with a purely chemical extraction, using co-precipitation techniques, performed earlier, and which occupied eight working days, this solvent method took 35 mins., excluding evaporation, with overall recovery of the P a better than 99%, of the Th, less than 1%.

Repeated extraction : In view of the preceding results, it was decided to treat the remainder of the material similarly. 13 ml. of the Th. solution were mixed with 18 ml. conc. HCl and 9 ml. of water, giving a solution 4.5 N in HCl. The total $\gamma$-count was 13600/mins. To see whether the partition coefficient might be highest at the beginning, volumes of MP K of only about one-third of the volume of the aqueous layer were used. The results are given in Table VII : there is no such initially high extraction, but, as mentioned on p.~~41~~51, the diminution of the organic layer is limited to the first pass.

The organic layers were combined and shaken with 50 ml. of water : no detectable activity was left with the solvent. The water extract was stripped twice with 40 ml. volumes of ether, which took less than 100 $\gamma$-cts./min. The aqueous residue gave 13,000 $\gamma$-cts./min. This was evaporated down with the residue for the previous run. The dish and the moist $ThCl_4$ residue were weighed, the salt extracted with water, and the dish reweighed. The difference was 161 mgm. The residue was re-cycled : on addition of ammonium fluoride to the final aqueous solution, a precipitate estimated at 2 mgm. of Th as fluoride was obtained. The solution was taken to dryness, a few drops of concentrated $HNO_3$ added, and evaporated down. This was repeated. The residue, after calcination to remove organic matter, which left a scarcely visible ring of matter, was taken up in ammonium fluoride solution. This formed a stock for the electrochemical work.

## Table VI

| MP K extract No: | 1 | 2 | 3 | Aqueous residue |
|---|---|---|---|---|
| $\gamma$-cts./min. | 7600 | 2200 | 400 | 60 |
| Volume | 3.8ml. | 5.5ml. | 5.6ml. | 5.4ml. |
| % Extraction | 75 | 81<br>of residual activity | 87 | -- |

## Table VII

| MP K extract Number | Vol. MP K added | Vol. MP K removed. | $\gamma$-cts./min. removed. | Total activity removed. |
|---|---|---|---|---|
| 1 | 15.0ml. | 8.5ml. | 2400 | 2400 |
| 2 | 11.0 | 11.0 | 3200 | 5600 |
| 3 | 10.0 | 10.0 | 1200 | 6800 |
| 4 | 12.0 | 12.0 | 2400 | 9200 |
| 5 | 32.0 | 32.0 | 2200 | 11400 |
| 6 | 32.0 | 32.0 | 1400 | 12800 |
| 7 | 27.0 | 27.0 | 400 | 13200 |
| Aqueous |  | 45ml. |  | 300 |

# SECTION III

## Applicability of the Nernst Equation at low concentrations.

### A. Introduction :

The validity of the Nernst Equation in concentrations greater than about $10^{-8}$ N hardly comes into question, since it is known to be obeyed above this range with non-radioactive isotopes, and it has also been verified for the radioactive isotopes of bismuth[23), 24)]. However, in concentrations less than this order, the quantity of material is barely sufficient to form even a monatomic layer on the electrodes, so that a sudden change of electrochemical behaviour in this region would not be surprising.

Since the quantity of ions in solution is then very small, and the electrolysis current corresponding to their transport insignificant compared with the total, due to $H^+$, $OH^-$, and impurities, it is not possible directly to determine the critical deposition potential by the potential-current method appliaable at macro concentrations.

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23) Hevesy and Paneth, Wien Ber., 1914. 123. 1909.

24) Haïssinsky, J.Chim.Phys., 1935. 32. 116.

Paneth and Hevesy[25] attacked the problem from a different aspect : they electrolysed for 24 hours a N/10 solution of Po in $HNO_3$ with gold electrodes, kept at definite potentials versus a reference electrode. By measuring the quantities deposited at different potentials, a curve was constructed, shewing a sharp rise corresponding to the critical potential for the discharge of the ions.

A further improvement by Joliot[26] consisted in devising an arrangement such that continuous monitoring was possible of the quantity of material deposited. His apparatus consisted of an electrolytic cell with metal foils as windows, thin enough to allow the passage of a proportion of the radiation from the deposited material. Atoms decaying in solution were recorded with very little (or, in the case of alpha-emitters, practically zero) efficiency, due to the absorptive effect of the solvent. By having ionisation chambers adjacent to the electrodes, the deposition could be directly and continuously measured. This principle of observation of velocity of deposition as a function of potential is the basis of all work so far published.

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25) Paneth and Hevesy, Wien.Ber.,1913.122.1037; 1914.123.1916.
26) J.Chim.Phys., 1930. 27. 119.

Previous workers have all used the natural radioactive elements : those with convenient periods lie in the range of Pb to U, but, of these, only Pb (ThB), Bi (RaE) and Po have properties suitable for tracers for electrochemical use.

The electrochemical deposition of polonium has been the most widely studied. Hevesy and Paneth 27), using $10^{-8}$ N solutions, found a cathodic deposition potential of + 0.63v. with respect to the normal hydrogen electrode. Wertenstein 28) using concentrations between $3.8 \cdot 10^{-9}$ and $3.8\ 10^{-11}$ N, found almost the same value and could not detect a potential shift greater than the experimental error of measurement, 30 mv. Joliot also, for concentrations of $1.1\ 10^{-8}$ to $6.10^{-10}$ N, could detect no shift. For a one hundred-fold change in concentration, a shift of only 28 millivolts is to be expected if polonium is tetravalent, or 56 mv. if divalent. These results, with such a large margin of error, give no certain indication of the applicability of the equation. Heal 29) using concentrations of $10^{-13}$ and $8\ 10^{-13}$ N found again a deposition potential of + 0.64 v.

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27) Wien.Ber., 1914. <u>123</u>. 1916.

28) Compt.rend.Soc.Sci.Warsovie, 1917. 10. 771.

29) National Research Council of Canada, Report MC-33.

and he considered this to disprove the applicability of the equation. at such low concentrations. However, taking account of the various ways in which curves can be drawn through his experimental points, the error is large and again no clear-cut decision is probable.

For the work on Bi 24) only the work of Haïssinsky with RaE and ThC is available : in the range of concentrations between $10^{-5}$ and $3\ 10^{-12}$ N he found critical potentials in good agreement with those calculated from the Nernst equation, and giving for the normal potential of the $Bi/Bi^{+++}$ electrode practically the same value as that found by Jellinek and Kühn 30) for macro quantities of Bi in reversible conditions.

The situation thus is that results for polonium, in several different conditions and concentrations, by different workers, lead to a denial of the Nernst equation at these low levels, but that, with Bi, the results of one worker lead to its confirmation. It is possible to find several explanations for this ambiguity. For example, Po is an element whose chemical behaviour is complicated by phenomena of hydrolysis, complex formation, adsorption

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30) Z.Phys.Chem., 1923. 105. 337.

and perhaps even aggregation into groups of atoms. Even yet, its valency states are not determined beyond question. Compared with the ease with which it may be handled in the vapour phase[31] its behaviour in solution is singularly difficult. With such an element, there may be difficulties, peculiar to itself, in the interpretation of its electrochemical behaviour. On the other hand, a concentration so low as "$10^{-12}$ N" (a microgram per cubic metre) of an element such as Bi, by no means uncommon, might well be spurious, in the absence of exceptional measures to exclude contamination from reagents and even from glassware and atmospheric dust.

The necessity for pushing the concentration limit down to such extremes is to get a shift so high as to be outside the region of experimental error. For this reason alone, both the trivalent Bi and the tetra-, tri-, or possibly di-valent Po are unsuited to the task.

In ~~a~~ recent publications[32], [33], Haïssinsky advances theoretical considerations why the Nernst equation should hold at these low concentrations when determined

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[31] Beamer & Maxwell : U.S.Atomic Energy Commission Declassified Document No.721.

[32] "Electrochimie des substances radioactives..."Hermann,Paris.

[33] J.Chim.Phys., 1946. 43. 21.

by such a method.

Herzfeld[34] modified the Nernst equation $E = \frac{RT}{nF} \ln \frac{P}{p}$ to take account of conditions where the amount of material is insufficient to form a monatomic layer on the electrode. The process is considered as dynamic, involving discharge of the ions at the electrode with simultaneous re-solution of some of those already deposited. Normally, with macro concentrations, one has a layer at least one atom thick and the number of ions passing back into solution is independent of the quantity already deposited. However, for solutions so dilute that such a layer cannot be formed, the amount of solution varies with the amount already deposited. Herzfeld then writes the equation

$$E = \frac{RT}{nF} \ln \frac{P'\pi}{p_o - \pi}$$

where p is the initial osmotic pressure, $\pi$ the fraction of the osmotic pressure corresponding to the maximum amount deposable at potential E.

Or, substituting for osmotic pressures the numbers of atoms,

$$E = \frac{RT}{nF} \ln \frac{P'x_m}{x_o - x_m}$$

expressing the dependence for each potential E of the

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[34] Physik.Z., 1913. 14. 29.

maximum number $x_m$ of atoms deposable at this potential upon the number initially present, $x_o$.

> Kinetic experiments by Joliot confirm this assumption to some extent. Using Po in nitric acid with a gold cathode, he plotted the amount deposited for different cathode potentials as a function of time. His results are summarised in Fig.9. For potentials more positive than the deposition potential (of 0.36 v. versus the N.C.E.), deposition stops after a time. At less positive values, deposition reaches a maximum which depends on the potential of the electrode. These curves follow an exponential growth
>
> $dx/dt = \alpha (kx_o - x)$ where k is a constant for each potential $= x_m/x_o$. $\alpha$ is a constant depending, inter alia, on the surface of the electrode.
>
> From his curves, the maximum quantities deposable at several different potentials may be calculated. From the modified equation, a plot of E versus $\ln \frac{x_m}{x_o - x_m}$ should be a straight line of slope RT/nF. Joliot's results lead to such a straight line, but yield a value of n, the electron transfer, of only 0.37. They thus confirm the modified equation qualitatively only.

The critical potential determined by the Paneth-Hevesy method is assumed by Haïssinsky from his results with Bi to give the true variation of potential with concentration down to $10^{-2}$ N. Since the method applies only to the beginning of deposition, Herzfeld's correction is negligible.

Haïssinsky's hypothesis may be summarised in this way :

The critical potential coinciding - in the absence

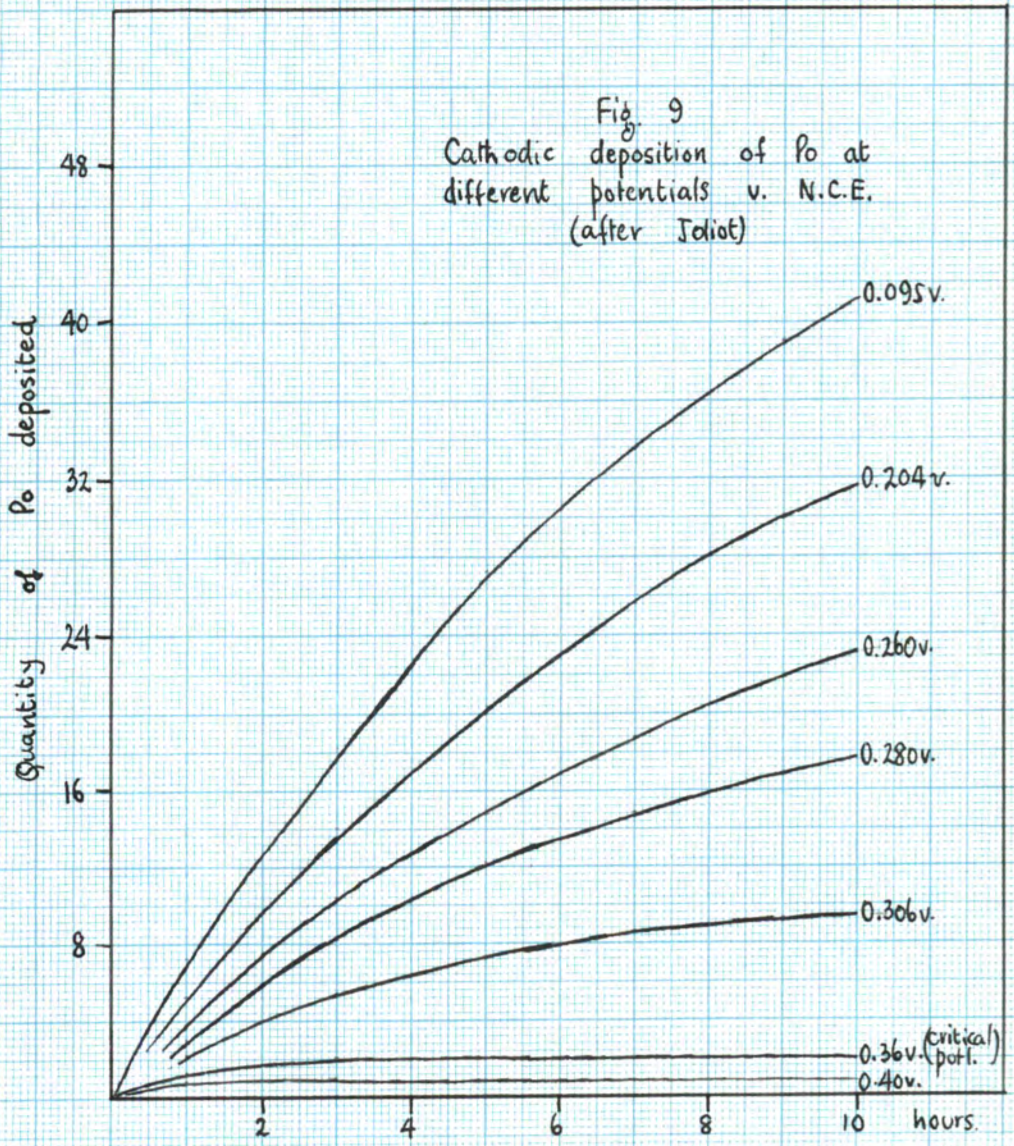
Fig. 9
Cathodic deposition of Po at different potentials v. N.C.E.
(after Joliot)
Quantity of Po deposited
48
40
32
24
16
8
2
4
6
8
10
hours
0.095v.
0.204v.
0.260v.
0.280v.
0.306v.
0.36v. (critical potl.)
0.40v.

of overvoltage - with the reversible electrochemical potential of the electrode is thus a measure of the free energy change in the electrode process. For example in the discharge of a monovalent hydrated cation :

$$(M^+)_{aq} + e^- \rightleftharpoons M$$

This may be split into the steps : 1) dehydration of the ion, involving expenditure of the heat of hydration, W; 2) removal of an electron from the electrode surface, with energy expenditure equal to the electronic work function, $\phi$, of the metal; 3) neutralisation by this electron of the ion formed in 1), yielding the ionisation energy of the atom, I; and 4) adsorption of this neutral atom on the electrode - the adsorption energy A is gained.

The overall energy expenditure on the system is therefore

$$= W + \phi - I - A$$

The variation in free energy is analogous, replacing the terms on the right by the partial free energies (entropy changes in the discharge of cations being small, one may identify changes in free energy with those of total energy).

He goes on to argue that, since W and I depend only on the ion discharged, and $\phi$ depends only on the electrode material, then, if the work function and the adsorption energy vary to the same extent with different metals, one can explain the independence of deposition potential from the nature of the support ( as observed by Hevesy and others). He goes on to shew from the work of Langmuir and Kingdon that one can practically identify A with $\phi$ . Further, experiments on volatilisation of radioelements from metallic supports by Bonet-Maury and others shew that the binding of even a single radioelement to a support is variable - one can volatilise at a given temperature from a solid support only a certain fraction of the element, and a higher temperature is necessary to increase the fraction. Some is more firmly bound to the surface than other - to active centres, Haissinsky maintains, and goes on to extend his argument to electrode surfaces.

For any support, there are a number of active centres for which $A = \phi$ , whereas for all other points on the surface $A < \phi$ . Thus, for deposition on active centres, the deposition potential depends only on the neutralisation potential of the ion and no activation energy is necessary. Therefore the critical potential, determined by the Paneth and Hevesy method, measuring as it does the minimum detectable deposit, is determined only by the neutralisation potential of the ion and, since $A = \phi$ , is independent of the nature of the electrode. Therefore the Nernst equation holds when applied in the classical manner and, in these conditions, Herzfeld's correction does not apply, the correction in $\pi$ being negligible.

For other points on the surface, less active than these centres, an activation energy must be supplied before deposition can occur. Curves of deposition versus potential, obtained with Joliot's apparatus, for Po and Bi, shew a "wave" similar to that obtained in polarography, and which have a breadth of 0.15 to 0.2 v. (or 3 to 5 calories). He points out that this is reasonable for differences of adsorption energy between different points of the same surface.

The following points need elucidation :

1) The discrepancy between the results for Po and Bi should be resolved by the use of another suitable radioelement as tracer,

2) The kinetics of deposition of different radioelements in different solvents, for a variety of electrode materials at different potentials, should be studied,

3) Experimental evidence should be sought for the existence of local centres of preferential deposit.

1) will be considered in detail in Section III b.

2) Since it was known that Haïssinsky and collabarators were working actively on these lines, no great amount of experimental work was done. What was performed is recorded, together with that coming under (3) in Section III c.

## B. Re-determination of the applicability of the Nernst Equation at low concentrations :

Optimum Properties of a Tracer Substance for this problem :

1) Since the potential change from, say, $10^{-8}$ to $10^{-11}$ N is only 174/n millivolts, choice is restricted to a mono- or di-valent cation for an unambiguous result (experimental errors being of the order of 30 mV.), but preferably the former,

2) To avoid complications due to the evolution of hydrogen at the cathode, the tracer must be fairly noble,

3) It must have a half-life convenient for the work; not too short, preferably, to avoid the fresh irradiation and extraction otherwise necessary for each determination (reproducibility might be endangered); and not too long, else the weight of material associated with a detectable activity of even the carrier-free nuclide might be inconveniently high. This consideration alone limits one to periods of, say, from rather less than a day to several months.

Other desiderata are that the electrochemistry in macro concentrations should be known and that the element should not be too common. For an element with no stable nuclide (such as polonium), the advantages arising from this latter outweigh the disadvantages of the former consideration.

A further limiting condition imposed at the time was the necessity of choosing a nuclide which could be made by neutron bombardment, since the only means of production of sufficiently high activities are bombardment in pile or accelerator, and the latter was not readily available. This, in turn, imposes the condition that, to get carrier-free material, only those neutrons reactions are permissible in which capture is followed by charged-particle emission to yield a different element. (We may discount the Szilard-Chalmers process since separation of the new atom is not absolute; only a concentration is effected).

The most desirable element, considering these points, would appear to be element 85, astatine, the lower homologue of iodine, produced by $Bi^{209}(\alpha,2n)At^{211}$. It is produced pure if the bombarding energy is between 21 and 28 MeV $\alpha$'s and separation from Bi is easily achieved by sublimation in vacuo at the melting-point of Bi. Experiments performed by Johnson, Leininger and Segre 35)

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35) AECD 1952, 10.5.48.

(from which the foregoing information is abstracted) shew that in 0.066 M.$HNO_3$ cathodic deposition is simple and reversible, at potentials of - 1.225 ± 0.025v. and - 1.220 ± 0.025v. for 2.8 $10^{-13}$ and $4.10^{-14}$ M. astatine solutions respectively. Even a single electron transfer would hardly shew a shift, discernible with such experimental errors, for such a low concentration range.

The only nuclide which fulfils all these severe limitations, however, is $Ag^{111}$, though several others are possible, but excluded on at least one count - e.g. $Zn^{65}$ and $Cd^{107,109}$ (both are cyclotron-produced).

$Zn^{65}$ was used by Haenny and Mivelaz 36) for verification of the Nernst Equation. The results presented, which they admit to be incomplete, shew, for an acetate-buffered solution which they claim to be $2.10^{-15}$ N in Zn, a critical potential of - 1.00 v. instead of the calculated - 1.18v. They had constant evolution of hydrogen from the cathode. Their value of $2.10^{-15}$ N may be contested on at least two grounds:

(1) no actual knowledge of the Zn content of their initial copper - though this was spectroscopically

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36) Helv. Chim.Acta, 1948. <u>31</u>. 633.

purd; with a target weight of even 100 mgm. and a lower limit of identification of 0.1 p.p.m., the inactive Zn is still present in overwhelming concentration.

(2) They counted their $Zn^{65}$ by means of the $\gamma$-rays. Reference to Fig.7 shews that they did not count any of the soft radiation and, considering that the efficiency of $\gamma$-counting is of the order of 1%, a further factor of several hundreds may be used to multiply their concentration, which was thus at least of the order of $10^{-12}$ N.

It was thought that, by the use of reagents whose purity with respect to silver might be put beyond question (e.g. by re-distillation of acids and use of gaseous reagents) and by the use of fused silica apparatus throughout in a room where silver had not been chemically treated, then the necessary low concentration might not be falsified by accidental contamination. For the activities to be expected, an upper limit for the silver content is $10^{-8}$ grams. Further, by keeping all conditions such as weight of material and irradiation time constant, using always the same batch of reagents, and varying only the neutron flux used - a factor of 100 is feasible - then, in the two cases, any accidental contamination would become apparent.

Two possibilities of preparing $Ag^{111}$ offer themselves : from irradiated Pd, or as a product of uranium fission.

*Preparation of $Ag^{111}$ from irradiated Pd* : Of the various isotopes of Pd, only two are of interest to us here, $Pd^{108}$ (27% abundance) and $Pd^{110}$ (13.5%).[37] The former yields $Ag^{109}$ (probably by $Pd^{108}(n, \gamma)Pd^{109} \rightarrow Ag^{109*} \rightarrow Ag^{109}$) which being stable, increases practically linearly with time, the intermediate species being short-lived. The isotopic cross-section for $Pd^{108}$ is 12.1 barns, which, corrected for abundance, gives 4.48 for the cross-section in natural Pd.

On the other hand, $Pd^{110}(n, \gamma)\ Pd^{111} \xrightarrow[26\text{ min.}]{\beta^-} Ag^{111}$, the isotope in which we are interested, and which undergoes an exponential build-up. The isotopic cross-section for this reaction is, however, only 0.63 barns,[37] which becomes only 0.085 barns when the abundance is considered. This means that one gram of pure Pd irradiated to saturation in a flux of $10^{10}$ neutrons/cm$^2$/sec. would give an activity of about 100 micro-curies of $Ag^{111}$. Assuming a bombardment of 1 gm.

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[37] MDDC - 626(b). Of the U.S.Atomic Energy Commission.

of pure Pd for one week, to half-saturation of $Ag^{111}$, we would have, from the former reaction, $2.10^{-8}$ gm. of $Ag^{109}$, and accruing from the latter, $2.10^{-10}$ gm. of $Ag^{111}$, with an activity of about 50 microcuries. This is already on the verge of the tolerance for inactive silver, or slightly above.

The main disadvantage, however, in the use of irradiated Pd as a source of $Ag^{111}$ is the necessity for reducing the inactive silver content to less than $10^{-8}$. No techniques apparent would guarantee the separation, apart from the impossibility of checking the purity of the material before bombardment.

In the Appendix (p. 121 ) is described a series of experiments on the precipitation of Pd - dimethylglyoxime from dilute acid solution. A considerable fractionation from silver, in trace amounts, is achieved.

Preparation of $Ag^{111}$ from irradiated uranium : A much more attractive proposition from the point of view of starting-material is the use of uranium, from which silver formed by fission (see below) might be extracted. It is known that uranyl nitrate may be extracted in a form of extreme purity by various organic solvents from dilute nitric acid solution, and it was felt that, with care, the inactive silver content might be held below the tolerance.

In the irradiation of uranium with slow neutrons, capture in $U^{235}$ probably first occurs, giving a compound nucleus of mass 236, which then undergoes fission, yielding two fragments whose masses total 236 - N, where N represents the number of fission neutrons liberated. These two fragments have both too high a ratio of neutron/proton for stability and consequently strive to reach a more stable nucleus by emission generally of beta-particles. We thus get chains of up to seven or eight members, with successive unit increase of atomic number, until a stable isotope is reached. The proportion of fissions which give rise to a given mass number is called the "fission yield" of the chain. Tables of nuclei formed in fission are given in the literature[38]. All elements from $_{30}Zn$ to $_{64}Gd$ are represented by at least one isotope, but the great majority of fission products lie in the ranges Br - Ru and Te - Pm. In Fig.10 is reproduced from Ref.38 the experimental dependence of fission yields upon mass number. $Ag^{111}$, it is seen, has a fission yield of only $\sim 1.8\ 10^{-4}$.

In addition to this $Ag^{111}$, there will be also present

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38) J.A.C.S., 1946. 68. 2416 - 2441.

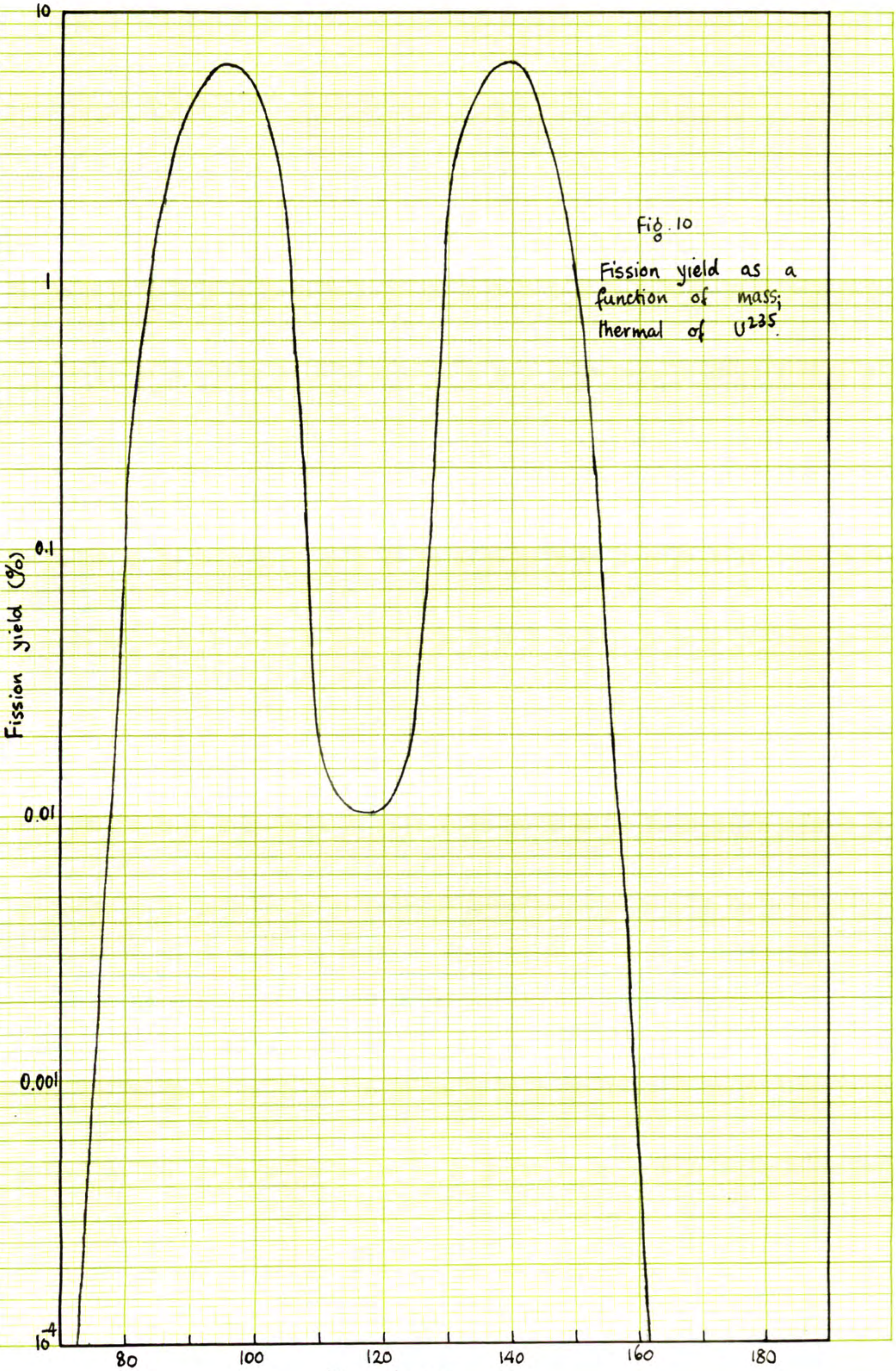

Fig. 10

Fission yield as a function of mass; thermal of $U^{235}$.

silver atoms, both active and inactive, arising from decay of other chains of different mass, but only the stable Ag isotopes will accumulate, the shorter-living Ag$^{112}$ (3.2 hrs.) decaying out to Cd$^{112}$.

Ag$^{107}$ would come from the chain of mass 107 whose first member is probably Tc$^{(107)}$, though this is uncertain. Pd$^{107}$ activity has not been detected; its half-life is either very short or greater than about 10$^{8}$ years. If the former, it would all go to Ag$^{107}$, if the latter, no Ag$^{107}$ would be formed. From interpolation in the graph, the fission yield of Ag$^{107}$ is thus either 2.10$^{-3}$ or zero.

Ag$^{109}$ is of much better-defined parentage, being the daughter of Pd$^{109}$ (13 hrs.) via an upper isomeric state Ag$^{109}$ (40 secs.). The fission yield of mass 109 is 2.8 10$^{-4}$.

From these considerations, Ag$^{111}$ is either about 0.18/2.16 or 0.18/0.46 of the total mass of fission silver present, i.e. about 7% or 40%. The activity of 0.5 millicurie (or 1.5 10$^{8}$ c.p.m. at 13% counter efficiency) estimated as probable would then be associated with 100/7 or 100/40 times its own mass of 10$^{-9}$ gm. Assuming 6.10$^{4}$ c.p.m. in 10 ml. as a reasonable working solution, this would correspond to a solution between

$10^{-11}$ and $10^{-12}$ M in silver, amply dilute for the purpose envisaged.

Thus it seemed from these considerations that the preparation from irradiated uranium, while chemically the more difficult, was likely to yield the higher specific activity.

## Extraction of carrier-free $Ag^{111}$ from irradiated uranium :

Samples of weight about 30 g. of $U_3O_8$ were irradiated in GLEEP for periods up to a month.

The general approach to the extraction was entirely chemical in nature, no attempt being made to utilise more physical methods. It was felt that the electrolytic extraction of the silver was not feasible, in view of the large excess of active Ru and inactive Pd present, both of which would be likely to co-deposit. Also it is known that traces of Te, Sb and Sn are easily brought down in the electrodeposition of copper (v., e.g., Allmand and Ellingham, "Applied Electrochemistry") and presumably would also co-deposit with Ag. In view of uncertainties such as these and indeed of the whole electro-deposition question at these concentrations, it was felt that such an electrolytic separation would itself be a long-term investigation.

It is first necessary, however, to remove the bulk of the uranium, leaving only the imponderables in solution. This was achieved by (1) extraction with diethyl ether of the bulk of uranyl nitrate from a concentrated solution about N/2 in free nitric acid, followed by (2) precipitation of uranium peroxide from the residual nitric acid solution with 100-vol. hydrogen peroxide. From considerations advanced on p. 83 , the adsorption upon $UO_4$ of cations which do not form peroxides insoluble in acid should be slight. Thus, of the possible elements present, only Th ($UX_1$) and, to a lesser extent Zr, should adsorb on the precipitated peroxide. (This was tested with a solution of radio-cerium containing only a fraction of a microgram of inactive cerium; 50 mgm. of uranium precipitated as peroxide from N/2 acid carried, after thorough washing with N/2 $HNO_3$ and $H_2O_2$ , less than 3% of activity ascribable to Ce).

In the various methods of extraction attempted, the following was adopted as a routine procedure :

> The $U_3O_8$ was dissolved in a minimal quantity of conc.$HNO_3$ under reflux, in a fume-cupboard with a strong draught, to avoid inhalation of the rare gases and halogens liberated 38) . In all but the first dissolution, about 20 mgm. of KI were added

to provide carrier for a source of active iodine required by another worker : the liberated iodine refluxed back into the flask. When solution was complete, the solution was cooled and the hold-up in the condenser carefully rinsed into the flask. The iodine was extracted by several washes with $CCl_4$ until no further visible extraction occurred.

The residue from the $CCl_4$ extraction was evaporated to dryness on a water-bath and taken up in the minimal amount of N/2 $HNO_3$. It was then extracted four times with volumes of ether roughly equal to that of the aqueous phase: this sufficed to remove the bulk of the uranyl nitrate. The residual aqueous solution was heated on a water-bath in a covered evaporating basin (to avoid spattering of solution by the breaking bubbles of ether). This done, the cooled solution was diluted to about 40 ml. with N/2 $HNO_3$ and treated with 100-vol. hydrogen peroxide until no further precipitation occurred. The suspension was allowed to stand one hour, then a further small amount of peroxide added to ensure complete precipitation of uranium. The precipitate was centrifuged off and washed thoroughly three times with N/2 + 5% of 100-volt peroxide. The residual solution plus washes was taken down to dryness, leaving an intensely active residue with a small amount of potassium nitrate. This was dissolved in N/5 HCl, and carriers added. These comprised 20 mgm. of La, and 5 mgm. each of Zr, Ru, Te and Cd; (Sb and Sn were omitted at this stage, to avoid the formation of troublesome insoluble acids). The Ia acts as hold-back carrier for the rare earths, Zr.for the Cb$^*$ present as well as for the Zr$^*$. $H_2S$ was passed in the cold for ten minutes to coagulate the precipitate and to ensure maximum co-precipitation of Ag$^*$ with the sulphide precipitate. This was centrifuged off, washed twice with N/5 HCl saturated with $H_2S$ and once with water. The precipitate was dissolved, still in the centrifuge cone, with 3 ml. conc. $HNO_3$ + a few drops of HCl and taken to dryness twice with conc. $HNO_3$ to remove sulphur. It was then taken up in conc.HCl, diluted to N/5, more La and Zr. added, and the Ru, Te and Cd. reprecipitated to reduce the rare-earth, Zr and Cb activity practically to zero. After washing and solution as before, a stock solution was obtained for further treatment.

Other fission products possibly present in this sulphide precipitate (except for traces of sulphide-soluble elements carried down by adsorption, and omitting stable isotopes) are the following 38) :

Table VIII.

| Isotope | Half-life | Fission Yield |
|---|---|---|
| $^{77}\mathrm{As}$ | 40 hrs. | $9\ 10^{-5}$ |
| $^{99}\mathrm{Mo}$ | 67 hrs. | $6\ 10^{-2}$ |
| $^{99}\mathrm{Tc}$ | $10^{6}$ yrs. | |
| $^{103}\mathrm{Ru}$ | 42 d. | $3.7\ 10^{-2}$ |
| $^{106}\mathrm{Ru}$ | 1.0 yr. | $5\ 10^{-3}$ |
| $^{103}\mathrm{Rh}$ | 50 min. | |
| $^{106}\mathrm{Rh}$ | 30 sec. | |
| $^{112}\mathrm{Pd}$ | 21 hrs. | $1\ 10^{-4}$ |
| $^{115}\mathrm{Cd}$ | 2.3 d. | $1\ 10^{-4}$ |
| $^{115}\mathrm{Cd}$ | 44 d. | $8\ 10^{-5}$ |
| $^{(121)}\mathrm{Sn}$ | 62 hrs. | $1\ 10^{-4}$ |
| $^{(121,123)}\mathrm{Sn}$ | 130 d. | $1\ 10^{-5}$ |
| $\mathrm{Sn}^{?}$ | 10 d. | $4\ 10^{-5}$ |
| $^{125}\mathrm{Sb}$ | 2.7 yrs. | $2\ 10^{-4}$ |
| $^{127}\mathrm{Sb}$ | 90 hrs. | |
| $^{127}\mathrm{Te}$ | 90 d. | $3\ 10^{-4}$ |
| $^{129}\mathrm{Te}$ | 32 d. | $2\ 10^{-2}$ |

Of this list, severalx elements may be discounted. $Tc^{99}$, despite its high fission yield, is only formed to a minute extent in a bombardment of a few weeks. As and Pd (also the Se and In formed) die out in a few days; Rh need not be separated, since it all comes from Ru parents, and, these being removed, will quickly die out. This leaves as possible contaminants : Te, Mo, Sb, Sn, Ru and Cd.

(Before proceeding further, a separation of silver was made from a portion of the solution, with 5 mgm. added silver carrier, to characterise the radiation. A count of $10^4$/min was obtained, shewing that silver was not removed with the $UO_4$ precipitate).

The proposed method of extraction was to remove as many as possible of these contaminants by specific treatments, leaving the silver behind, and to bring the silver down from the residual solution with some suitable non-isotopic carrier, which might then be removed.

I. <u>Distillation methods</u> : A survey of methods given in standard texts 39),40),41) on analysis of the rarer elements shewed that Ru is generally removed as the volatile

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39) Noyes & Bray :"Qualitative Analysis for the Rarer Elements"

40) Schoeller & Powell :"Analysis of Minerals & Ores of the Rarer Elements".

41) Beamish et al.,Ind.Eng.Chem.,Anal.Ed.,1940. <u>12</u>. 561.

tetroxide, $RuO_4$, from boiling perchloride acid solution. Noyes and Bray also recommend as "fairly satisfactory" for the removal of Sb, Sn and Ru a distillation in a current of steam and hydrogen chloride.

(i) To one-half of the stock "sulphide group" solution prepared as above were added 5 mgm. each of Sn and Sb, and the solution evaporated just to dryness. The residue was washed into the distilling flask of the apparatus shewn in Fig.11, and 5 ml. of fuming perchloric acid added. The temperature was raised gradually until the yellow colour of the distillate shewed $RuO_4$ to be passing over into the trap of 6N.NaOH (this also removes Tc). When distillation of Ru ceased, the flask was cooled and 5 mgm. more of Ru added, and distilled off in turn. This step was repeated. At this point, the distillate and residue were allowed to stand overnight to allow Rh daughters to die in the solution and to grow in the distillate. A measurement of comparative $\gamma$-activities next day shewed that only some 15% of the $\gamma$-activity was removed with the Ru. The residue in the distillation flask was a pale brown suspension in perchloric acid. This was

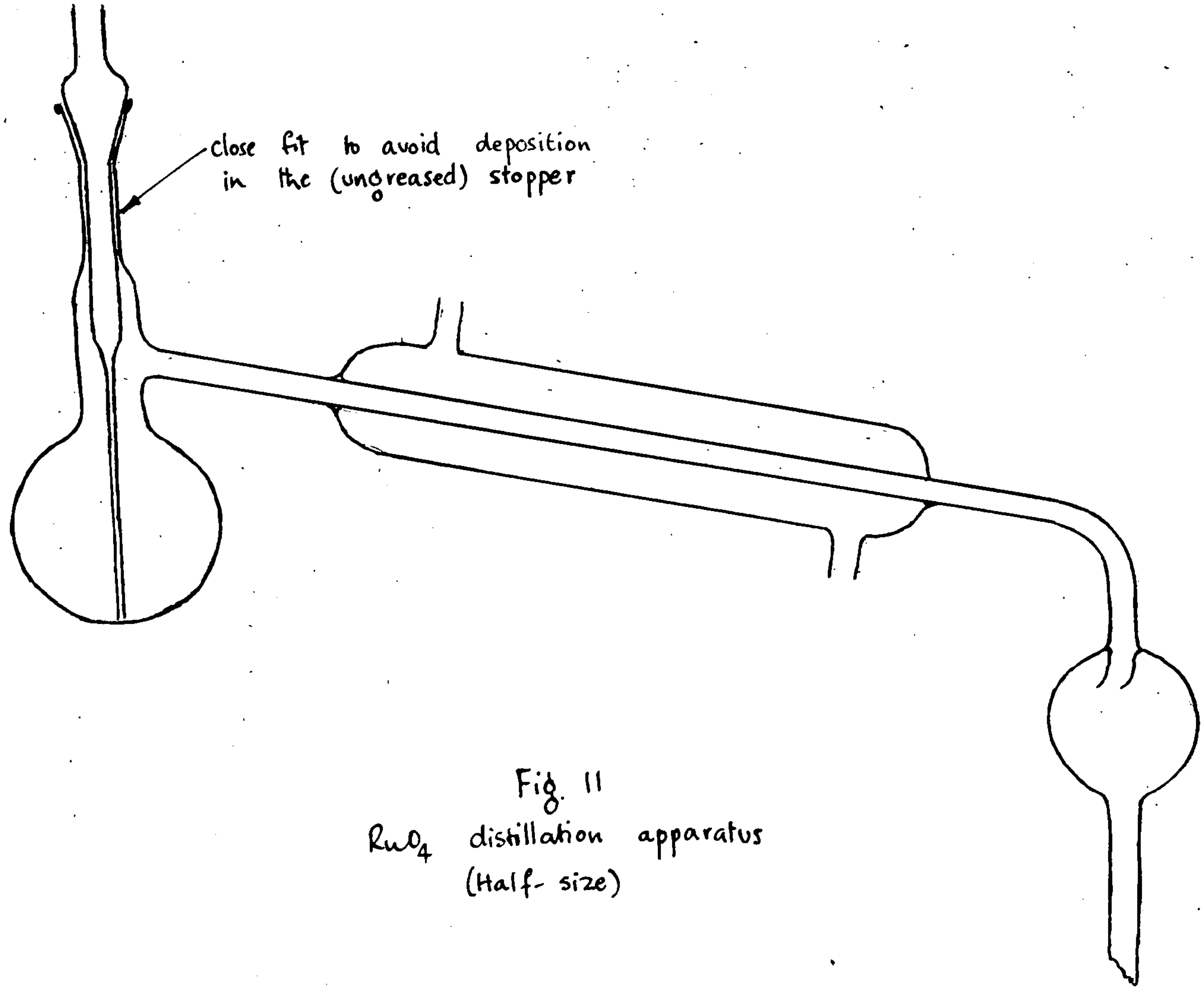

Fig. 11

$RuO_4$ distillation apparatus

(Half- size)

heated to boiling and a stream of hydrogen chloride passed through by boiling conc. HCl in a separate flask. Distillation was carried on for an hour without any apparent diminution of the solid residue in the flask, and the experiment was stopped at this point.

(ii) It was thought that the precipitate might consist of stannic and antimonic acids brought down by the fuming perchloric acid. The experiment was performed in inverse order, following the advice of Noyes and Bray 39) to keep the temperature of the solution between 170° and 180°. This was done, using a hot paraffin bath, and passing HCl gas through from the start. Even in these conditions, precipitation was visible in 15 mins.and the brown colour of the Ru still persisted in the flask. Distillation was carried on for 40 mins. by which time a precipitate much as in (i) was obtained, and separation of Ru was visibly incomplete.

(iii) Instead of the strongly oxidising fuming perchloric acid, which might cause the excessive precipitation, another run was made using sulphuric acid. A portion of stock sulphide group solution, in 5 ml. conc. HCl, was added to the distilling flask, 1.0 ml.

of conc. $H_2SO_4$ added and the whole saturated with HCl gas in the cold. The mixture was distilled down to about 2 ml. bulk, cooled, more conc. HCl added, and re-distilled. No great turbidity was observed in the residue, but only a faint opalescence was found in the NaOH trap : the liquid, however, did assume a faint yellow colour, perhaps due to some Ru distillation. With this was associated about 10% of the total $\gamma$-activity. The Ru was distilled as previously, with $HClO_4$, and a further 15% of the $\gamma$-activity collected. The large bulk of the activity was with the residue in the flask still.

II. *Chlorination methods* : It was felt inadvisable to continue these distillation experiments further, in view of the poor success obtained.

A characteristic of most of the important contaminants listed in Table VIII is the volatility of the chlorides.

(i) To a portion of the solution was added another 5 mgm. of Ru and 1/2 mgm. each of Sb, Sn and Te. This was evaporated almost to dryness and transferred to a micro porcelain boat, and dried on a steam-bath. It was then heated in a stream of chloride, dried with conc.$H_2SO_4$ and $P_2O_5$, for an hour at temperatures gradually increasing from 310° to 520°, and bubbling through water traps. On cooling, it was found that a small white sublimate had passed to the cool part of the tube, but that the dark Ru was still present in the boat and that with it was associated almost all of the activity.

(ii) A second run was made, taking great precautions to avoid dampness. The apparatus was dried with acetone and ether and the tube baked out. To the active material was added now only 1 mgm. of Ru, but 4 mgm. each of Sb, Sn and Te, with 2 mgm. of Cd. The dried mass was placed in the tube and heated to 290° in a stream of dried air. The air was then displaced with chlorine in the cold : a light yellow oil distilled into the traps and produced a faint turbidity. On raising the temperature to 390° for 50 mins., a white sublimate formed, which was chased along the tube into the traps.

The measured activity of the precipitate in the water traps was again only a few percent of the total, the dark Ru residue containing practically all.

III. Co-precipitation Experiments : The early work of Fajans[42] and Paneth[43] led to the formulation of a rule which states that invisible quantities of a cation are generally carried down with a precipitate whose anion forms with this cation a compound insoluble in the medium concerned. On the basis of this, silver should be carried down by insoluble chlorides, bromides and iodides, and perhaps by insoluble sulphates. A series of experiments was therefore made, using as tracer the sulphide group minus Ru (from earlier experiments). Duplicate runs were made in each case. In parallel experiments, 5 mgm. of Pb was precipitated as chloride, bromide, or iodide from 8 ml. of solution by 100% excess of precipitant, in the cold, having previously added a suitable measured quantity of the active solution (generally around 100,000 cpm.). There was no regularity apparent in the amounts of activity carried down, these being uniformly low and in the region of 5 - 15% of the amount added. Duplicate, and even quadruplicate, experiments varied within these limits. Moreover, the absorption in aluminium shewed a complex curve, and decay curves on each sample shewed no recognisable seven-day period.

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[42] Fajans, Ber., 1915. 48. 700.

[43] Paneth, Physik.Z., 1914. 15. 924.

Lead sulphate, on the other hand, carried much more of the activity, averaging about 50% of the total. This is certainly due to partial adsorption of probably all the activities present.

These tentative experiments shewed little hope of cleaning the silver by such means - with the unavailability of silver of very high specific activity, no more precise measurements were possible.

IV. Solvent extraction of Silver : It is known (v.,e.g. "Handbook of Chemistry and Physics", 1946) that silver perchlorate is soluble in benzene, toluene and xylene. Experiments were made to see if this might be made a basis for extraction.

Inactive silver perchlorate was added to solutions containing sodium perchlorate (to act as a salting-out agent) and perchloric acid in varying proportions, at as high a concentration as possible. The solutions were shaken with benzene or toluene, the supernatant organic layer removed and chloride added. No precipitate was obtained in any case. Work was discontinued.

In view of these unpromising results, after several month's intermittent work, the attempt to extract carrier-free silver was abandoned. The method of co-precipitation was, however, successfully used at a later stage : using mercury carrier in a cyclical precipitation of sulphide, iodide and metal, a clean $Ag^{111}$ activity was obtained. This is described in Appendix (p. 121 ).

Other methods : In the last few weeks of work reported here, but too late for work to be done on the subject, there appeared in the literature44) a series of papers by American workers on the separation of inorganic ions by means of synthetic ion-exchange resins. By means of these, e.g., even the most closely similar rare earths can be separated in amounts ranging from carrier-free material up to kilogram quantities. These resins consist of insoluble and infusible phenolic resins containing free methylene sulphonic acid groups, the hydrogen of which may be exchanged, on a strict Mass Action basis, with inorganic cations present in solution. On the addition of a solvent containing inorganic cations to the top of a column of resin, exchange occurs and hydrogen is displaced. The greater the valency of the ion and the smaller the (hydrated) ionic radius, the stronger the affinity between resin and cation. Thus we have, e.g.,

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44) J.A.C.S., 1947. 69. 2769 - 2881; MDDC 1447, Nov.1947.

$Th^{4+} > La^{3+} > Al^{3+} > Ba^{2+} > Na^{+} > H^{+}$. Anions, including anionic forms of metals, flow through the column without exchange. The essential procedure in the work so far reported is "complexing elution"; for example, having adsorbed, say a mixture of zirconium and lanthanum, even in a carrier-free state, at the top of the column, by the action of dilute oxalic acid the zirconium is converted to the very stable anionic oxalate complex and is eluted, while the lanthanum is essentially unmoved.

It would seem that this is a most suitable method for tackling the problem under discussion: it is easy to envisage ways of separation of the silver from most other contaminants, either by complexing anionic elution or by simple displacement by another cation on a mass-action basis. For example, on the results of the American work, where it is found that both Te and Ru washout with acids - presumably in the form $TeCl_6^{--}$ with HCl - it may be expected that Sb and Sn will behave similarly. This would leave then only the separation of Cd and Ag, and a problem thus greatly simplified.

## C. The Spontaneous Deposition of Protactinium on Metal Foils :

For the experiments on electrodeposition of $Pa^{233}$ in $NH_4F$ and $H_2SO_4$ solution, to be described in Section IV, it was necessary to investigate the spontaneous deposition on various metals in these electrolytes, since the absence of any appreciable spontaneous deposition greatly facilitates the estimation of the "knickpunkt", where the sudden rise of deposition occurs. Preliminary studies shewed the kinetics of this deposition, and the amount of activity taken up, to be widely different for the different metals and to depend partially on the preliminary treatment of the metal surface.

Depite the fact that radioelements have been available for several decades, little attempt has been made to use them to investigate the early stages of electrodeposition. Joliot 26), Haïssinsky 45),46) and Tammann and Wilson 47) have investigated the kinetics of the deposition of Po in various conditions and for various substrates. Flagg and Bleidner 48) measured the deposition of element 43 ("technetium") at different times, for varying potentials (they give few

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45) J.Chim.Phy., 1932. 29. 453.

46) ibid., 1933. 30. 27.

47) Z.Anorg.Chem.,1928. 173. 137.

48) J.Chem. Physics, 1945. 13. 269.

experimental points, and the errors, which are rather large, make their results of little value for comparative purposes). Joliot's results have been summarised already (p. 60 ): they lead to the equation

$$dx/dt = \alpha\ ( kn_o - x)$$

which may be compared with Tammann and Wilson's equation

$$dx/dt = k\alpha\ (n_o - x)$$

where $\underline{x}$ is the number of atoms deposited, $\underline{\alpha}$ a constant depending on the experimental conditions ( $\alpha = DS/\delta V$, where $\underline{D}$ is the diffusion coefficient of the ions, $\underline{S}$ the surface of the electrode, $\underline{\delta}$ the thickness of the diffusion layer near the electrode, and $\underline{V}$ the volume of the solution). $\underline{k}$ is a constant for each potential and represents the maximum fraction of the total activity deposable at that potential. For conditions favourable to deposition, $\underline{k}$ tends towards unity , and the two equations tend to identity.

Or,

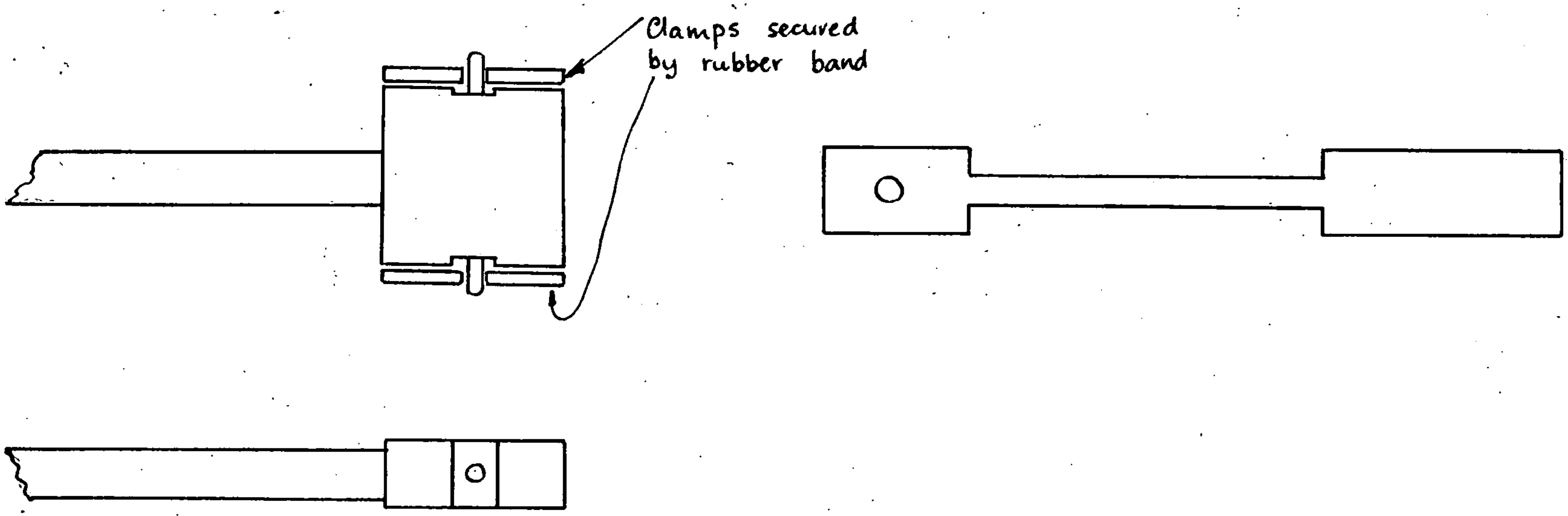
$$x = n_{max.} (1 - e^{-\alpha t}).$$

Tammann and Wilson consider that the spontaneous deposition of Po on Au, Pt and Pd is due only to adsorption and not to an eletrochemical displacement.

Little has been reported on the spontaneous deposition of Pa - Haïssinsky and Emmanuel found it to deposit very badly on Pb, Fe and Zn in $H_2SO_4$ solution, better on Zn in HF solution, but again with a moderate yield. Bouissières found it to be excellent on Be in slightly acid HF solution. The work done here agrees in the main with these conclusions.

Experimental : This was extremely simple, consisting only of a metallic foild suspended in a stirred solution of $Pa^{233}$, at the desired concentrations of Pa and ammonium fluoride. To ensure reproducibility of stirring and to simplify operation, a device due to Heal 29) was used. Rather than stir the solution or rotate the electrode, as in previous work, he kept the stirrer and electrode fixed with respect to one another, dipping in a beaker which revolved at constant speed. In the present system, the electrode(s) were clamped in a perspex holder with no metal fittings (to avoid contact potential differences); the 25 ml. vessel used was held with plasticene on a 2" turntable attached to a 24v. motor which, by gearing and a potentiometer, could be revolved at speeds between 60 and 120 rpm. - in general, a speed of 96 rpm. was standard. Where successive measurements involved removal and replacement of electrodes from the solution, care was taken to replace them in the same position as before with respect to both stirrer and solution. The standard size of electrode used and the perspex holder are shewn in Fig. 12. The hole in the lug serves to locate the electrode correctly in the holder, by means of a spigot in the latter.

Electrodes were cut with scissors from a sheet or foil of thickness about 0.005". A thin coat of "Brushing Belco" enamel was applied to cover the shank and obverse side of the electrode and, as far as possible, the raw edges left on cutting. This enamel was baked on with an infra-red lamp. Were some such insulator not employed, errors might arise if large amounts of activity were deposited on each side of a foil, for, while one side was being counted, radiation from $Pa^{233}$ deposited on the other side might otherwise penetrate the foil and be counted. The amounts of material which are adsorbed by the enamel in the solvents used are quite small - a copper foil, painted on both sides, adsorbed an average of 90 cpm./$cm^2$ in 12 hours immersion. Since the adsorbed material is on the obverse side of the foil, the radiation would be diminished on passing through to the counter. The diminution of counting-rate of a strong source of $Pa^{233}$ by the various foils used was also investigated.



A. Electrode holder (full size)
Perspex

Fig. 12

B. Electrode (twice size)

## Table IX

| Metal | None | Ni | Cu | Zn | Ag | Cd | Pt | Pb |
|---|---|---|---|---|---|---|---|---|
| Thickness (mgm/cm$^2$) | | 214 | 74 | 64 | 130 | 425 | 280 | 150 |
| Counts/min | 9900 | 0 | 74 | 104 | 46 | 82 | 71 | 47 |
| % passing | | 0.0 | 0.8 | 1.1 | 0.5 | 0.8 | 0.7 | 0.5 |

This shews that adsorption on the enamel, when filtered through the foil, is quite insignificant.

The standard method of preparation of the electrode surface was to clean with the finest emery paper after baking, to produce a smooth matte finish, and final polishing was made with paper worn by rubbing against another sheet. In various specific cases, this treatment was followed by immersion in the inactive solvent.

Autoradiographs were made by clamping the sample face to face with a small piece of "Kodak" Lantern Plate, and exposing for from 4 to 30 hours, dpending on the surface density of Pa$^{233}$. There is no point in using any emulsion other than this, since only very energetic radiation is involved, and the relative insensitivity of these plates makes manipulation in a subdued light convenient. Development in undiluted Kodak D-11 developer gave a suitably contrasty image.

a linear increase of deposition with time was apparent. While this method of removal and replacement is open to criticism, it was felt to be a reasonable compromise between those methods which use separate foils for each determination for a particular time, and those methods involving continuous monitoring of deposition, and which, unless much time is spent in preparing extremely thin foils for each metal, are relatively insensitive.

Results are shewn in Tables X to XXV, and graphically in Figs.14 - 18.

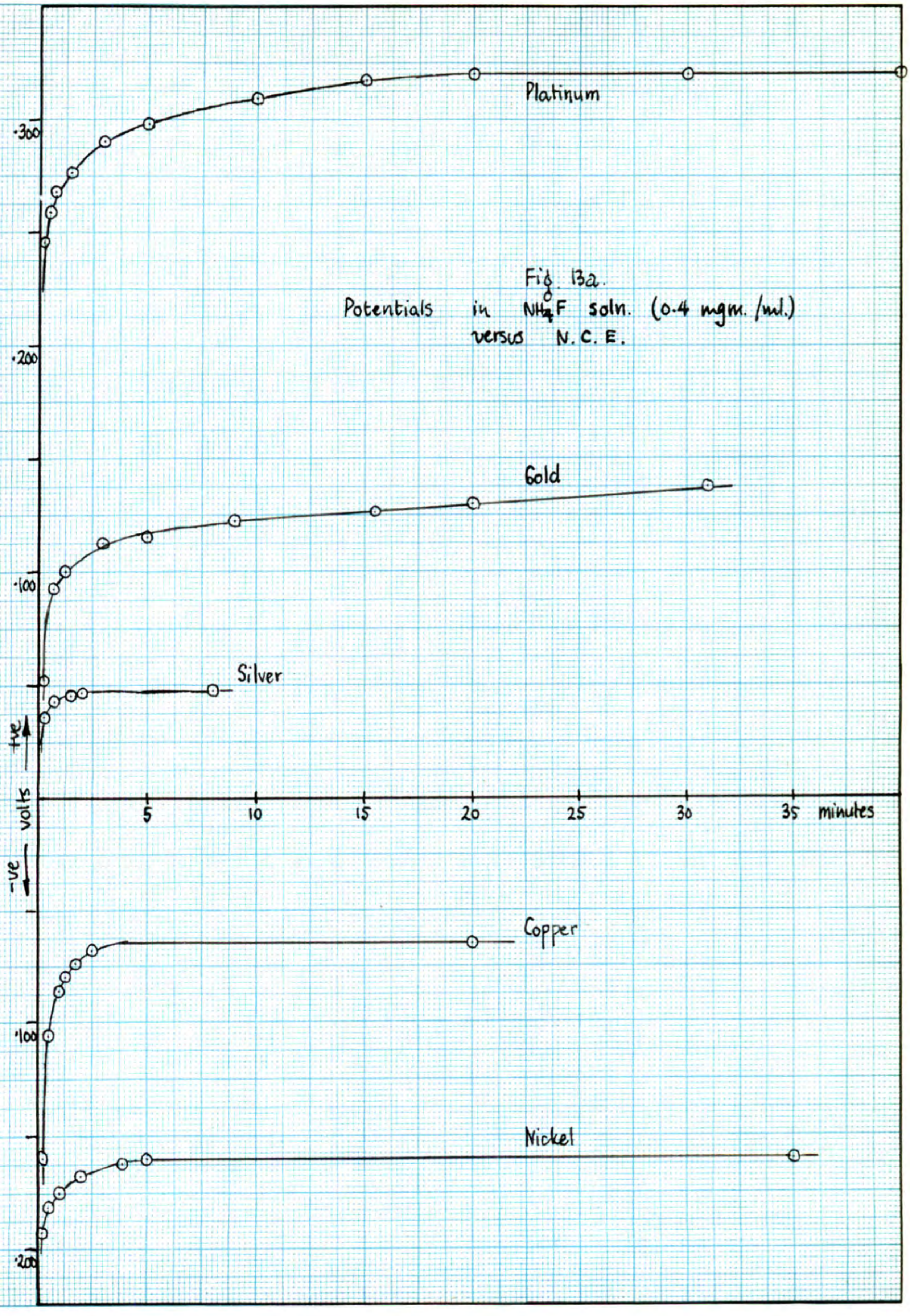


Fig. 13a.

Potentials in $NH_4F$ soln. (0.4 mgm./ml.) versus N.C.E.

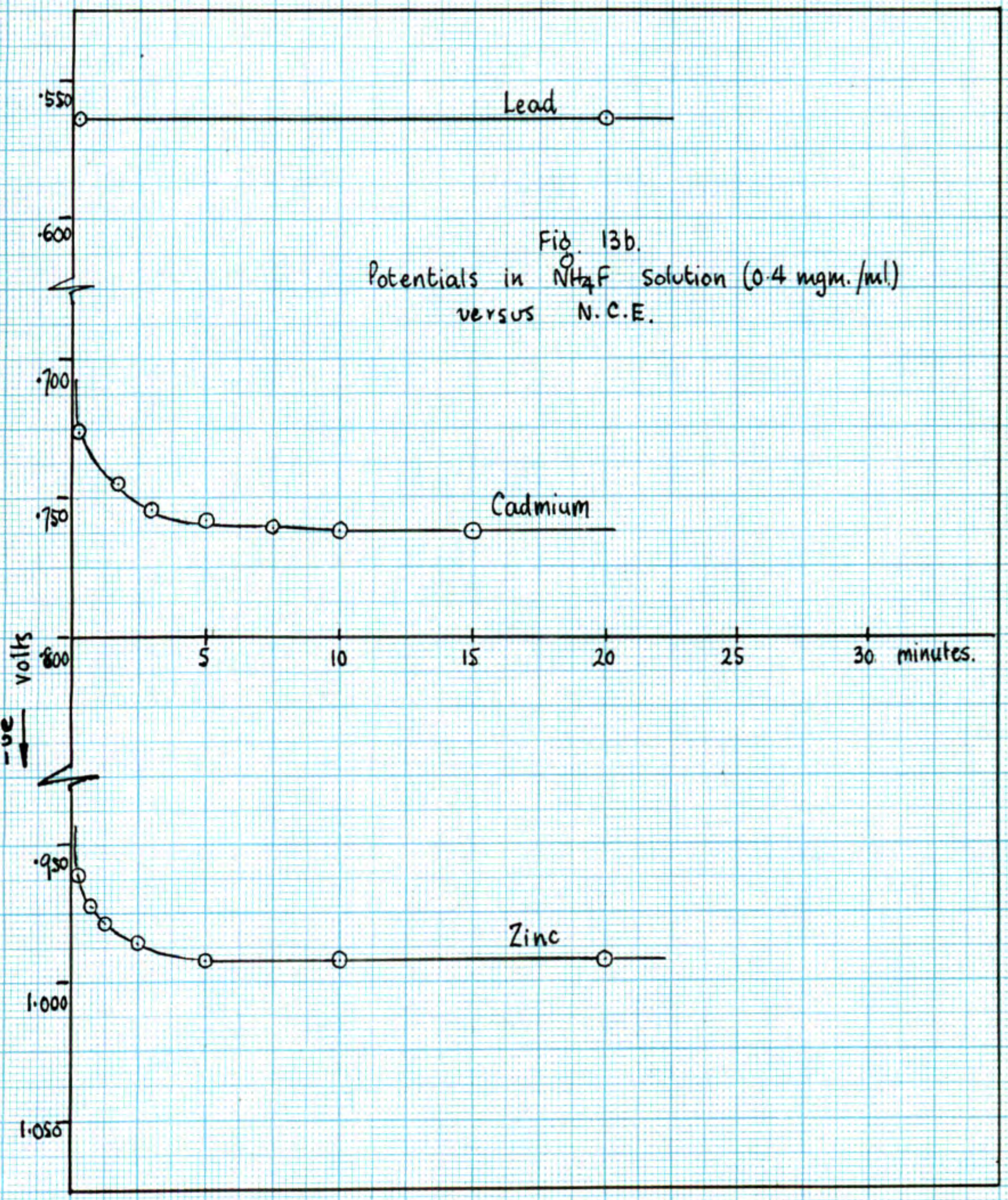


Fig. 13b.
Potentials in $NH_4F$ solution (0·4 mgm./ml.)
versus N.C.E.

## Table X

Solution : $NH_4F$ containing 5.71 $10^{11}$ atoms Pa/ml.

Electrode material : Platinum, superficial area 96 $mm^2$.

Pretreatment : Clean with emery, then 60 mins. in $NH_4F$.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 20 | 20 | 1.28 $10^8$ |
| 72 | 92 | 3.28 |
| 60 | 152 | 4.28 |
| 60 | 212 | 4.32 |
| 100 | 312 | 4.60 |
| 90 | 402 | 5.38 |
| 120 | 522 | 5.21 |
| 78 | 600 | 6.30 |

## Table XI

Solution : $NH_4F$ containing 4.12 $10^{11}$ atoms Pa/ml.

Electrode material : Gold, superficial area 100 $mm^2$.

Pretreatment : I. Clean with emery, then 2 hours in $NH_4F$.

II & III. Hot 8N.$HNO_3$ for 5 mins, hot satd.$NH_4F$ for 5 mins.

| | Time interval (secs) | Total time (secs) | Atoms deposited |
|---|---|---|---|
| I. | 60 | 60 | 3.85 $10^8$ |
| | 60 | 120 | 4.38 |
| | 120 | 240 | 4.00 |
| II. | 10 | 10 | 2.21 $10^9$ |
| | 10 | 20 | 1.80 |
| | 20 | 40 | 1.68 |
| | 60 | 100 | 1.41 |
| | 300 | 400 | 1.20 |
| | 4800 | 5200 | 1.17 |
| III. | 10 | 10 | 1.42 $10^9$ |
| | 10 | 20 | 1.19 |
| | 10 | 30 | 1.09 |
| | 10 | 40 | 1.01 |
| | 20 | 60 | 0.93 |

## Table XII

Solution : $NH_4F$ containing 5.65 x 10" atoms Pa/ml.

Electrode material : <u>Silver</u>, superficial area 96 $mm^2$.

Pretreatment : Clean with emery.

| Time interval (mins) | total time (mins) | Atoms deposited |
|---|---|---|
| 10 | 10 | 3.2 $10^7$ |
| 20 | 30 | 8.5 |
| 30 | 60 | 1.16 $10^8$ |
| 40 | 100 | 1.26 |
| 100 | 200 | 1.60 |
| 100 | 300 | 1.64 |
| 100 | 400 | 1.80 |
| 180 | 580 | 1.80 |

## Table XIII

Solution : $NH_4F$ containing 4.10 $10^{11}$ atoms Pa/ml.

Electrode material : <u>Copper</u>, superficial area, 96 $mm^2$.

Pretreatment :
I. Clean with emery
II. Clean with emery, then 15 hrs.in $NH_4F$
III. Clean with emery, then 48 hrs.in $NH_4F$ (corrosion visibly beginning)

| | Time interval (secs) | total time (secs) | Atoms deposited |
|---|---|---|---|
| I. | 30 | 30 | 1.63 $10^8$ |
| | 60 | 90 | 1.58 |
| | 210 | 300 | 1.76 |
| | 120 | 420 | 1.64 |
| II. | (mins) | (mins) | |
| | 10 | 10 | 8.30 $10^8$ |
| | 10 | 20 | 9.2 |
| | 20 | 40 | 9.7 |
| | 60 | 100 | 9.3 |
| III. | 10 | 10 | 2.60 $10^9$ |
| | 10 | 20 | 2.58 |
| | 20 | 40 | 2.68 |
| | 85 | 125 | 2.60 |

## Table XIV

Solution : $NH_4F$ containing $5.68\ 10^{11}$ atoms Pa/ml.

Electrode material : Nickel, superficial area 96 $mm^2$.

Pretreatment : Clean with emery, then 60 mins. in $NH_4F$.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 10 | 10 | $2.10\ 10^8$ |
| 20 | 30 | 3.40 |
| 35 | 65 | 5.8 |
| 25 | 90 | 5.3 |
| 50 | 140 | 5.6 |
| 65 | 205 | 4.7 |
| 95 | 300 | 4.7 |
| 120 | 420 | 4.8 |

## Table XV

Solution : $NH_4F$ containing $4.10\ 10^{11}$ atoms Pa/ml.

Electrode material : Lead, superficial area 24 $mm^2$.

Pretreatment : Clean with emery.

| Time interval (secs) | Total time (secs) | Atoms deposited |
|---|---|---|
| 10 | 10 | $3.35\ 10^9$ |
| 10 | 20 | 4.90 |
| 10 | 30 | 5.87 |
| 30 | 60 | 7.00 |
| 40 | 100 | 8.45 |
| 50 | 150 | $1.08\ 10^{10}$ |
| 50 | 200 | 1.30 |
| 50 | 250 | 1.56 |
| 150 | 400 | 2.42 |

## Table XVI

Solution : $NH_4F$ containing 4.20 $10^{11}$ atoms Pa/ml.

Electrode material : Cadmium, superficial area 96 $mm^2$.

Pretreatment : Clean with emery.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 0.5 | 0.5 | 2.78 $10^{10}$ |
| 0.5 | 1.0 | 4.98 |
| 0.5 | 1.5 | 5.68 |
| 0.5 | 2.0 | 6.10 |
| 0.5 | 2.5 | 6.21 |
| 1.0 | 3.5 | 6.21 |
| 5.0 | 8.5 | 6.80 |
| 10.5 | 19.0 | 8.50 |
| 11.0 | 30.0 | 1.03 $10^{11}$ |
| 5.0 | 35.0 | 1.26 |
| 5.0 | 40.0 | 1.33 |

## Table XVII

Solution : $NH_4F$ containing $5.70\ 10^{11}$ atoms Pa/ml.

Electrode material : Zinc, superficial area 96 $mm^2$.

Pretreatment : Clean with emery, then 30 hrs. in $NH_4F$.
(surface visibly attacked).

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 10 | 10 | $1.34\ 10^{11}$ |
| 4 | 14 | 1.56 |
| 6 | 20 | 1.63 |
| 10 | 30 | 2.12 |

## Table XVIII

Solution : $NH_4F$ containing $4.10\ 10^{11}$ atoms Pa/ml.

Electrode material : Zinc, superficial area 24 $mm^2$.

Pretreatment : II. Clean with emery.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 2 | 2 | $1.89\ 10^{10}$ |
| 2 | 4 | 5.74 |
| 2 | 6 | $1.00\ 10^{11}$ |
| 2 | 8 | 1.47 |
| 1.5 | 9.5 | 1.75 |

## Table XIX

Solution : 0.3 N $H_2SO_4$ containing $2.11\ 10^{10}$ atoms Pa/ml.

Electrode material : Lead, superficial area 96 $mm^2$.

Pretreatment : Clean with emery.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 2 | 2 | $1.91\ 10^{8}$ |
| 2 | 4 | 2.33 |
| 6 | 10 | 2.76 |
| 10 | 20 | 3.00 |
| 20 | 40 | 3.16 |
| 20 | 60 | 3.65 |
| 20 | 80 | 3.63 |
| 30 | 110 | 3.60 |
| 70 | 180 | 3.64 |

## Table XX

Solution : 0.3N $H_2SO_4$ containing $3.55\ 10^{11}$ atoms Pa/ml.

Electrode material : Gold, area 192 $mm^2$.

Pretreatment : Plated on in hot HCl-KCN electrolyte.

| Time interval (mins) | total time (mins) | Atoms deposited |
|---|---|---|
| 5 | 5 | $9.7\ 10^{7}$ |
| 10 | 15 | $1.55\ 10^{8}$ |
| 21 | 36 | 2.20 |
| 50 | 86 | 2.16 |

### Table XXI

Solution : 0.3N $H_2SO_4$ containing $4.70\ 10^{10}$ atoms Pa/ml.

Electrode material : Silver, superficial area 192 $mm^2$.

Pretreatment : Clean with emery.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 1.25 | 1.25 | $4.05\ 10^7$ |
| 2.0 | 3.25 | 5.55 |
| 6.75 | 10.0 | 8.35 |
| 25 | 35 | $1.12\ 10^8$ |
| 35 | 70 | 1.28 |
| 35 | 105 | 1.44 |
| 60 | 165 | 1.56 |
| 90 | 255 | 1.47 |

### Table XXII

Solution : 0.3N $H_2SO_4$ containing $3.12\ 10^9$ atoms Pa/ml.

Electrode material : Silver, as for XXI , from adjacent part of sheet and treated simultaneously.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 1 | 1 | $9.5\ 10^7$ |
| 2 | 3 | $1.89\ 10^8$ |
| 5 | 8 | 3.30 |
| 5 | 13 | 4.13 |
| 7 | 20 | 4.53 |
| 15 | 35 | 5.30 |
| 60 | 95 | 6.30 |
| 100 | 195 | 8.40 |

## Table XXIII

Solution : 0.3N $H_2SO_4$ containing 1.07 $10^{11}$ atoms Pa/ml.

Electrode material : Silver, as for XXI , from adjacent part of sheet and treated simultaneously.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 0.5 | 0.5 | 3.25 $10^{9}$ |
| 1.0 | 1.5 | 8.40 |
| 2.5 | 4.0 | 1.21 $10^{10}$ |
| 5 | 9 | 1.57 |
| 11 | 20 | 1.76 |
| 20 | 40 | 1.95 |
| 40 | 80 | 2.21 |
| 80 | 160 | 2.50 |

## Table XXIV

Solution : 0.3N $H_2SO_4$ containing 3.65 $10^{9}$ atoms Pa/ml.

Electrode material : Silver, as for XXI , from adjacent part of sheet and treated simultaneously.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 1 | 1 | 4.16 $10^{8}$ |
| 4 | 5 | 8.65 |
| 10 | 15 | 1.22 $10^{9}$ |
| 25 | 40 | 1.57 |
| 50 | 90 | 1.86 |

## Table XXV

Solution : 0.3N $H_2SO_4$ containing 2.40 $10^{8}$ atoms Pa/ml.

Electrode material : Silver, as for XXi , from adjacent part of sheet and treated simultaneously.

| Time interval (mins) | Total time (mins) | Atoms deposited |
|---|---|---|
| 2 | 2 | 2.2 $10^{7}$ |
| 5 | 7 | 5.7 |
| 21 | 28 | 1.17 $10^{8}$ |
| 65 | 93 | 2.05 |

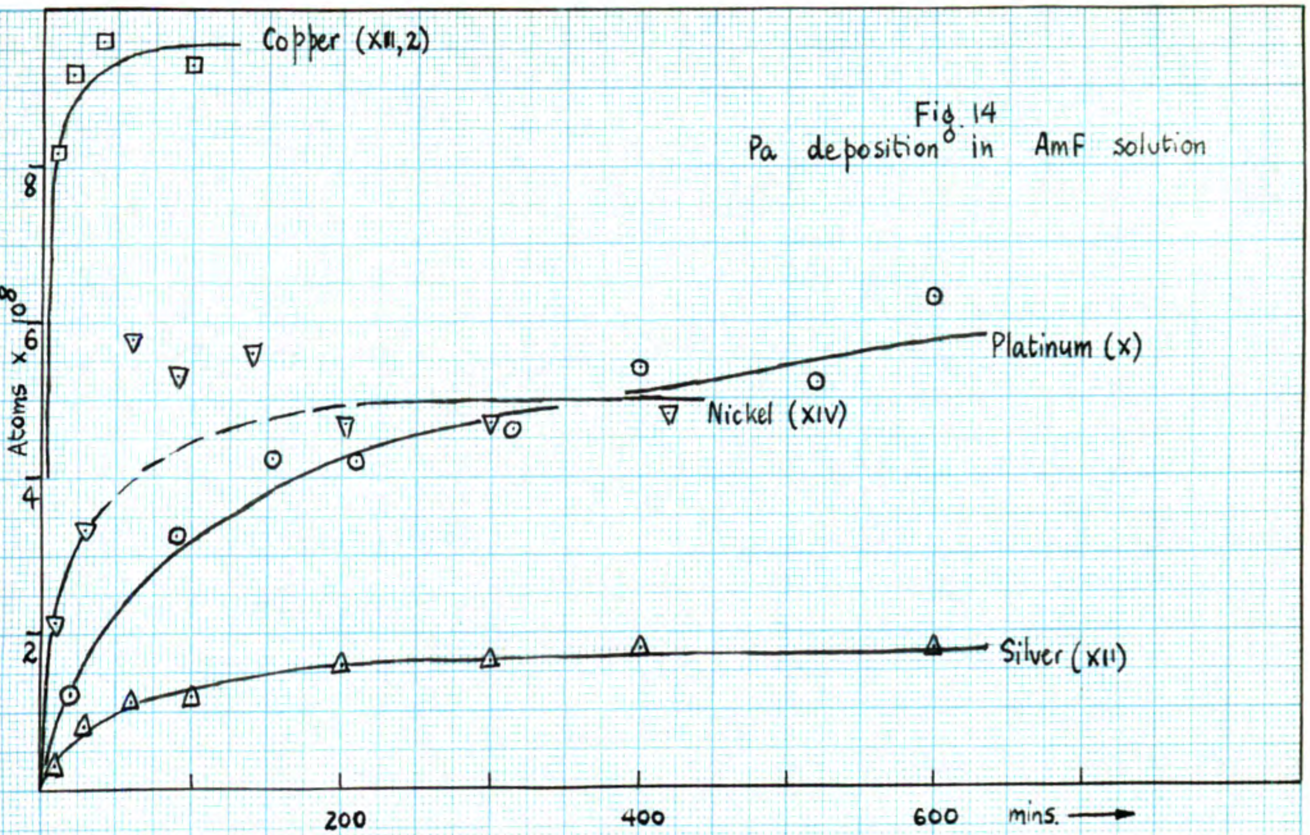


Fig. 14
Pa deposition in AmF solution

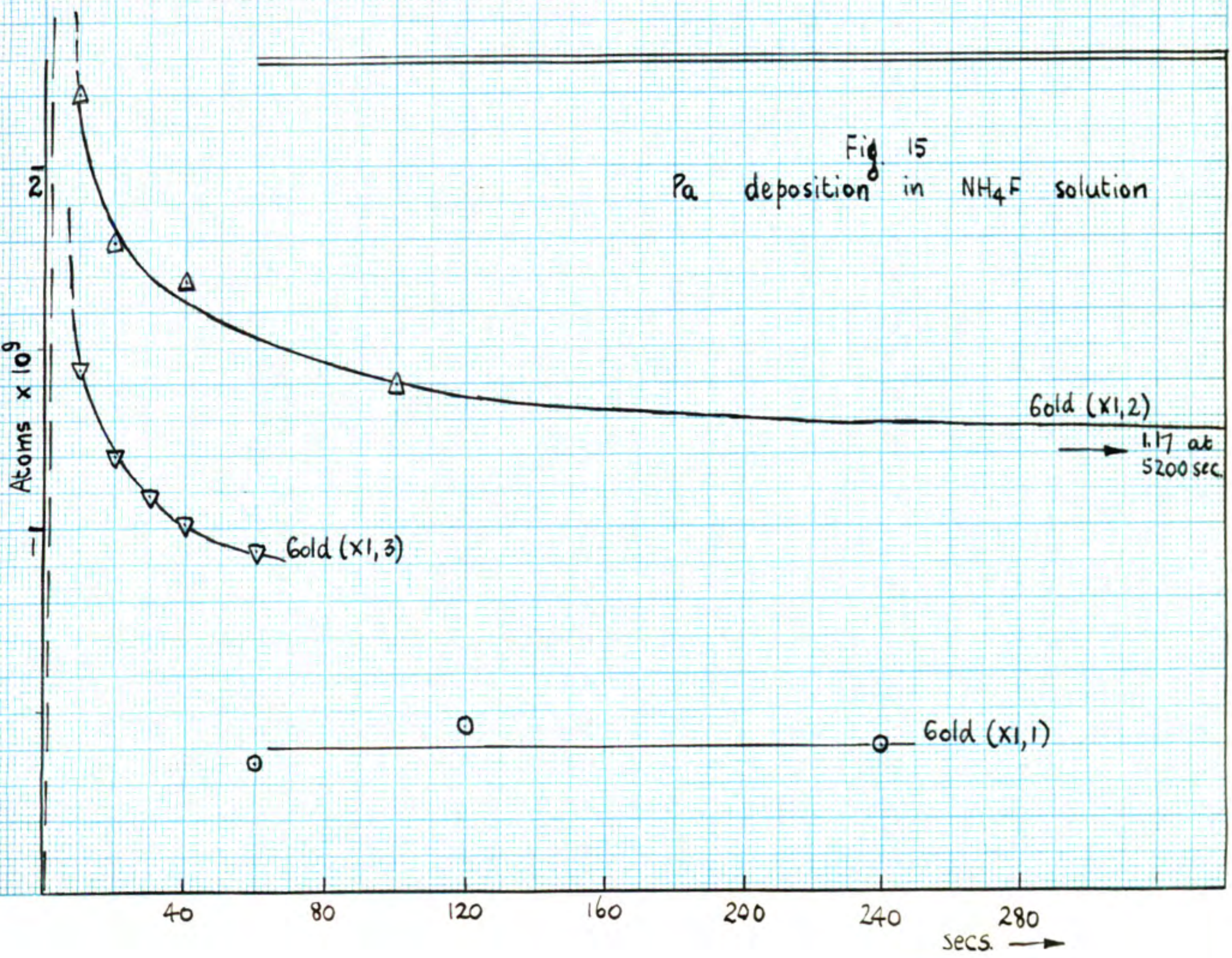


Fig. 15
Pa deposition in $NH_4F$ solution

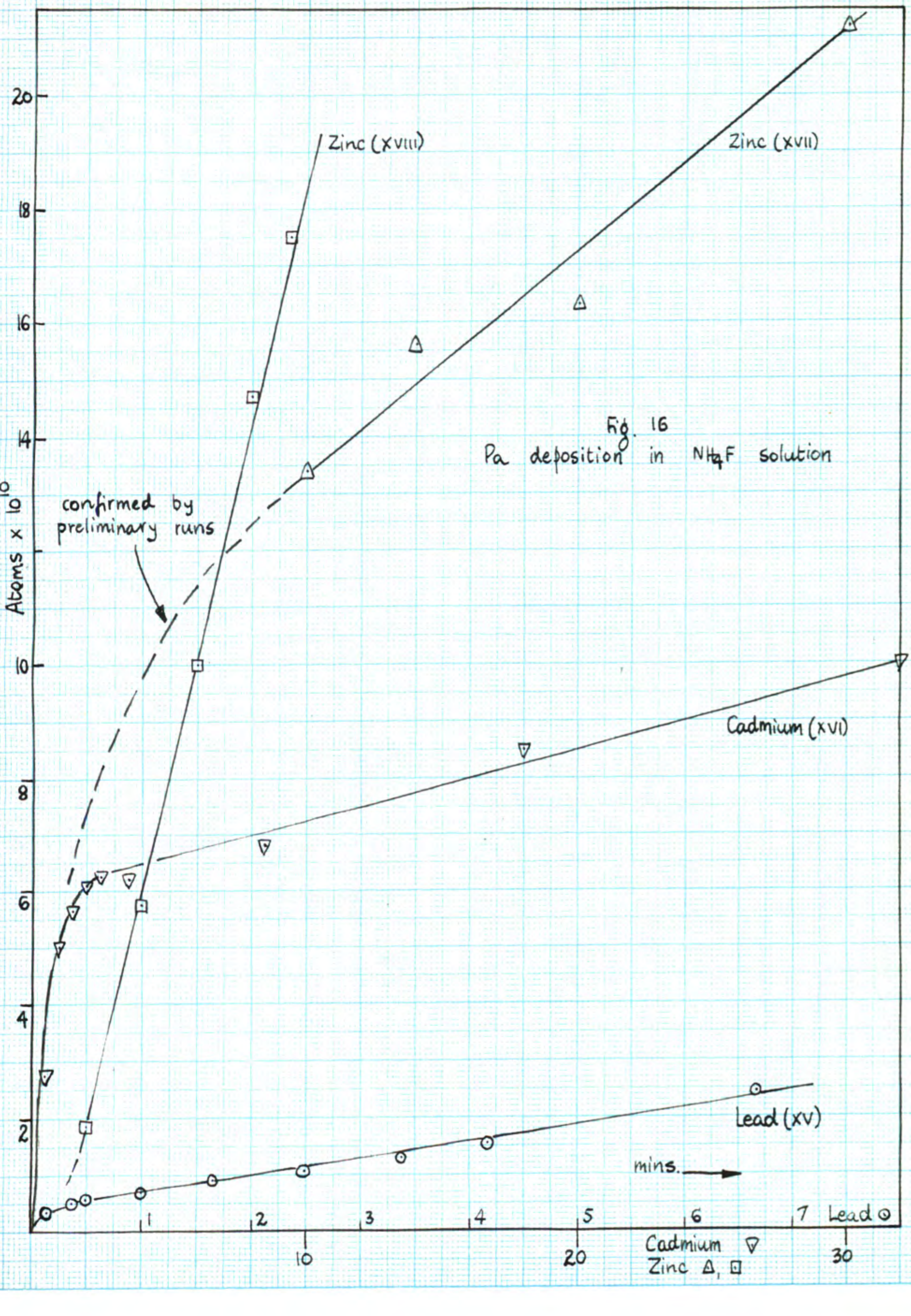


Fig. 16
Pa deposition in $NH_4F$ solution

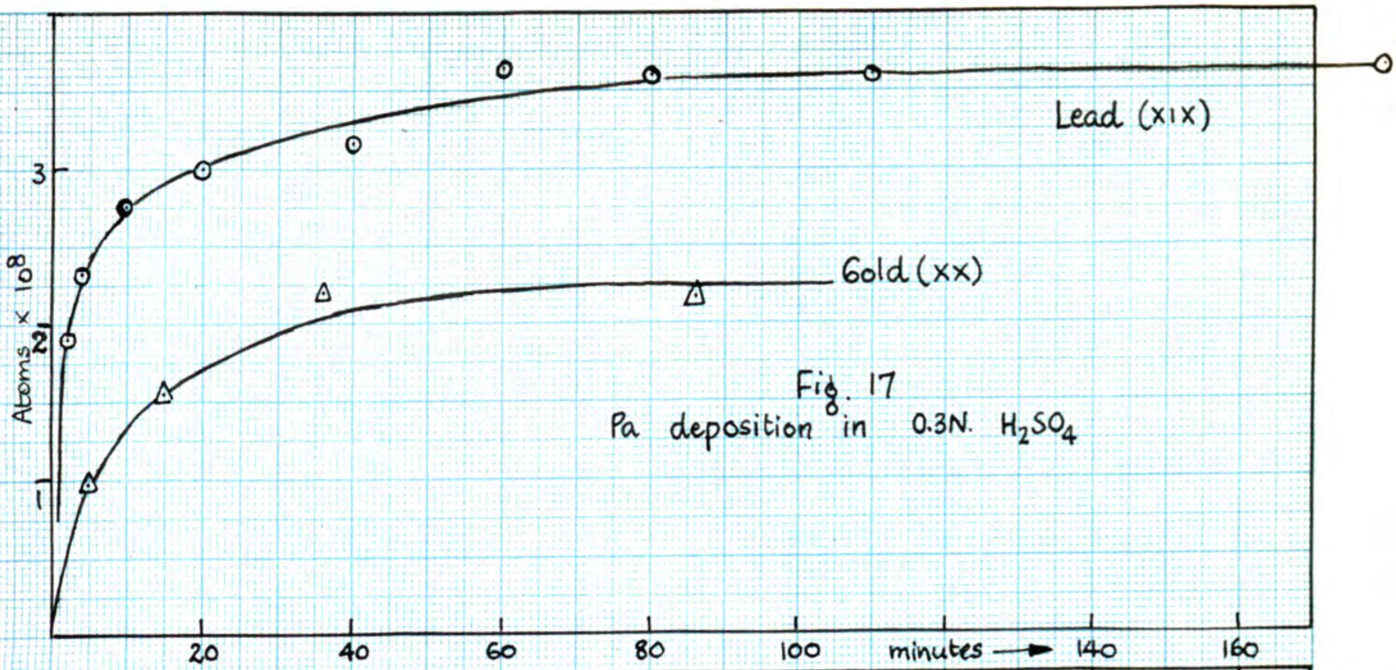


Fig. 17
Pa deposition in 0.3N. $H_2SO_4$

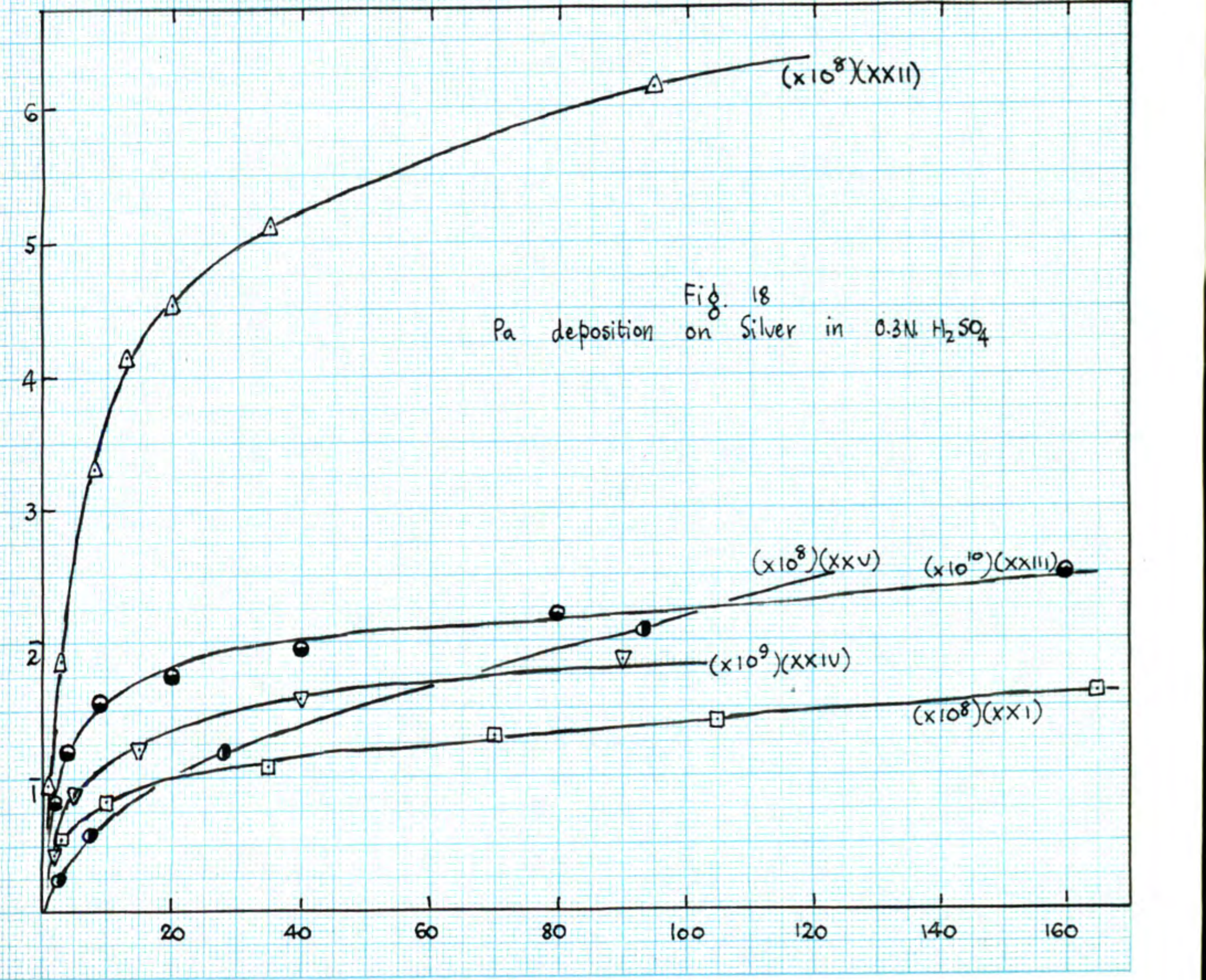


Fig. 18
Pa deposition on Silver in 0.3N $H_2SO_4$

Discussion of Results :

Ammonium Fluoride solutions : It is seen that, with the exception of Au, the results fall into two distinct classes : (1) Pt, Ni, Ag, and Cu, where there is an exponential growth to a maximum value, and (2) Pb, Cd, and Zn, where the initial exponential growth is followed by an almost linear portion; in this second group, amounts deposited are also considerably higher than in the first. In addition, these latter metals attain potentials in the ammonium fluoride solution much more negative than those of the former group.

These results are interpreted in the following way : With metals more noble than Pa (or the form which deposits) in the medium concerned, those of the first group, only a small proportion of the Pa atoms striking the surface are deposited; alternatively, there are a number of localised centres where deposition may occur and, as these become saturated, with no new centres being formed, deposition tends to a limiting maximum value. With metals less noble, such an initial process takes place - though now the exponential growth takes only minutes, as opposed to hours previously - with a superimposed or subsequent true electrochemical deposition, accounting for the linear growth. (Attempts were made to perform similar experiments with Al and Mg foils: these, however, decomposed the solution with evolution of gas, but it was found that deposition was extremely rapid - for example, 100 $mm^2$ of Mg deposited $3 \ 10^{10}$ atoms of Pa in 15 seconds - which agrees with the more extended observations).

The critical potential for the deposition of Pa from $NH_4F$ (0.4 mgm./ml) would thus lie between +0.136 and - 0.56 v. with respect to the normal calomel electrode.

The activities of the Pa deposited were, in the case of the more noble metals, much too low to permit of identification of such centres of deposition. It was thought, however, in the case of Zn, where the amounts deposited were high, that autoradiographs might prove a useful means of observation. Accordingly, such autoradiographs were made of two zinc electrodes which had exhibited rather different behaviour.

The results shewn in Table XVII, which are typical of several performed in practically the same way, were obtained with a foil which, prior to Pa deposition, had been soaked for about 30 hours at room temperature in a Pa-free ammonium fluoride solution of the standard concentration. A small amount of etching took place, the surface being visibly dulled from its previous brightly-polished appearance. Autoradiographs made with exposures of 4 and 19 hours respectively are shewn in Figs. 19 - 20. It is seen that localisation of deposit (white areas) has occurred and that this is in comparatively random spots. Deposition is also evident on a few scratch marks from the emery used in the polishing and which survived the etching with ammonium fluoride. The series of parallel lines across the plate probably represent lines introduced in the preparation of the foil[*] and which, due to the rolling process employed, may be slightly harder, and hence less noble, than the surrounding body of metal. On standing for several days, in moist air, this electrode gradually attained a greyish-white coating in spots which are practically superimposable on the autoradiograph - this isshewn in Fig. 21 as white marks on the prevailing dark grey background.

By contrast, the results shewn in Table XVIII were made with a rather smaller Zn foil which was immersed in Pa-$NH_4F$ solution immediately after scouring. In this case , there should be a much larger number of fresh centres exposed, and the autoradiograph (Fig.22) shews the deposit to be more evenly distributed over the surface. The graph of

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[*] According to Messrs.Johnson Matthey, the makers, this consisted of 99.9% Zn foil prepared by the "normal melting, casting and rolling."

Fig. 19

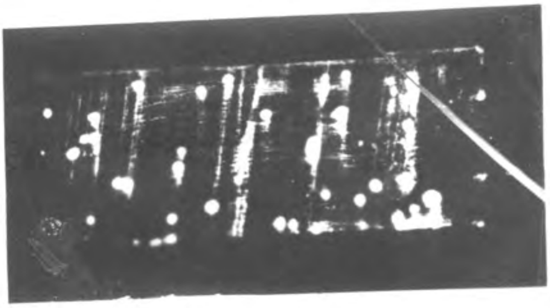


Fig. 20

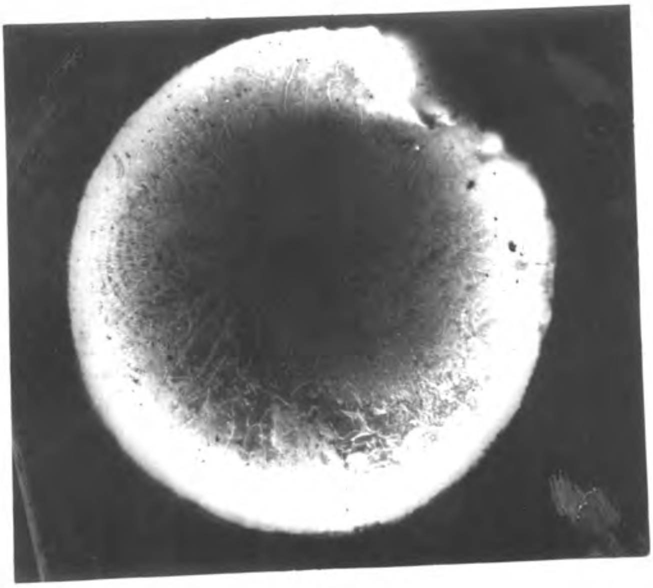


Fig. 23

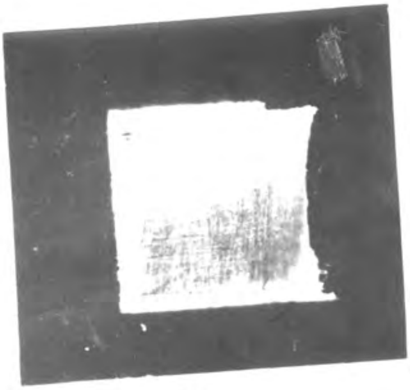


Fig. 22

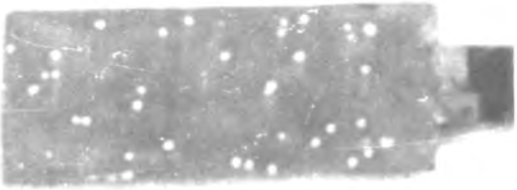


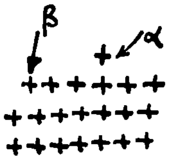
Fig. 21

deposit against time is now also linear, with no initial exponential growth.

To see if there were any localisation due to crystal orientation in the zinc surface, two experiments were made of which the more convincing may be quoted. A quantity of As-free zinc (AnalaR) was melted and held at 416° (m.pt. 419°) for three hours, at the end of which it was cooled and a section cut. This was polished with emery and a very fine alundum stone to a bright mirror finish, and etched with $HNO_3$-$K_2Cr_2O_7$ reagent. The autoradiograph obtained (Fig.23) was compared with a photograph of the surface - it is evident that preferential deposition has occurred round the edges of the crystals. (The much greater deposit on the outside edges of the sample is probably due to the increased stirring at the edge, due to the experimental set-up).

In support of this hypothesis, we may consider the results of Tammann and Wilson (loc.cit.) who believe, on the basis of results with Polonium, that Pt, Au and Pd adsorb the radioelement and that electrochemical displacement (as suggested by Hevesy) does not occur. They found that Ni, Cu and Ag, on the other hand, did displace polonium from solution electrochemically.

It is generally accepted also that the potential of even a pure metal surface varies from point to point - we may quote Butler ("Electrocapillarity",p.170) : "Only liquid and soft metals such as sodium and lead give rise to well-defined potentials. With hard metals, the reversible potential has generally been measured on a finely-divided material and massive places of the metal do not usually have exactly the reversible potential, at least not without careful preparation. ..... At such electrodes, the rate of deposition of the metal atoms may well be influenced by the circumstances of crystal growth. At the surface of a hard metal, the potential energy probably varies from point to point. Isolated atoms ( $\alpha$ ) on the surface of a completed plane will have a higher energy than those ( $\beta$ ) which are partially surrounded by others at the edge of an incomplete plane. At a given V, deposition will take place preferentially at the points of lowest energy available, i.e. at the edges of growing layers rather than haphazardly on the surface."



The results presented here are not quite in agreement with those of Joliot (loc.cit.) where, in particular, the shape of curves at potentials favourable to deposit is different. The same general type of behaviour occurs, however, and the divergences observed may be due to differences in surfaces of electrodes. (The mode of preparation of his thin gold windows is not revealed, but such thin windows are often made by sublimation of gold in vacuo on to a mica surface, from which it is subsequently removed by penetration with water. This would be expected to yield a surface rather free of inhomogeneities.)

The case of Au in $NH_4F$ solution presents a different problem. Here, an initially inactive foil rapidly charges itself with Pa to an undetermined degree and within a few seconds (Table XI ) is already shedding the deposit; eventually a steady minimum value is reached. The very rapidity of the process makes it seem plausible that possibly the potential of the gold is the determining factor and that initially the potential is much more negative than the equilibrium value, with much deposition occurring. Or possibly the gold charges itself with fluoride ions initially, which are in great excess, and which draw with them perhaps by some electrostrictive effect the Pa, which immediately begins to release itself.

The same may not be said, however, of the experiments by Haïssinsky 49) on deposition of ThC on a gold cathode from

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49) J.Chim.Phys., 1935. <u>32</u>. 120.

$10^{-12}$ N solution. Here, over a period of many minutes, the cathode acquires relatively important quantities of the radioelement, immediately after introduction of the solution, at potentials much more positive than the critical potential. The speed of this deposit gradually slows and stops, and the deposit finally redissolves almost entirely. His graphs are shewn in Fig.25, deposition only occurs at this normality at - 0.25 v. versus the S.C.E. No immediate explanation of these results is obvious.

Sulphuric acid solutions: With Pb, Au and Ag we have only the case where the deposition tends to a rather low, limiting maximum; the slow rise with silver is probably due to slight surface attack. This is in conformity with the explanation advanced above, since cathodic deposition (see below) is not readily obtained in sulphuric acid solution.

In contrast to the results in ammonium fluoride solution, the gold foil now shews no anomalous behaviour.

Influence of impurities : In a series of preliminary experiments with silver foils in sulphuric acid solution, with varying concentrations of Pa, other things being equal, it was found that there was no clear dependance of amount of deposit on the concentration of Pa used. This is brought out in Tables XXI - XXV with silver electrodes cut from adjacent

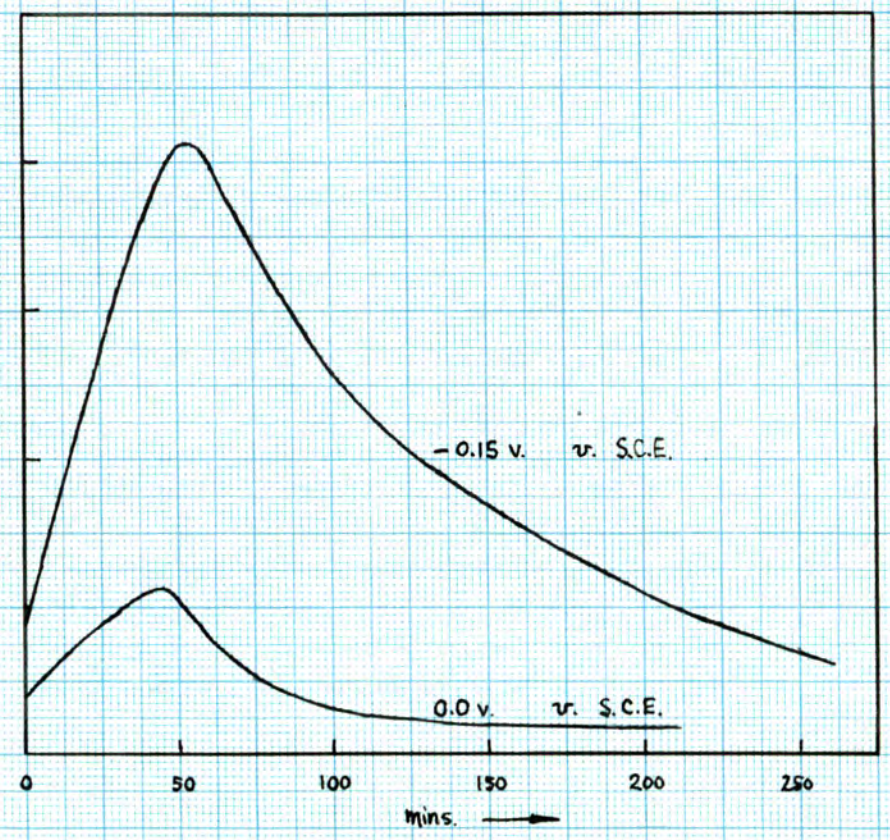

Fig. 25. Deposition of ThC on Gold.

parts of the same sheet, after identical treatment. In XXI and XXII, a tentimes more dilute solution is seen to give a five-fold higher deposition. This solution was evaporated to dryness, and a barely visible film of tarry organic matter - probably only a fraction of a milligram from 15 ml. of solution, and most likely arising from the solvent extraction process used to prepare the tracer - was obtained. The material was calcined, and taken up afresh in 0.3N $H_2SO_4$ and the results shewn in Tables XXIII - XXV obtained. Here the maximum quantities deposable are more nearly proportional to the concentration, though not exactly so. For example, the ratios of maximum atoms deposable/ atoms per ml. are about 0.88, 0.50, and 0.23 for solutions of strengths 1 : 15 : 445 respectively. This again agrees with a localised deposition (as do the comparable results of Tammann and Wilson with polonium on Pt, Au and Pd). Also, in the cleaned solution, the half-lives for deposition are all in the region of five or six minutes whereas in the untreated solution containing organic matter, they are about three times this value.

Returning now to the hypothesis of Haïssinsky, that the critical potentials obtained by the Paneth-Hevesy technique are governed with respect to concentration by the

Nernst Equation, and that deposition only occurs in localised areas of the electrode surface, it is seen that the present results are quite in conformity with this. Such centres can come from surface imperfections, variations in hardness or crystal boundaries in the material substrate.

## SECTION IV

### Electrochemistry of Protactinium.

It was explained in an earlier passage that Pa is element extremely rare in macroscopic amounts, due to the long life and difficult chemistry of the element. The chemical work which has been performed has utilised as tracers the beta-emitting isotopes $UX_2$ (1.14 mins) and UZ (6.7 hrs): more recently the artificially-produced $Pa^{233}$ has been used. Though the chemical properties have thus been partially elucidated, very little is known about the electrochemical behaviour of the element, since the short-living isotopes do not lend themselves to electrochemical studies, which are generally time-consuming compared with chemical co-precipitation experiments, and since the weak radiation of $Pa^{231}$ does not allow of the study of the more dilute solutions. Besides, the salts of Pa in aqueous solution have a great tendency to hydrolysis, which renders them difficult to manipulate, particularly from an ionic and electrochemical view-point.

One must generally treat the element as far as possible in fluoride solution, despite the volatility of the fluoride, this being almost the only solution in which Pa does not easily adsorb on almost any precipitate present (v.I.Joliot-Curie, "Les Radioelements Naturels", pp.45-47). For this reason, practically all electrochemical studies carried out on Pa have used a fluoride-containing solution, although the situation is thereby rather obscured : the Pa is presumably in the complex $PaF_7^{--}$ anion, yet, at sufficiently high applied voltages, the deposition is all at the cathode. The electrolysis used in the preparation of the $Pa^{233}$ tracer (v.p.3 ) illustrates this. The precise nature of the deposit is not clear - Haïssinsky and Emanuel 50) mention two types of deposit, a heavy white one, or a fine black coating, depending on conditions of pH, of ammonium fluoride concentration, of stirring, and so on. It is suggested that the white deposit is of oxide or basic salt, the black of metal. Practically all the work reported has been by Haïssinsky and co-workers 51),52) using less than milligram quantities of the element, containg Ti and Zr as impurity.

In addition to the above results with ammonium fluoride, it has also been reported that, in sulphuric acid solution, Pa may be deposited on both anode and cathode.

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50) J.Chim.Phys., 1937. <u>34</u>. 641.

51) Emanuel and H., Comptes Rendus, 1938. <u>206</u>. 1102.

52) H., Nature, 1945. <u>156</u>. 423.

Haïssinsky(53) reports the results of measurements carried out in N. $H_2SO_4$ solution. Here the anode was of Pt covered with $PbO_2$, the cathode of Pt or Ni. Three experiments were performed, using the same concentration of Pa ($10^{-5}$ g./ml., i.e. $4.1 \; 10^{-5}$ M): these yielded values for a critical potential of 1.54, 1.60 and 1.70 volts. In this case, his experiments were complicated by the no means negligible spontaneous adsorption on the $PbO_2$ (about 20%). No other quantitative data have been determined, and Haïssinsky himself states ("Electrochimie des Substances Radioactives", 1946. p.39) " It is still impossible to draw any conclusions (from these experiments) regarding the possibility of important electrochemical preparations of Pa".

It was decided to investigate the deposition of the element both in ammonium fluoride and in sulphuric acid solution.

Earlier experimenters thus suffered under the disadvantage of too much material and too little activity : the author on the other hand, found the difficulty with $Pa^{233}$ to be the reverse, with too little bulk associated with a high activity. For example, a monatomic layer of $Pa^{233}$ to cover a metallic foil of superficial area 1 $cm^2$ represents

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53) H., J.Chim.Phys., 1946. 43. 66.

an activity of about a millicurie. For this reason, none of the experiments to be described ever entailed covering the electrodes with even a single monatomic layer on the average. The most desirable solution would be to use a mixture of natural $Pa^{231}$ with artificial $Pa^{233}$ in a ratio of about $10^6$ atoms of the former to one of the latter. Unfortunately, no $Pa^{231}$ was available for the present work; experiments were made to separate the element from a concentrate, but these were not successful, since the work was performed "blindfold" with no possibility at the time (due to lack of an alpha-counter) of checking the distribution of the Pa in the many chemical questions involved. (The source material was a concentrate from the final silica residues of uranium extraction : its previous history and composition were unknown).

## A. Electrodeposition in Ammonium Fluoride solution :

A series of preliminary experiments were made, using various metal electrodes and an electrolyte consisting of 1 mgm./ml. ammonium fluoride.

Silver electrodes : In two hours electrolysis with 0.5 v. applied potential, the solution became cloudy and a grey deposit appeared on the anode. The cathode potential was far from steady, with much wild fluctuation about a mean which itself gradually drifted. Tiny gas bubbles appeared at the cathode, probably of hydrogen. The~~y~~ grey anode deposit is probably of oxide due to secondary reaction of liberated fluorine with water.

*Ni electrodes* : It was difficult to obtain a balance for the cathode, there being a potential more negative than the 1400 millivolts capacity of the measuring instrument (v.p. 92 and below) to the N.C.E. With about 5 v. applied potential, a black cathodic deposit was obtained.

*Gold electrodes* : These shewed a very heavy polarisation; even with 5 volts applied potential, it was impossible to get a balance of the cathode with the reference electrode. In addition, at this applied potential, the cathode rapidly acquired a black surface coating.

*Summary* : With Ni, Au, and Cu (v.p. 43 ) a black cathodic deposit is formed. It is difficult to see why - since two different samples of AnalaR ammonium fluoride both produced the deposit, it is probably not due to any deposable impurity; - it may be due to liberated atomic axygen, which produces oxidation. Such an attack is also found in the preparation of strong electrolytic sources of Po - here the ozone from radiation decomposition of water is to blame. It was intended to perform a series of experiments with hydrofluoric acid, keeping below its decomposition potential, to minimise attack. At the time, however, since the tracer supply on hand was much diminished, it seemed more reasonable to use the apparatus for the experiments with sulphuric acid, where no difficulty was anticipated, This was done, and subsequently lack of time prevented a return to the HF system.

## B. Electrodeposition in Sulphuric acid solution :

**Apparatus :** This included the perspex electrode holder and the solution vessel previously described. To the mounted electrodes were applied varying potentials from a 4 v. accumulator connected across a $10^5$-ohm potentiometer - even if current were to flow, it would be small. In practice, voltages less than the decomposition potential of 0.3 N.$H_2SO_4$ were applied and the electrodes were permanently polarised. Any measuring device drawing appreciable amounts of current would upset the equilibrium of the gas layers adsorbed on the electrodes: the millivolt scale of a "Cambridge" pH meter was used. (This is a vacuum-tube millivoltmeter employed as a null instrument). Occasionally, sharp fluctuations were observed when equipment was switched on in the same mains circuit, but these were compensated for, and the potentials of the electrodes found to be unaltered; these were measured by glass capillaries joining to a mercurous sulphate electrode through a bridge beaker of 0.3 N.$H_2SO_4$; the reference electrode itself was made up with 0.3 N acid - its potential, measured against a hydrogen electrode, was found to be + 0.696v. at 17°C.

For switches, mercury pools in a block of paraffin wax were used, connection being made by amalgamated copper wires. Two were used - a selector switch to measure either anode or cathode, and a reversing switch to ensure the right polarity at the millivoltmeter.

No attempt was made at thermostatting - the cool weather prevailing, with suitable adjustment of room heating, held the temperature within 16 to 20°C.

The electrodes were of Pt foil, shaped as previously, but with surfaces 6 mm. x 8 mm. Gold was plated onto the Pt for 10 mins. from a bath of $HAuCl_4$ + a five-fold excess of 50% KCN. A gold foil anode was used, with no agitation, at 60°C. The deposit was heated in a hydrogen flame until the gold melted and alloyed with the Pt. A further Au deposit was then made for 10 mins.; this gives a pale yellow matte finish. If agitation was used, the deposit was much coarser and reddish. The electrodes were boiled 15 mins. in ammonium fluoride (2 mgm./ml.) before use. No cellulose enamel was used here to isolate one surface.

Procedure : The electrodes were assembled in the holder and the connections soldered. The measured volume of 0.3 N $H_2SO_4$ was placed in the vessel and the electrodes immersed as far as the shoulder. The assembly was left with the vessel rotating until steady potentials were reached at the electrodes; this, in practice, meant until a drift of less than 1 millivolt per 10 mins. occurred, and necessitated in general about two hours. (It was part of the standard procedure to keep undisturbed at the end of an experiment the potentiometer setting for the applied voltage, and this was re-applied at the beginning of the next run for an hour to make sure that the same potentials as before were reached. Differences might occur due to the cleaning treatment employed, to faulty soldering of connections, etc. In practice, it was found that for identical treatment of the electrodes, and for temperatures between 16 and $20^{\circ}$ settings were reproducible to better than 10 mv. A new voltage was then applied). To ensure that the electrode surfaces had not undergone an alteration in surface during a series of experiments, the following method was used : the approximate critical potential being known from preliminary experiments, potentials for the anode were selected to cover a range about this approximate value and applied alternately at the low and high ends of the scale, drawing nearer together in the course of the series. This was held to be necessary in view of the ease with which the spontaneous adsorption on the electrodes could be altered (v.inf.).

When a steady state had been reached, the tracer solution was added in small volume (generally 0.15 ml.) of 0.3 N. acid. This caused a small fluctuation of a few millivolts in the electrode potentials, but in a few minutes the old values were obtained plus or minus a millivolt or two. Electrolysis was continued for an hour in all cases; it was found that, if there had been allowed initially sufficient time for equilibrium to be attained, the drift during electrolysis was less than five millivolts and frequently zero. Readings of potentials were made at 10-min.intervals.

At the end of 60 mins., the electrodes were withdrawn from the solution without removing the applied potential : this was then removed, and the electrodes plunged into 0.3 N.acid to remove adhering solution without hydrolysis. They were then thoroughly washed back and front with a fine spray from a hand wash-bottle, dipped in methyl alcohol, and dried by presing between sheets of soft paper tissue. The connections were then unsoldered. Face and obverse sides of both electrodes were counted, the foil being thick enough, as shewn previously (p. 91 ) to cut out radiation from the side away from the counter. A standard count and a background count were both made, to correct results.

After counting, the electrodes were boiled in ammonium fluoride solution (2 mgm./ml.) for ten minutes, changing the solution once, half-way. They were then well washed with water, rinsed with methyl alcohol, and dried as before. They were once more counted, and a background determination made: if the difference between these was significant, further cleaning was done. The electrodes were then ready for the next experiment. This method of cleaning was found to be most suitable - the little alteration in the deposition values at the cathode during a large number of repeated cleanings shews the surface of the electrode to be little affected by the cleaning process. By contrast, cleaning with nitric acid, between two series of readings in a preliminary run, was found to be harmful. After a series of eight experiments in which this spontaneous adsorption was in all cases close to the average of 2.9%, the electrodes were cleaned with hot 8N.$HNO_3$ for 5 mins. In the three subsequent runs, the values found were 30, 18, and 28% in the same time of contact. Presumably there had been some solution of the gold and an increase in the effective area of the electrodes. This may explain the dispersion of experimental points in the graphs of Heal[29], who used such a cleaning procedure, boiling with concentrated nitric acid.

Results are summarised in Tables XXVI - XXVIII, and shewn graphically in Fig.26. To save space, actual counter readings are not shewn, but values corrected for background and counter efficiency. Corrections for decay of the Pa are small (of the order of a few percent for the few days a series of experiments took) but are applied to the initial Pa content of the solution. When a count was made, this was for a sufficiently long time to give better than 2% statistical accuracy in the final result : with the solutions used, this rarely necessitated counting for more than a few minutes.

## Table XXVI

$0.3$ N $H_2SO_4$

Concentration of Pa: 63500 c.p.m. in 13.25 ml. = 3.0 $10^{-12}$ M

| Potential referred to $Hg_2SO_4$ electrode | Counts deposited (corrected values) | | | | Mean %'s deposited per side |
|---|---|---|---|---|---|
| | I(F) | I(O) | II(F) | II(O) | |
| 1.201 | | | 6160 | 8530 | 11.5 |
| 1.101 | | | 4470 | 3560 | 6.5 |
| 1.066 | | | 4130 | 3350 | 5.9 |
| 1.052 | | | 3230 | 2850 | 4.7 |
| 1.034 | | | 1156 | 1100 | 1.74 |
| 0.984 | | | 1505 | 1130 | 2.04 |
| 0.918 | | | 788 | 575 | 1.05 |
| 0.573 | | | 318 | 344 | 0.58 |
| 0.038 - | 323 | 215 | 308 | 184 | 0.40 |
| 0.293 - | 380 | 277 | | | 0.50 |
| 0.307 - | 235 | 99 | | | 0.26 |
| 0.346 - | 445 | 375 | | | 0.63 |
| 0.360 - | 450 | 310 | | | 0.58 |
| 0.400 - | 435 | 322 | | | 0.57 |
| 0.429 - | 411 | 340 | | | 0.57 |
| 0.439 - | 338 | 350 | | | 0.48 |
| 0.520 - | 466 | 421 | | | 0.67 |

## Table XXVI a

Conditions as for Table XXVI; a few more results were obtained at more negative values, using (1) a Pt anode with a Au electrode, (2) Ni electrodes. The Pt and Ni were scoured with fine emery before use. Allowing for superficial area differences, the results are in good agreement with those shewn above.

| | | Potential | Corrected Counts | | | | Mean %'s deposited |
|---|---|---|---|---|---|---|---|
| | | | I(F) | I(O) | II(F) | II(O) | |
| 1. | (Pt) | 1.246 | | | 8700 | | 14.7 |
| | (Au) to | 0.732 -<br>0.696 - | 411 | 356 | | | 0.58 |
| 2. | (Ni) | 0.460 | | | 376 | 252 | 0.51 |
| | (Ni) | 1.100 - | 215 | 186 | | | 0.34 |

## Table XXVII

$0.3$ N $H_2SO_4$

Concentration of Pa : 405,000 cpm. in 8.75 ml. = $2.96\ 10^{-11}$ M.

| Potential referred to $Hg_2SO_4$ electrode | Counts deposited (corrected values) | | | | Mean %'s deposited per side |
|---|---|---|---|---|---|
| | I(F) | I(O) | II(F) | II(O) | |
| 1.177 | | | 28000 | 26000 | 6.7 |
| 1.132 | | | 21100 | 21500 | 5.3 |
| 1.072 | | | 8300 | 8300 | 2.1 |
| 1.027 | | | 6000 | 5800 | 1.5 |
| 0.387 - | 4100 | 4040 | | | 1.0 |
| 0.405 - | 2900 | 3600 | | | 0.8 |
| 0.432 - | 3000 | 2760 | | | 0.7 |
| 0.461 - | 3260 | 3460 | | | 0.8 |

## Table XXVIII

0.3 N $H_2SO_4$

Concentration of Pa : $3.48\ 10^{6}$ cpm. in 8.75 ml. = $2.55\ 10^{-10}$ M.

| Potential referred to $Hg_2SO_4$ electrode | Counts deposited (corrected values) | | | | Mean %'s deposited per side |
|---|---|---|---|---|---|
| | I (F) | I(O) | II(F) | II(O) | |
| 1.152 | | | 304000 | 319000 | 9.00 |
| 1.116 | | | 90000 | 95000 | 2.65 |
| 1.074 | | | 43000 | 52600 | 1.38 |
| 1.020 | | | 73200 | 55000 | 1.80 |
| 0.424 - | 10850 | 16900 | | | 0.40 |
| 0.426 - | 25400 | 26000 | | | 0.75 |
| 0.444 - | 27500 | 33000 | | | 0.8 |
| 0.466 - | 39200 | 40600 | | | 1.1 |

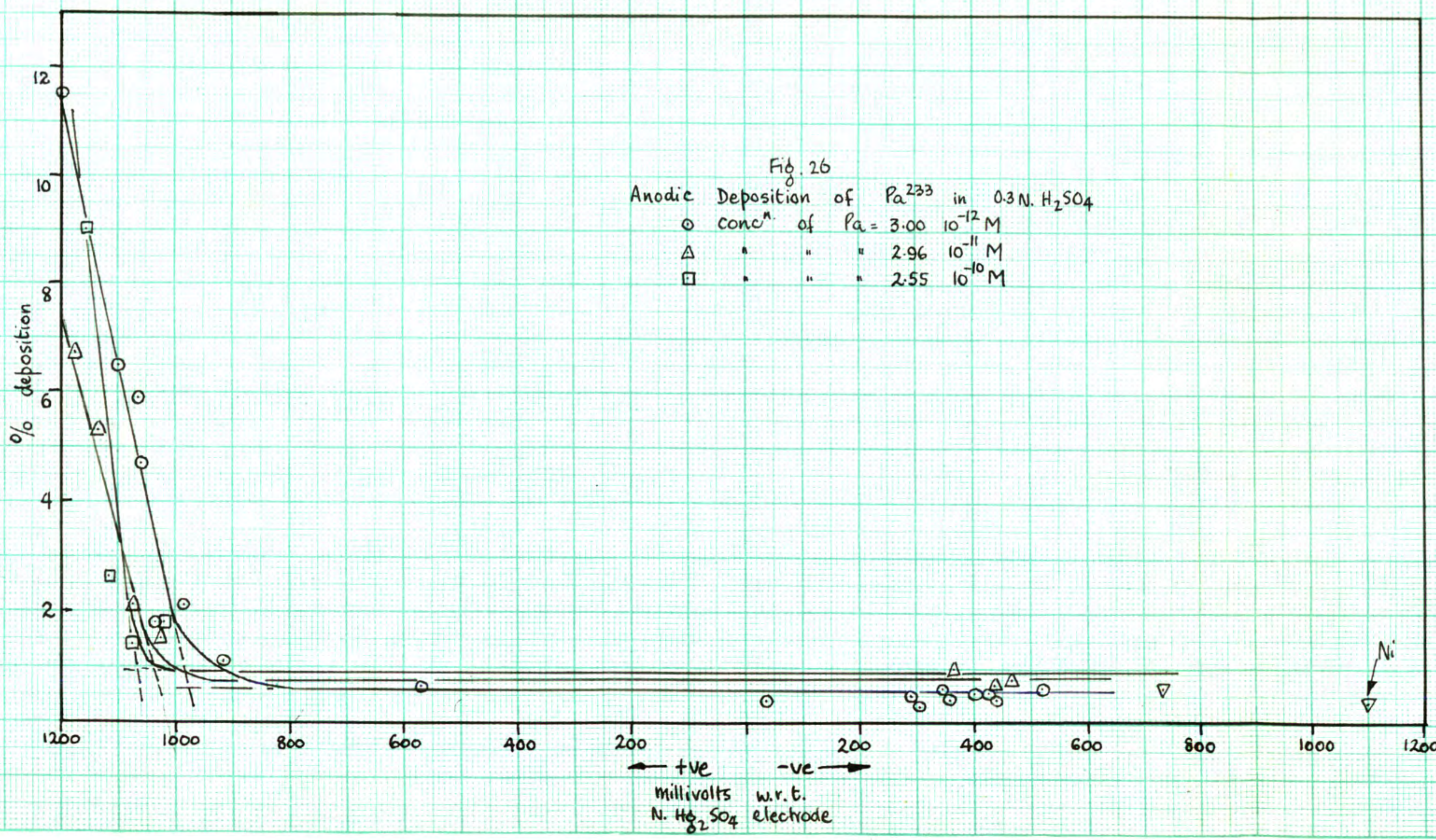


Fig. 26

Anodic Deposition of $Pa^{233}$ in 0.3 N. $H_2SO_4$

<u>Discussion</u> : 1) There is no cathodic deposit even at potentials of 1.100 v. negative with respect to the mercurous sulphate electrode, or 0.404 v. negative with respect to the normal hydrogen electrode.

2) It would appear from the above results that there is a pronounced shift in the critical potential as the concentration is varied. It is seen from the graph that, for a ten-fold change in concentration, between $3.10\ 10^{-12}$ and $2.96\ 10^{-11}$ M, there is a 70 mv. shift, and for an 8.5-fold change in concentration, between $2.96\ 10^{-11}$ and $2.55\ 10^{-10}$ M, a shift of 55 mv. These would compare with values calculated from

$$E = E_0 - RT/nF \ln C \text{ (for anode)}$$

of 58 and 52 mv. respectively for a single electron transfer. This shift, however, cannot be valid.

Firstly, if there were a Nernst shift of potential with concentration, it would be in the opposite direction.

Secondly, the critical potential is near that at which oxygen liberation is to be expected. If some secondary reaction were involved, such as liberation of oxygen followed by adsorption of Pa probably as a hydrolysed salt or oxide, in this case, no great variation of critical potential with concentration would be expected, and such variation not governed by the Nernst Law.

Thirdly, it is difficult to envisage any procedure by which Pa could deposit anodically unless by some secondary reaction : the valency of the element is five and, while no evidence is available as to its state of existence in dilute sulphuric acid, it is probably a hydrolysed compound such as $Pa(OH)(SO_4)_2$ or $Pa(OH)OSO_4$. In any case, the formation of a higher oxide, as with Pb or Po, seems out of the question.

4) Further, the most dilute series of experiments was performed with a stock solution of Pa prepared from thorium irradiated at an earlier date and extracted by an entirely different method. If any real shift occurred with concentration, this most dilute curve should be reproducible. A solution of this most dilute concentration ($3.0\ 10^{-12}$ M) was made by dilution of the strongest ($2.55\ 10^{-10}$ M) and a few points redetermined: they are shewn in Table XXIX. Comparison with Table XXVI shews a great divergence.

Table XXIX

$0.3\ N\ H_2SO_4$

Concentration of Pa : $3.0\ 10^{-12}$ M.

| | | | | |
|---|---|---|---|---|
| Potential of anode w.r.t. $Hg_2SO_4$ electrode. | 0.820 | 1.006 | 1.114 | 1.172 mv. |
| Mean %'s of activity deposited. | 2.6 | 2.5 | 4.0 | 3.8 |

This divergence is due to one or both of two factors : (1) to change of the surface of the electrode between the series, or (2) to the presence in one set of experiments of a small trace of impurity such as ammonium sulphate - even a few micrograms would be in overwhelming concentration compared with the Pa and some complexing might be expected. Change of surface cannot be excluded - it is seen that as one passes through Tables XXVI, XXVIII, and XXVII (the chronological order of the work), the residual deposition tends to increase, perhaps due to a slow increase in the specific surface in the cleaning process.

From these arguments, and from the last-mentioned results, it seems that no true shift of potential occurs, that observed being due either to impurities or to a change in electrode characteristics.

To test this, a series of experiments were made at a potential of 1.010 v.-ve, where, for a change in concentration, the relative deposition should alter most. Results are shewn in Table XXX. For the 35-fold change in concentration, a four- or five-fold change in deposition should occur. In fact, the values observed are practically the same; the order in which the experiments were performed precludes any change in electrode characteristics during the series.

Taken in conjunction with the results of Haïssinsky 53) though these were in different experimental conditions, the range is extended from $10^{-5}$ to $10^{-12}$ M. Results are consolidated in Table XXXI. The final result indicates that a surface reaction is responsible for the anodic deposition of Pa, that the critical potential is independent of concentration and close to the potential for oxygen liberation. The overlap of experimental values for the critical potential at widely different concentrations, shews its lack of thermodynamic significance.

## Table XXX

| Potential referred to $Hg_2SO_4$ electrode | Concentration of Pa | Mean %'s deposited |
|---|---|---|
| 1.020 | $1.25\ 10^{-12}$ M | 11.8 |
| 1.015 | $4.4\ 10^{-11}$ M | 10.2 |
| 1.009 | $4.4\ 10^{-11}$ M | 9.7 |
| 1.004 | $1.25\ 10^{-12}$ M | 11.2 |

## Table XXXI

| Concentration of Pa | Acidity | Anode | Critical Potential | Observer |
|---|---|---|---|---|
| $4.1\ 10^{-5}$ M | 1 $N.H_2SO_4$ | $PbO_2$ | 1.54 | Haïssinsky |
| $4.1\ 10^{-5}$ M | " | " | 1.60 | " |
| $4.1\ 10^{-5}$ M | " | " | 1.70 | " |
| $2.55\ 10^{-10}$ m | $0.3N.H_2SO_4$ | Au | 1.79 | Present work |
| $2.96\ 10^{-11}$ M | " | " | 1.73 | " |
| $3.0\ 10^{-12}$ M | " | " | 1.66 | " |

# Appendix

## Separation of Carrier-free Ag-111.

Abstract : This appendix discusses in a semi-quantitative way the extraction of carrier-free $Ag^{111}$ from fission products and from irradiated Pd. In the first case, a cyclical precipitation process, using mercury carrier, as sulphide, iodide and metal, gives a pure silver activity on removal of the mercury. In the second case, precipitation of Pd-dimethylglyoxine from slightly acid nitric solution achieves a substantial concentration of silver in the solution.

Experimental : (1) From fission products : 2 gm. $UO_3$ irradiated four days at $10^{11}$ n/cm$^2$/sec. and cooled 24 hours, was used as starting-material. (a) Chemical Extraction for reference purposes : to an aliquot of the material, converted to nitrate, were added 10 mgm. each of La, Ce, Ru, Sr, Zr, and Cs, and 20 mgm. of Ag. AgCl was precipitated from N/4 $HNO_3$ solution, washed, dissolved in ammonia, and 2 mgm. La added to scavenge the solution. The $La(OH)_3$ ppt. was washed with dilute ammonia and the wash added to the supernatent solution, from which AgCl was reprecipitated. Four cycles such as this were made. The final silver chloride precipitate was dissolved in ammonia and silver sulphide precipitated. This was dissolved in conc.$HNO_3$ and the sulphide reprecipitated. This gave sample Ag.1.

(b) without addition of carrier silver : to a portion of the material, brought into 1 N acetic solution were added 50 mgm. of Cd and 10 mgm. each of La, Ce, Zr, Sr and Cs. CdS was pptd., washed and dissolved in conc. HCl, with evaporation to dryness. La, Ce, Cs, Zr and Sr carriers were again added and CdS repptd. from 1 N, acetic acid. Four precipitations in all were made. The final ppt. was dissolved in conc.HCl and converted to nitrate by repeated evaporation with nitric acid. 50 mgm. mercuric ion and 10 mgm. La ion were added and the whole taken to dryness. The residue was dissolved in ca. N/2 acetic acid and $NgI_2$ precipitated with as little excess KI as possible. (In these conditions, silver forms on the macro scale the compound $HgI_2.2AgI$.) The washed precipitate was dissolved in N/2 acetic and excess KI and the mercury precipitated with 50% hydrazine solution. The washed mercury precipitate was dissolved in nitric acid, and the cycle repeated three times in all. This gave sample Ag.2. The mercury was precipitated with $Cl^-$, and digestion with 2N. ammonia gave sample Ag.3.

(2) From irradiated palladium : 50 mgm.Pd sponge were irradiated four days at $10^{11}$ $n/cm^2/sec.$ and cooled 24 hours. Samples of varying strength, were followed for decay, to establish the initial concentration of silver. (Samples Pd IV, a, b, and c.)

(a) Chemical extraction for reference purposes : from an aliquot, 20 mgm. of Ag were precipitated as chloride from N/4 $HNO_3$ solution. This was converted to nitrate, 50 mgm. of Pd added, and AgCl reprecipitated, giving sample Pd 1.

(b) Dimethylglyoxime precipitation : The Pd solution in nitric acid was brought to 200 ml. of N/4 $HNO_3$ and precipitated at $60^o$ with excess saturated solution of dimethylglyoxime in ethyl alcohol. After a brief digestion, the suspension was cooled and filtered through a fine sintered filter. The precipitate was washed thoroughly with hot water. Samples of this Pd once precipitated were taken, (Pd III and Pd V a and b for the two runs made). A sample of the clear supernatant solution was taken (Pd II and Pd VI). The solution was evaporated to dryness, fumed down with conc.$HNO_3$, 20 mgm. Pd added and precipitated as before. Samples of the precipitate (Pd VII) and solution (Pd VIII) were taken.

Discussion.

(a) The silver from both fission and Pd yield practically identical curves (graphs 27 a and 29a, 28 and 29b).

(b) Carrier-free from fission products - from the decay and absorption curves of samples Ag.1, Ag.2, and Ag.3 (graphs 27 and 28) it seems that the final sample Ag.3 approximates very closely to the chemically-extracted form, Ag.1, though there is a small amount of a short-lived, more energetic product, which is more evident in Ag.2, before the ammonia leach. A small trace of perhaps $\mathrm{Mo}^{99}$ would agree with the estimated 60-70 hr.period of this contaminant (f.y. of $\mathrm{Mo}^{99} = 6.4\%$, of $\mathrm{Ag}^{111}$ 0.018%).

(c) Carrier-free from irradiated Pd : The decay curves in the various samples graphed (Fig.30) shew a decided fractionation in the ratio Pd:Ag, referred to zero time of the pile.

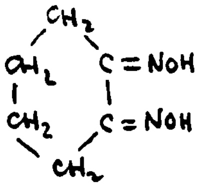
| Sample | History | Pd/Ag. |
|---|---|---|
| Pd IV | Gross mixtures before treatment | 260 |
| Pd V | Once precipitated Pd (Runs 2) | 2600 |
| Pd III | Once precipitated Pd (Run 1) | 10000 |
| Pd VI | Residual solution | 8.3 |

corresponding to roughly a 30-fold enrichment.

That separation of the Ag from the Pd is virtually complete is shewn by the identity of decay curves Pd, VI, VII and VIII - the first residual solution, the second Pd precipitate from it, and the second residual solution respectively.

Notes.

(The Pd sponge used for irradiation was Johnson-Matthey "Specpure" grade, though the analysis showed a "strong" silver line. The use of "Nioxime" - 1, 2 cyclohexanedionedioxime - as recommended by Voter, Banks, and Diehl[54] may effect better separation still, since it is water soluble, but yields an even more insoluble Pd complex.)



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[54] U.S.Atomic Energy Commission Document MDDC - 1095.