THE

OXALATE COMPLEXES

OF

THORIUM

- by -

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SUMMARY.

(1) The ammonium, potassium and sodium salts of three complex thorium oxalates were prepared and studied.

(2) Their solubilities and conditions of stability were studied.

(3) The reaction between thorium and excess oxalate, and vice versa, was studied by means of conductivity and high frequency conductivity measurements.

(4) The formation constant of $Th(C_2O_4)_4^{4-}$ and $Th(C_2O_4)_3^{2-}$, and the solubility product of $(NH_4)_2Th_2(C_2O_4)_5$, were determined by a solubility method.

INTRODUCTION AND REVIEW OF LITERATURE.

The solution of thorium oxalate in warm ammonium oxalate was first observed by Bahr(1) in 1864. Bunsen(2) observed that the solution of yttrium and cerium earths in warm ammonium oxalate, when diluted by a moderate amount of water, were largely precipitated whilst the solution of thorium oxalate was unaffected. He used the reaction to separate thorium from the rare earths, but found it necessary to carry out the precipitation many times to get rid of the last traces of lanthanum and cerium.

B. Brauner(3) was the first person to investigate this reaction quantitatively with a view to preparing pure thorium compounds. He has described the preparation of $(NH_4)_4Th(C_2O_4)_4.7H_2O$ and $(NH_4)_4Th(C_2O_4)_4.4H_2O$, giving the latter as the stable form. He has also given an account of the hydrolysis of the above salt to $(NH_4)_2Th_2(C_2O_4)_5.7H_2O$, by treating the solid compound with water. Brauner suggested that the compound $H_2Th_2(C_2O_4)_5.9H_2O$, as opposed to the compound $H_2Th(C_2O_4)_3.3H_2O$, is formed on treating a solution of thorium oxalate in ammonium oxalate with strong mineral acid. The formation of $H_2Th(C_2O_4)_3.3H_2O$ was described by Glaser(4) in the previous year. Brauner makes no mention of the ion $Th(C_2O_4)_3^{2-}$.

The results of Brauner were confirmed, but without extension, by the findings of Rosenheim, Samter and Davidsohn(5).

- The compounds -

The compounds $K_4Th(C_2O_4)_4.5H_2O$ and $Na_4Th(C_2O_4)_4.6H_2O$, formed by dissolving thorium oxalate in hot concentrated potassium and sodium oxalates, were first described by Cleve (6) and Rosenheim, Samter and Davidsohn(7) respectively.

In 1908 Hauser and Wirth(8) and Wyrouboff and Verneuil(9) gave an account of the formation of an oxalochloride of thorium, $Th_4(C_2O_4)_6Cl_4.20H_2O$, by treating thorium oxalate with hydrochloric acid of concentration greater than 20%.

The first investigation of the solubility of the system $Th(C_2O_4)_26H_2O$ - $(NH_4)_2C_2O_4$ - H_2O was carried out by Hauser and Wirth(10), together with an investigation of the solubility of thorium oxalate in mineral acid and oxalic acid solutions. They described the compounds $(NH_4)_2Th_2(C_2O_4)_5.7H_2O$, $(NH_4)_2Th(C_2O_4)_3.3H_2O$ and $(NH_4)_2Th(C_2O_4)_4.7H_2O$, and their solubilities in ammonium oxalate. They postulated that, at 25°C, the only possible solid phases are $(NH_4)_2Th_2(C_2O_4)_5.7H_2O$ and $(NH_4)_2Th(C_2O_4)_3.3H_2O$ and $Th(C_2O_4)_2.6H_2O$, and that the latter can only exist in very dilute oxalate solutions.

They postulated the following equilibria:-

$$Th(C_2O_4)_2 \rightleftharpoons Th^{4+} + 2C_2O_4^{2-}$$

$$2Th^{4+} + 5C_2O_4^{2-} \rightleftharpoons Th_2(C_2O_4)_5^{2-}$$

$$Th^{4+} + 3C_2O_4^{2-} \rightleftharpoons Th(C_2O_4)_3^{2-}.$$

- Assuming the -

Assuming the chief source of thorium in the solution of thorium oxalate in excess oxalate to be $Th_2(C_2O_4)_5^{2-}$ and $Th(C_2O_4)_3^{2-}$, then :

$$[Th]_{TOTAL} = [Th_2(C_2O_4)_5^{2-}] + [Th(C_2O_4)_3^{2-}]$$

$$= \left(\frac{K_{s.p.}^{2}}{K_1} + K_{s.p.} \right) \frac{[C_2O_4^{2-}]}{K_2}$$

where $K_{s.p.} = [Th^{4+}]\,[C_2O_4^{2-}]^2$

$$K_1 = \frac{[Th^{4+}]^2\,[C_2O_4^{2-}]^5}{[Th_2(C_2O_4)_5^{2-}]}$$

and $$K_2 = \frac{[Th^{4+}][C_2O_4^{2-}]^3}{[Th(C_2O_4)_3^{2-}]}$$

From these relations

$[Th]_{TOTAL}$ = Constant x oxalate concentration and

should be directly proportional to the oxalate concentration. The much more rapid increase in solubility with oxalate concentration was attributed to the influence of the $Th(C_2O_4)_4^{4-}$ ion and to the polymerisation of $Th(C_2O_4)_2$ to $[Th(C_2O_4)_2]_4$. This was deduced from a hydrate, $3Th(C_2O_4)_2.4H_2O$, which they prepared,and the oxalochloride $3Th(C_2O_4)_2.ThCl_4.2OH_2O$, of Wyrouboff and Verneuil(9).

The most complete account of the oxalate chemistry of thorium is found in the textbook of R. J. Meyer and O. Hauser, Die Analyse der seltenen Erde und der Erdsaüren(11). An expanded version of the above work, together with an account of the precipitation of thorium oxalate from strongly acidified solutions of thorium oxalate complexes is given.

James, Whittemore and Holden carried out a phase rule investigation of the system $Th(C_2O_4)_2.6H_2O$ - $(NH_4)_2C_2O_4$ - H_2O(12) at 25°C. From the points of intersection they deduced that the only stable phases were $(NH_4)_2Th_2(C_2O_4)_5.7H_2O$ and $(NH_4)_2Th(C_2O_4)_3,3H_2O$. The latter however was incorrectly given in the original reference as $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.2H_2O$(12b).

The system $Th(C_2O_4)_2.6H_2O$ - $Na_2C_2O_4$ - H_2O was investigated by Britton and Jarrett(13) in 1936. The only solid complex isolated was $Na_4Th(C_2O_4)_4.6H_2O$, at pH ca. 7 and 25°C. However mixtures of the latter and $Th(C_2O_4)_2.6H_2O$ and $Na_2C_2O_4$ were reported. Unfortunately the pH is too high to allow these results to be compared with those of Hauser and Wirth.

No phase rule studies of the corresponding $K_2C_2O_4$ - $Th(C_2O_4)_2$ - H_2O system have been carried out. The compound $K_4Th(C_2O_4)_4.6H_2O$ has been prepared by Cleve(6) in his investigation of solution of thorium oxalate in potassium oxalate. A tartrate complex $K_2Th(C_4H_4O_6)_3.?H_2O$ was also prepared by Cleve(14). Another bidentate thorium potassium complex of the same form is the catechol complex of Rosenheim, Raibmann and Schendel(15), $K_2Cat_3Th.7H_2O$, formed by adding KOH to a 1 : 8 molar mixture of thorium nitrate and catechol in 5 moles water.

- The quantitative -

The quantitative insolubilities of thorium oxalate in oxalic acid(16) and mixture of sulphuric and oxalic acid(17) were determined by Colani and F. Wirth respectively. The method of Bunsen(2) of separating thorium from the rare earths by extracting thorium oxalate by concentrated ammonium oxalate was criticised by Benz(18), who, in 1902, found contamination by cerium earths and serious losses of thorium, even after repeated extraction and precipitation. The method was also critisised by Bonardi(19), Little(20), Meyer and Hauser(11) and Spencer(21). Since 1920 this method of separation has found no application, and from 1920 to 1940 with the loss in interest in the incandescent gas mantle little work on thorium complexes has been carried out.

Since 1940, however, the possible importance of the thorium nucleus in fission studies has refocussed interest in thorium. In 1948 the first reviews of thorium chemistry, dealing chiefly with analytical and separational procedures, (22), (23), (25) appeared.

The quantitative precipitation of thorium as thorium oxalate has been re-examined by Willard and Gordon(27), Kall and Gordon(28), and Carron, Skinner and Stevens(26). Precipitation was carried out by the sudden addition of a saturated solution of oxalic acid, solid oxalic acid, or a solution of methyl oxalate in alcohol(27) to acidified solutions of thorium salts, usually 4 - 5% in nitric acid. In discussing the precipitation of the oxalate, Rider and Mellon(29) stress the effect of the volume of the supernatant liquid. This is of significance because of the quantitative insolubility of thorium oxalate with oxalate concentration.

Since 1941, when the use of thoron (APANS) as a colorimetric reagent for thorium was first proposed by Kuznetsov(30), many articles have been published about colorimetric methods for the determination of thorium. These are far too numerous to review here. The reagents proposed are various azo-dyes which are usually derivatives of chromotropic acid, viz:

These form very stable 2 : 1 complexes with thorium. A typical example is thoron itself which is 1-(o-phenylazo-)-chromotropic acid. In one case, that of Thoron II, viz. bis 1-(o,o'diphenyldiazo-)-chromotropic acid, the 1 : 1 complex formed is so strong that oxalic acid is used to mask interfering elements, e.g. Ti and Zr.

The same group of dyes have been used as indicators in the complexometric titration of thorium with EDTA or potassium fluoride. A critical review of the complexometric methods for determining thorium has been given by Přibil(32).

In 1935 Brintzinger and Eckardt(24) investigated the dialysis coefficient between 0.04 to 0.2 M Thorium nitrate in

- M $(NH_4)_2C_2O_4$ and -

M $(NH_4)_2C_2O_4$ and water. They revealed the existence of a dinuclear ion $Th_2(C_2O_4)_8^{8-}$. This has been confirmed in a more recent study using a cellophane membrance by B. Frank(24b).

The oxalate complexes of thorium have been investigated by Bose and Chowdhury(34) using a thermometric method i.e. Job's method of continuous variation applied to molecular properties (in this case, the freezing point of the 12% KNO_3 - ice cryohydrate(35)). On titrating 0.12 M potassium oxalate with 0.3 M thorium nitrate, pH not specified, they obtained breaks in the freezing point curve corresponding to thorium : oxalate ratios of 1 : 8, 1 : 4, 1 : 3 and 1 : 2 moles, indicating the formation of $Th(C_2O_4)_4^{4-}$, $Th(C_2O_4)_3^{2-}$ and $Th(C_2O_4)_2$. They interpreted the 1 : 8 break as the initiation of $Th(C_2O_4)_4^{4-}$ formation, and the formation of $Th(C_2O_4)_8^{8-}$. They obtained no break at 2 : 5 and concluded that Brauner's compound, $(NH_4)_2Th_2(C_2O_4)_5.7H_2O$, is a double compound of $(NH_4)_2Th(C_2O_4)_3$ and $Th(C_2O_4)_2$ in the solid phase, i.e. $(NH_4)_2Th(C_2O_4)_3.Th(C_2O_4)_2.7H_2O$. On addition of potassium oxalate to thorium nitrate, they obtained indications of a polymeric complex ion $(ThC_2O_4)_n^{n+}$.

Bose and Chowdhury(36) have used the same method to calculate the stability constant of the $Th(C_2O_4)_4^{4-}$ ion, which they give as $-\log K = 24.48$, with temperature and total ionic concentration not specified. Owing to the slow rate of dissolution of thorium oxalate the equilibrium was studied on the basis of hydrolysis. The pertinent equilibria are :-

$$Th(C_2O_4)_4^{4-} \rightleftharpoons Th(C_2O_4)_3^{2-} + C_2O_4^{2-}$$
$$Th(C_2O_4)_3^{2-} \rightleftharpoons Th_2(C_2O_4)_5^{2-} + C_2O_4^{2-}$$
$$Th_2(C_2O_4)_5^{2-} \rightleftharpoons Th(C_2O_4)_2 + C_2O_4^{2-} .$$

No intermediate formation constants were given.

Thorium oxalate complexes have also been studied by the means of "heterometry",(40) this method consists of measuring the optical density of a suspension of a solid compound in aqueous media. Interferences due to colouration are removed by filters or by masking. A titration is carried out in a similar manner to a colorimetric titration, the optical density in the well-stirred titration vessel being continuously measured. The method differs from turbidimetry in that the light absorbing particles are supposed to be the primary particles formed in the reaction and not the microcrystals formed from them, hence the optical density depends on the chemical nature of the primary particles rather than their physical size. Similarly, the heterometric optical density is independant of the rate of stirring over a wide range. Heterometric titrations are carried out rapidly and without the addition of protective colloids.

The breaks occuring in the plots of optical density vs. moles of reagent added correspond to the change from one species of primary particle to another.

Using this method the citrate(41), maleate(42), phthalate(42), tartrate(43) and oxalate(44), (45) complexes of thorium have been studied.

On adding 0.5 M potassium oxalate solution to 0.01 M thorium nitrate in an acetic acid solution of pH 1.7, Bobtelsky and Ben-Bassat(44) found complex formation to commence at a ratio of 1 : 1 moles of thorium and oxalate respectively, corresponding to the ion $ThC_2O_4^{2+}$. The optical density curve then rose gently to a ratio of 1 : 2, i.e. corresponding to the compound $Th(C_2O_4)_2$. From minor breaks in this curve they postulated the existence of $Th_2(C_2O_4)_3^{2+}$ and $Th_3(C_2O_4)_5^{2+}$ as insoluble complexes. i.e. the following reactions occur :

$$Th^{4+} + C_2O_4^{2-} \rightleftharpoons ThC_2O_4^{2+}$$

$$2ThC_2O_4^{2+} + C_2O_4^{2-} \rightleftharpoons Th_2(C_2O_4)_3^{2+} + C_2O_4^{2-} \rightarrow 2Th(C_2O_4)_2$$

$$3ThC_2O_4^{2+} + 2C_2O_4^{2-} \rightleftharpoons Th_3(C_2O_4)_5 + C_2O_4^{2-} \rightarrow 3Th(C_2O_4)_2.$$

At pH greater than 7 they postulated the formation of various polymeric complexes, and depending on pH and oxalate concentration, contained thorium and oxalate in the ratios 4 : 1, 3 : 1, 3 : 2, 2 : 1, 2 : 3 and 1 : 1 moles. The solubility, or otherwise, of these chains depends on the presence of Th - O - Th links, derived from the original partially hydrolysed thorium solutions.

The evidence from the optical density curves seems insufficient to prove the existence of complex ions other than $ThC_2O_4^{2+}$, and in the case of insoluble complexes precipitated above pH 7, there appears to be no proof that the structures are in fact polymeric. They have not been mentioned by any other source.

A similar determination by Komatsu, Taki and Takoda(46), employing the turbidometric titration of 0.005 M $Th(NO_3)_4$ with 0.05 M ammonium oxalate in the presence of M acetic acid and 0.1% polyvinyl alcohol, revealed only the break at 1 : 1 moles.

The more recent general reviews of thorium chemistry comprise those of Seaborg and Katz(56), Kuznetsov, Savvin and Mikhailov(57); and Gmelin's Handbuch, 8 Auflage, Thorium und Isotope. A useful review of the complex chemistry of the oxalate ion is that of Krishnamurty and Harris(58).

REVIEW OF METHODS AVAILABLE FOR INVESTIGATION OF THORIUM OXALATE COMPLEXES.

(a) SOLVENT EXTRACTION.

Although solvent extraction has been applied to the study of the complexes between thorium and chelating agents such as oxine and cupferron(37), (38), (39), and acetylacetone(39), it has not been applied to oxalate complexes. In the above measurements the distribution of the thorium- organic chelating agent complex between water and organic solvents was studied by a radiometric technique using Th^{234}. This method is not suitable for the study of oxalate complexes since their solubility in organic solvents is very low.

(b) CONDUCTIVITY.

Conductivity studies of the ionic species present in thorium nitrate solutions made by Krauss and Holmberg(47) indicate the presence of polymeric hydroxy ions. Sirkka Hietanen(48) by the same method deduced the presence of $Th[(OH)_3Th]_n^{4+n}$ and $Th[O(OH)Th]_n^{4+n}$ in a thorium nitrate solution in equilibrium with hydrous thorium oxide. These results were later confirmed by Dey(49).

Other conductiometric studies of thorium and oxalate solutions have been made only with regard to the quantitative determination of thorium.

Menon and Singh(50) have determined thorium conductiometrically in solutions 0.00033 M with respect to oxalic acid with an error of ± 0.5%.

Conductivity offers a suitable method of investigating the oxalate complexes of thorium, the great difference in conductivities between the thorium ion and the various oxalate complexes being readily measurable under controlled conditions.

(c) HIGH FREQUENCY CONDUCTIVITY.

This has the advantage that no actual physical contact with the solution is necessary, thus eliminating electrode effects. Furthermore the conductivity depends on the dielectric constant of the solution which may change by a large amount on the substitution of one ionic species by another.

The high frequency titration of thorium with EDTA has been discussed by Hara and West(51), and in rather more detail by Pungor and Zapp(52).

(d) ION EXCHANGE.

Although the elution of thorium from cation exchange resins has been discussed(59), ion exchange techniques have not been applied to thorium oxalate complexes. The difficulties associated with the ion exchange behaviour of small amounts of thorium have been overcome by A. Zielen(53) in the radiometric cation exchange study of the reactions :-

- $Th^{4+} + HSO_4^-$ -

$$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{++} + H^+$$

$$ThSO_4^{++} + HSO_4^- \rightleftharpoons Th(SO_4)_2 + H^+$$

The ion exchange behaviour of thorium is at present being studied in the chemistry department of Rhodes University.

(d) SPECTROPHOTOMETRY.

Owing to the colourless nature of thorium and complex thorium oxalate ions, the absorption spectra of the thorium oxalate system have not been studied. However Tolmacher(54) has investigated the carbonate complex in the ultra violet region, 2200 A.U., and assigned a structure $Th(CO_3)_4(OH)_2^{6-}$.

(e) STEREOISOMERISM.

The stereochemistry of thorium complexes in general has been ignored, but the analogous tetra-oxalato uranium IV compound, $K_4U(C_2O_4)_4.5H_2O$, has been resolved into 4 optical isomers, thus eliminating the possibility of a cubic type structure for the ion.

(f) TURBIDOMETRY or HETROMETRY.

These methods do/seem to be able to offer much scope for the investigation of oxalate complexes.

1. PREPARATION AND STABILITY OF THORIUM OXALATO COMPLEXES.

1.1 METHODS OF ANALYSIS OF COMPLEXES.

1.11 Thorium.

Three methods are available :

(a) IGNITION TO THORIA.

This is the classical method used by Brauner, Hauser and Wirth and others, and has the advantage of simplicity. However it breaks down when traces of alkali metals or rare earths are present, and when only small amounts of sample are available. Thorium oxalate decomposes to the oxide between 200-250°C according to Duval(60) and Beckett and Winfield(61). ThO_2 is stable up to very high temperatures but loses the last traces of water very slowly. The optimum ignition conditions, limited by evaporation of platinum, are 30 mins in a closed platinum crucible at 850 ± 25°C.

(b) COLORIMETRIC DETERMINATION.

Small amounts of thorium in the presence of rare earths and simple cations can be determined by this method. However, the oxalate, fluoride and nitrate ions interfere by competing with the colour reagent, or by oxidising it. A wide variety of reagents are available for the determination of thorium, e.g.

Thorin, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulphonic acid, also known as Naphtharson, Thoron, Thoronol, and APANS.

Arsenazo, 2,7-di-(4-sulphononaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid, also known as SNADS.

Methods for the determination of thorium by thorin have been described by Thomason, Perry and Byerly(62), Banks and Byrd(63), Clinch(64), and Grimaldi and Fletcher(65).

Methods using arsenazo by Kuznetsov and Nikol'skya(66), Kuznetsov and Savvin(67) and S. K. Datta(68).

Procedure adopted.

The removal of oxalate: Thomason, Perry and Byerly(62) recommended the wet oxidation by evaporation of the sample in a mixture of 0.5 ml conc. nitric acid, 0.05 ml water and 1.0 ml 70% perchloric acid under an infra-red lamp. It was found that in the presence of more than 0.1 g oxalic acid this had to be repeated 10 times to give a constant result.

A simpler procedure which gives satisfactory results in the presence of unlimited amounts of oxalic acid is as follows :

The sample is evaporated to dryness in a silica dish, and placed in a well ventilated oven at 170 ± 5°C for 30 mins. 5 ml fuming nitric acid is added and the sample evaporated to dryness under an infra-red lamp.

Since oxalic acid sublimes at 150°C, and thorium oxalate is stable up to 200°C, fairly accurate temperature control is needed. All solid thorium complex oxalates are stable with respect to ThO_2 to at least 200°C.

- Colour development -

Colour Development.

The residue from the above treatment (less than one drop nitric acid should remain) is dissolved in 1 ml conc. HCl and diluted to the required volume. A sample containing 100 to 400 μg ThO_2 is placed in a 50 ml flask together with 20 ml water, 1 ml conc. HCl, 5 ml 0.1% freshly prepared aqueous thorin, and 20 ml absolute alcohol. The volume is made up to 50 ml by the addition of water. The transmittance is measured at 545 mμ against a reagent blank 1 hour after making the solution. The colour remains stable for 5 hours.

The procedure using arsenazo is the same except that the absolute alcohol is omitted and the transmittance measured at 600 mμ.

Of the two methods the latter is slightly less sensitive to traces of oxalate and nitric acid than the former which, however gives more consistant results, and was therefore used throughout the subsequent work.

Effect of oxalic acid on the colorimetric determination of thorium.

50 μg sample of ThO_2 in 50 ml flasks.

	% Transmittance.	
mg oxalic acid added.	Thorin.	Arsenazo.
Blank	72.0	76.4
0.5	72.0	76.4
1.0	72.5	76.5
2.0	73.5	77.0
4.0	75.7	77.5
10.0	77.0	79.2

Effect of adding conc. nitric acid.

50 μg sample in 50 ml flask.

ml conc. HNO_3 added.	% Transmittance Thorin	% Transmittance Arsenazo.
0.1	72.0	6.4
0.2	72.0	76.4
0.3	73.0	76.7
0.4	73.9	77.0
0.5	74.8	77.8

This effect is not due to any change in pH since adding an equivalent amount of conc. HCl produced no effect.

(c) COMPLEXOMETRIC DETERMINATION.

This offers a quick method (± 1% accuracy) of determining amounts of thorium over 10 mg.

Reagent.

Only EDTA was used. A 0.01 M solution was prepared and standardised by weighing out the pure disodium salt (Merck). A check using pure magnesium sulphate with eriochrome black T indicator revealed no significant difference.

Indicator.

Among the numerous indicators suggested Alizarin Red S(69) screened with methylene blue was found the most suitable.

Procedure.

The sample was evaporated under an infra-red lamp with 1 ml conc. nitric acid, 1 ml 70% perchloric acid, and 0.5 ml water.

- If much free -

If much free oxalic acid was present the sample was first heated at 170°C to sublime the excess. The residue was dissolved in 3 drops conc. nitric acid and transferred to a conical flask with 25 ml water. 3 drops alizarin red S, and 4 drops of 1% methylene blue solution were added. 0.01 M EDTA was run in until a grey colour appeared, when the pH was adjusted (pH meter or test paper), to 3 by addition of 1 : 1 aqueous ammonia solution. EDTA was added dropwise. The end-point colour was purple to green (very similar to the screened methyl red acid-base indicator). No interference was produced by the presence of 0.5 g oxalic acid or 1 ml nitric acid in the titration vessel.

1.12 OXALATE.

Brauner and Hauser and Wirth determined oxalate by direct titration with potassium permanganate solution or by back titration with ferrous ammonium sulphate solution. However, the oxidation of insoluble oxalates by permanganate is slow, and the end-point uncertain.

Four methods were compared :-

(a) Oxidation by hot potassium permanganate solution followed by back titration with ferrous ammonium sulphate solution.

(b) Oxidation by hot ceric sulphate solution. Back titration with ferrous ammonium sulphate solution using ferroin as indicator.

(c) Catalytic oxidation by warm ceric sulphate solution. ICl was used as a catalyst and the end-point was determined electrometrically.

(d) Catalytic oxidation by cold ceric sulphate solution. The catalyst was OsO_4 and the end-point was determined electrometrically.

<u>Preparation of 0.05 N ceric sulphate solution</u>.

175 g of B.D.H. anhydrous ceric sulphate was dissolved in 300 ml of 1 : 1 aqueous sulphuric acid solution and any insoluble matter was filtered off. The solution was made up to 10 litres and 5 g chrome alum added to complex the phosphate present. The solution was left a week and filtered before standardising, after which the strength was constant.

<u>Preparation of ferroin indicator</u>.

0.700 g ferrous sulphate and 1.485 g o-phenanthroline monohydrate were dissolved in 100 ml of water.

<u>Preparation of 0.001 M ICl catalyst</u>.

0.1395 g KIO_3 and 0.0890 g KI were dissolved in 100 ml water and 125 ml conc. HCl added. The solution was adjusted to an electrometric end-point by the addition of very dilute KIO_3 solution. It was then diluted to 250 ml by the addition of water.

<u>Preparation of 0.01 M osmium tetroxide catalyst</u>.

0.25 g Eastman-Kodak white label OsO_4 was dissolved in 100 ml N H_2SO_4 and stored in a black bottle.

Standardisation of ceric sulphate solution.

0.125 g AR.As_2O_3, previously dried at 105-110°C for 2 hours, was dissolved with gentle warming in 20 ml 5% NaOH, 100 ml water followed by 25 ml N SO_2 - free H_2SO_4 added. 3 drops OsO_4 catalyst were added and the solution was titrated using either ferroin (2 drops) as indicator or determining the end-point electrometrically.

End-points.

The ferroin end-point colour change is from orange to light blue. A blank of 0.04 ml was measured.

The electrometric end-point occured when a small drop of reagent produced a voltage change (of the order of 100-200 mV) between platinum and saturated calomel electrodes.

Comparison of methods.

The oxalate content of a sample of pure thorium oxalate, $ThOx_2.6H_2O$, Lindsay Chemical Co., kept over silica gel, was determined by the following methods :-

(a) 0.02 g of sample was added to 10 ml of ceric sulphate and 5 ml of N H_2SO_4 solutions. This was heated at 80°C for 30 mins, cooled and titrated with ferrous ammonium sulphate solution using 1 drop of ferroin indicator.

(b) As above with 0.05 N $KMnO_4$.

(c) 0.02 g of sample was added to 10 ml water, 5 ml ICl catalyst added and warmed to 55°C. The end-point was determined electrometrically.

- (d) 0.02 of -

(d) 0.02 g of sample was added to 10 ml water, and 5 ml SO_2 - free H_2SO_4 solution, and 3 drops OsO_4 catalyst added. The end-point was determined electrometrically.

A 10 ml burette reading to 0.02 ml was used in all titrations.

Method	Wt. $ThOx_2 6H_2O$ g.	Titre mls.	% $C_2O_4^{2-}$.	
(a)	0.02210	1.70	34.10	
	0.01685	2.58	34.18	
	0.01972	2.10	34.08	
	0.01204	3.38	34.12	Mean 34.12%
(b)	0.01889	3.08	34.09	
	0.01363	3.90	34.14	
	0.01772	2.26	34.10	
	0.02382	2.32	34.10	Mean 34.11%
(c)	0.01916	2.85	34.09	
	0.02152	3.20	34.09	
	0.02537	3.78	34.12	
	0.05954	2.90	34.05	Mean 34.11%
(d)	0.01957	2.92	34.09	
	0.02142	3.18	34.10	
	0.02294	3.38	34.12	
	0.02021	3.00	34.10	Mean 34.10%

The two direct methods, (c) and (d), compare well in accuracy and reproducibility of results with the indirect and more time consuming methods, (a) and (b). Method (d), the simplest of the four, was chosen.

- 1.13 DETERMINATION -

1,13 DETERMINATION OF AMMONIUM ION CONTENT.

The ammonium ion content was determined in a Kjeldahl semi-micro distillation apparatus. The sample was weighed out, dissolved in a small amount of conc. HCl and transferred, with the minimum amount of water, through the funnel into the vacuum-jacketted steam distillation vessel. The receiver contained 25 ml 1% boric acid solution. 25 ml 10% NaOH solution was added and the ammonia was distilled over into the receiver. After about 50 ml of distillate were collected, the contents of the receiver were titrated with approximately 0.01 N H_2SO_4 using screened methyl red indicator. The apparatus was thoroughly steamed out before and after use.

The sulphuric acid solution was standardised using Bakers Analysed borax, twice recrystallised according to Vogel, and stored over saturated sugar and salt solution. Screened methyl red was used as the indicator.

1,14 DETERMINATION OF NITRATE ION CONTENT.

The nitrate content was determined by Devarda's method, i.e. reduction of the nitrate to ammonia, using the above apparatus.

The sample was dissolved in a few drops of conc. HCl and washed into the distillation vessel with the minimum amount of water. 2 g of Devarda's alloy powder was washed in using 5 ml water, 25 ml 20% NaOH was slowly added, and the apparatus left for 90 mins.

- The distillation -

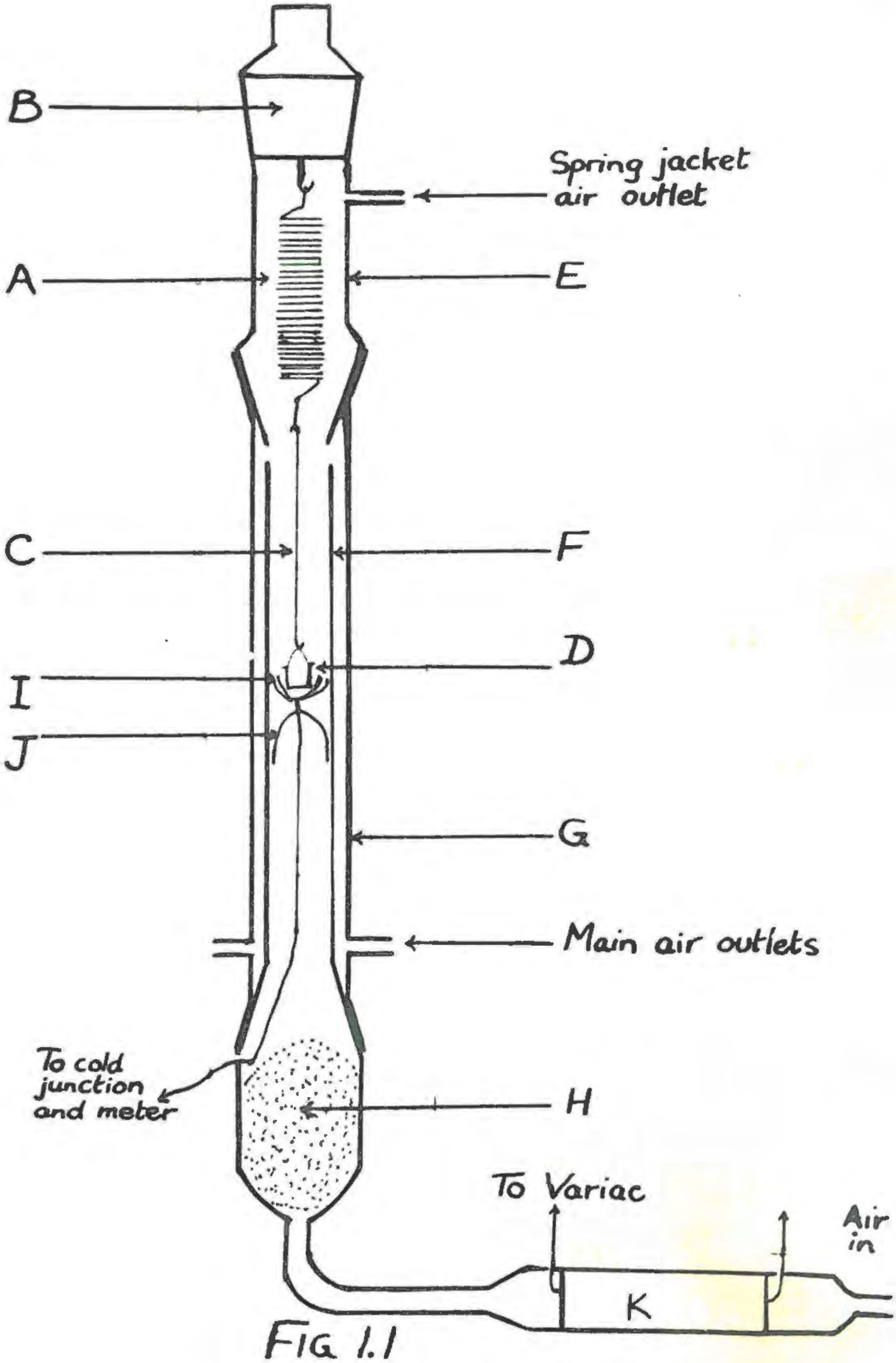

B
Spring jacket air outlet
A
E
C
F
D
I
J
G
Main air outlets
To cold junction and meter
H
To Variac
Air in
K

FIG 1.1

The distillation was carried out for 25 mins. The distillate was collected in a receiver containing 25 ml of 1% boric acid. Titration of the resulting solution was carried out as above.

1.15 DETERMINATION OF WATER CONTENT.

Experiments with heated vacuum desiccators and ovens proved unsuccessful owing to (a) lack of temperature control, (b) the fact that some complex oxalates are hygroscopic and (c) some oxalates tend to loose ammonia on heating in vacuo. Consequently a thermobalance was devised; a simple design which was first tried was based on one described by Delhez(70). This consisted of a vertical glass tube containing a quartz helical spring and suspended bucket, warmed by the passage of hot air. However it was found that the temperature gradient of approximately 5°C along the tube was too great.

A double jacketted arrangement was finally designed and constructed, Fig. 1.1. With this apparatus the temperature gradient was reduced to 0.4°C in 25 cm.

Description of apparatus. (Fig. 1.1)

A. Quartz Spring.

This was obtained from the Thermal Syndicate. The specifications were, diameter 1 cm, length 2.5 cm, sensitivity 3.65 mm/mg, and a maximum extension of 20 cm.

The springs were shipped in glycerine. Before use they were washed repeatedly by decantation with warm distilled water. When dry they were lifted by passing an L-shaped glass rod horizontally through them and lifting them in a horizontal position. This procedure was adopted as the weight of water adhering to them would have exceeded the maximum load. Before use they were dried and subsequently aged in an air oven for 48 hours at 120°C.

B. Suspension.

The spring was suspended from a platinum wire hook sealed onto a B24 glass stopper. This was firmly clamped in a stand.

C. Stirrup.

This was a very thin glass rod 0.2 mm in diameter and 6 cm in length. The ends were hooked and rounded into knobs. The weight was 8 mg.

D. Bucket.

The bucket was made from 48 gauge nickel foil and was a 2 mm cube. The seams were spot welded by a 6 v accumulator and silver wire electrode. The handle was made of stainless steel wire. Both were aged at 120°C and checked for constant weight. The weight of the bucket and handle was 18.5 mg.

E. Spring jacket.

It was decided to keep the spring at sample temperature and apply a correction for loss of elasticity due to temperature changes. This was done by a small vent in this section of the vertical tube, comprising a B24 socket and cone separated by 3 cm of 1.5 cm diameter tubing.

F. Inner Jacket.

The inner jacket consisted of a glass tube 1.2 cm internal diameter, 18 cm long, joined to the small end of a B24 cone. The large end was joined to a 4 cm length of 2 cm diameter glass tubing containing a plug of quartz wool, H, to diffuse the heating air, and an inlet hole for the thermocouple leads. It was joined via a length of asbestos lagged tubing and a B10 cone and socket to the heater K.

G. Outer jacket.

The outer jacket consisted of a tube 2 cm in diameter, and 18 cm long, terminating at both ends in B24 sockets. The lower end contained the four diametrically opposed main air outlet holes.

I. Temperature measurement.

The temperature was measured by ten copper-constantan thermocouples soldered in series. One set of ends was formed into a ring and held in position immediately below the bucket by four stainless steel wire sliders, J. The ring of thermocouples surrounding the bucket could be slid up or down the inner tube pushing or pulling the wires through the entry hole. The other set of ends were insulated by epoxy resin and placed in a Dewar flask in crushed ice. The emf was measured by a stabilised valve voltmeter. A calibration curve was prepared by placing a standardised thermometer between the thermocouples. The temperature could be read to 0.2°C and held constant to 0.5°C.

K. Heater.

The heater consisted of a 10 cm length of 1 cm diameter pyrex tubing, joined to the inner jacket by a B10 cone. It was lined with a roll of asbestos paper to protect the glass from the heating element, which consisted of a coiled 8 cm length of Nichrome wire connected to a Variac. Maximum current of 2 amps produced a temperature of 150°C.

Air Supply.

Compressed air at 5 atm was reduced in pressure to 80 cms Hg pressure by a diaphragm valve. It was then passed into a 10 litre expansion chamber and out through rubber tubing onto which was fastened a screw clip. This further reduced the pressure. The gas was then passed into another expansion chamber, and then through two drying towers, one containing P_2O_5 and the other cotton wool (to act as a filter), and finally through a flow-meter.

Measurement of extension.

A vertical travelling microscope, focussed on the bucket hook, was used to measure the spring extension. The spring

- suspension, -

suspension, B, was clamped to the microscope stand and any expansion which occured merely displaced the jacket downwards.

1.151 OPERATION.

Loading.

The bucket was placed on a flat surface. The suspension stopper with spring and stirrup was withdrawn from the apparatus and hooked under the bucket handle. The whole was gently lifted and replaced.

Readings.

Readings could be made either with the airstream on or off. Although the bucket remained virtually steady, more reliance was placed on results obtained with the air stream off. Air was passed at a standard rate of 2 litres per minute and readings were taken, with power and air turned off, immediately the bucket came to rest.

Correction for effect of temperature on spring.

The coefficient of Youngs modulus, E, with temperature, t, of quartz is negative.

$$E_t = E_{15}[1 - a(t - 15)]$$

where

$$E_{15} = 8 \times 10^{10} \text{ dynes/cm}^2$$

$$a = -1.3 \times 10^{-4}/^{\circ}\text{C} \quad (71)$$

Hence for a temperature rise of 100°C :

$$E_{115} = E_{15}\,(1 + 1.3 \times 10^{-4} \times 100)$$

$$= E_{15} \times 1.013$$

i.e. E, the elasticity increases by 1.3%. This is offset by the linear expansion of the stirrup and mountings, so that the overall correction is low.

Corrections:

Load.	Temperature Range. 20-80°C.	20-100°C.	20-120°C.	20-140°C.
0 mg	-0.00cm	-0.05 cm	-0.10 cm	-0.14 cm
25	-0.00	-0.05	-0.10	-0.14
50	-0.00	-0.07	-0.13	-0.15
75	-0.02	-0.08	-0.15	-0.17

If readings are taken with the airflow on, the corrections are approximately twice as great.

Accuracy.

The spring had a sensitivity of 36.5 cm/g i.e. 27.40 mg/cm. Since the cathetometer could be read to 0.01 cm, this corresponds to 0.3 mg sensitivity, i.e. 0.3% on a 0.1 g sample.

1.2 PREPARATION AND ANALYSIS OF COMPLEX THORIUM OXALATES.

1.21 Preparation of M_4ThOx_4.

Heterogeneous preparation.

The primary products formed on the dissolution of thorium oxalate in hot concentrated oxalate solutions were prepared as follows :-

> 1 mole of thorium oxalate was boiled with 3 moles of ammonium oxalate crystals dissolved in 100 ml water. The slurry was washed through a Whatman No. 44 paper (the washings were discarded) and after ignition the residue was found to correspond to 4.86 g thorium oxalate. On cooling the solution, small, well formed, needle-like crystals were produced.

The supersaturation noted by Brauner was not observed, and only a few crystals were obtained on further cooling and seeding. The crystals were collected and cautiously washed with a little cold water. The crystals were dried on filter paper and stored over silica gel in a desiccator.

The experiment was repeated with potassium and sodium oxalates, and oxalic acid in equivalent amounts. In the case of sodium and potassium oxalates small needle-shaped crystals were obtained; oxalic acid produced an amorphous precipitate. The composition of the products formed in these experiments are shown in the following table.

- table follows -

"Solvent"	Wt $ThOx_2$ dissolved.	Composition of Complex							
		% Th	Moles	% Th	Moles	% NH_4^+	Moles	% H_2O	Moles
$(NH_4)_2Ox$	0.24 g	29.59	1.00	45.25	4.05	9.05	3.93	16.01	6.91
Na_2Ox	0.13 g	28.85	1.00	43.98	3.93	-	-	18.9	5.33
K_2Ox	0.17	26.62	1.00	39.72	3.90	-	-	17.6	5.42
H_2Ox	0.08	No agreement on different samples.							

Preparation from homogenous solution.

If an oxalate solution is added to a strong thorium nitrate solution the precipitate initially formed soon redissolves.

5.5 g $Th(NO_3)_4.4H_2O$ (1 mole) was dissolved in 10 ml water, the solution heated to near boiling point and the calculated amount, 4 moles, of ammonium oxalate added. A definite slurry of thorium oxalate remained.

As the complex is evidently stable only in the presence of an excess of oxalate, an attempt was made to determine the critical concentration. A strong standardised solution of ammonium, potassium, and sodium oxalates was added dropwise to the above solution until the solution was clear. This was repeated at different temperatures. The clear solution was evaporated to 10 ml and the crystals treated as before. The results obtained are given in the following tables.

- tables follow -

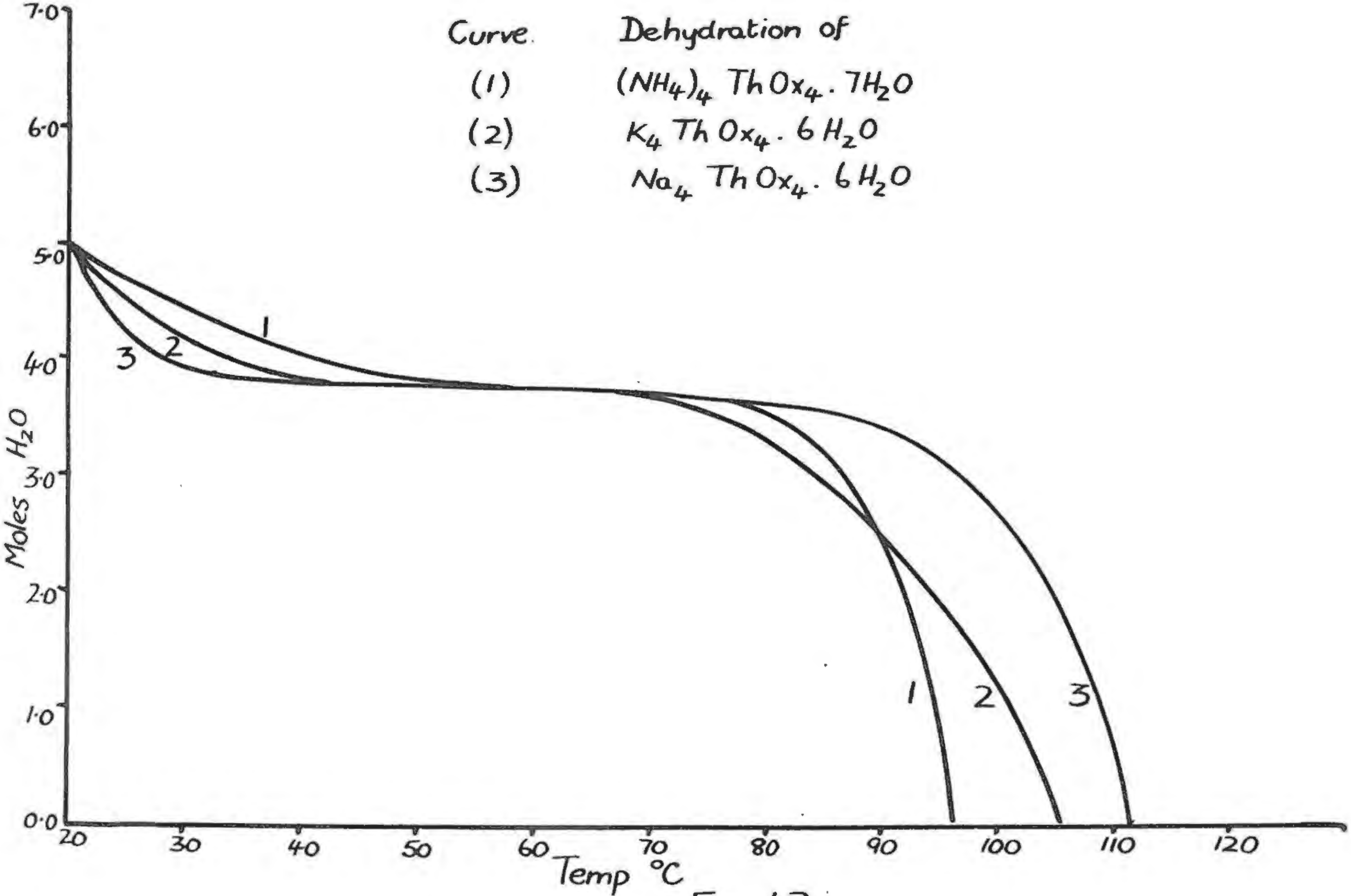

Curve
Dehydration of
(1) $(NH_4)_4\ ThOx_4 . 7H_2O$
(2) $K_4\ ThOx_4 . 6H_2O$
(3) $Na_4\ ThOx_4 . 6H_2O$
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
Moles H_2O
20
30
40
50
60
70
80
90
100
110
120
Temp °C
1
2
3

FIG 1.2

Oxalate used :	Critical Concentration at 80°C.	Composition of product, molcs. Th	Ox	NH_4	H_2O	NO_3
Ammonium	0.32 M	1.00	3.65	3.82	6.71	0.02
Potassium	0.27	1.00	3.69	-	5.82	0.02
Sodium	0.36	1.00	3.60	-	5.63	0.01

In each case the minimum temperature required to redissolve the precipitate was about 76°C.

Temperature.	Critical concentration of ammonium oxalate.
90°C	0.24 M
85	0.28
80	0.32
76	0.35

The decreased amount of oxalate required at higher temperatures indicates a higher stability at higher temperatures.

Dehydration of $M_4ThOx_4 \cdot 7H_2O$.

The compounds, air dried at room temperature, contained between 5 and 6 molecules of water per molecular formula. In their dehydration curves (Fig. 1.2), there are inflexions at 30, 42 and 47°C for the NH_4, K and Na compounds respectively. Unlike thorium oxalate they all form stable anhydrides at 92, 101 and 110°C respectively.

- The 4- hydrate -

The 4-hydrate was prepared by using the thermobalance and is completely stable at room temperatures, the 7-hydrate loses water very slowly at room temperature.

1.22 Preparation of M_2ThOx_3.

(a) Hydrolysis of $ThOx_4^{4-}$.

0.1 g $(NH_4)_4ThOx_4.7H_2O$, as prepared above, was placed in 100 ml water at room temperature. The substance rapidly dissolved producing a milky suspension, which settled after 3 days.

The precipitate was coagulated by boiling (without change in composition) and filtered with difficulty. A similar precipitate was formed by adding the thoroxalate to boiling water. The mother liquid contained only 2.2 mg thorium, i.e., 22 mg/litre. The precipitate was washed cautiously with cold water and dried on filter paper and stored over silica gel in a desiccator.

Under the microscope the crystals were seen to consist of extremely small plate-like crystals.

The potassium and sodium analogues of the above also produced precipitates similar to the above. The composition of the hydrolysis products were as follows :

	Percentage.	Moles.
Th	48.55	1.00
C_2O_4	46.37	3.18
NH_4	6.52	2.19
H_2O	8.50	2.74

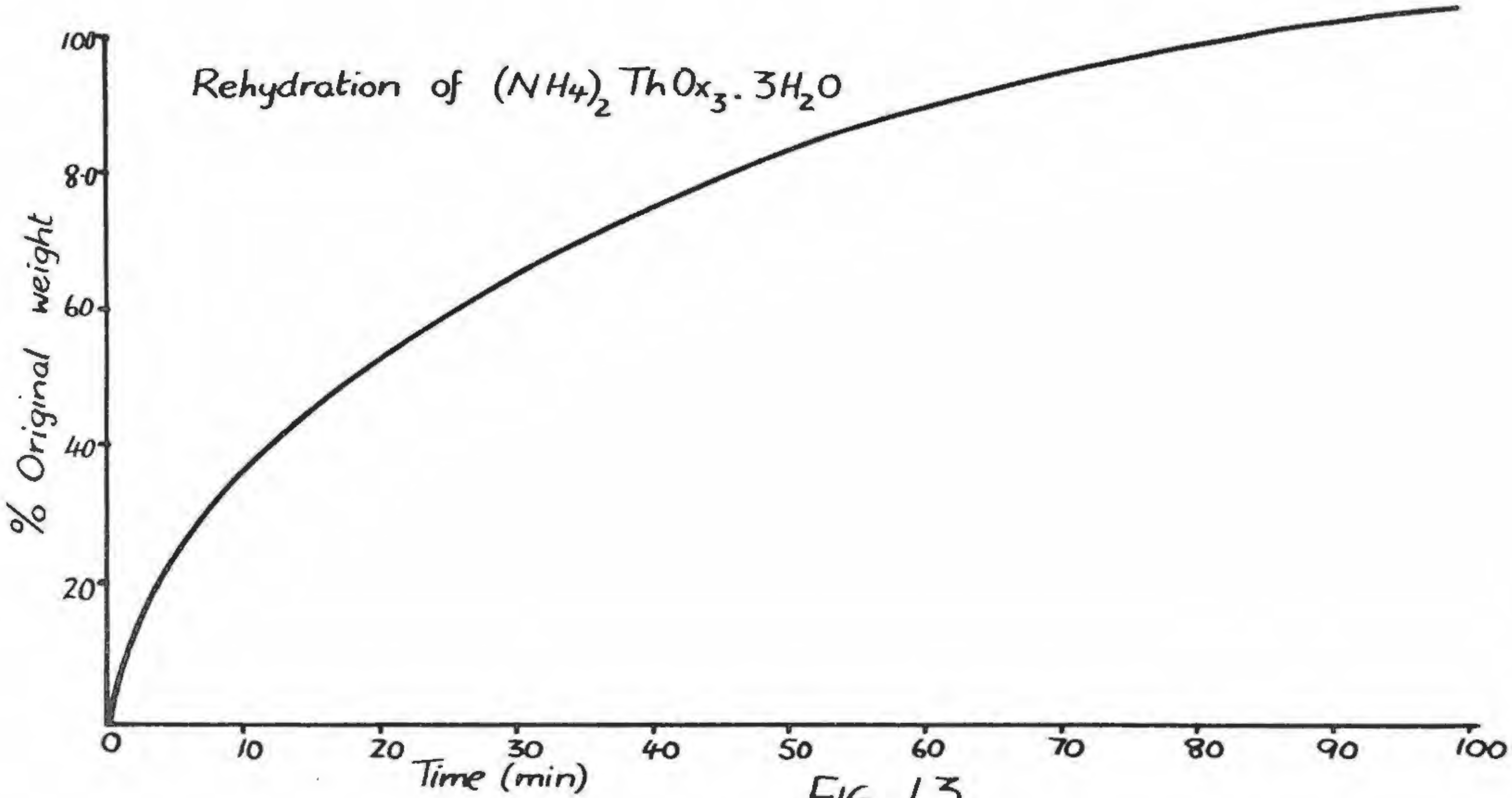

Rehydration of $(NH_4)_2ThOx_3 . 3H_2O$

FIG 1.3

The sodium and potassium precipitates showed an indefinite water content, the thorium/oxalate ratios were 1 : 3.4 and 1 : 3.5 respectively.

(b) Dehydration of $(NH_4)_2ThOx_3 3H_2O$.

When the precipitate was spread out on watch glass over P_2O_5 in desiccator and left overnight, the decrease in weight indicated the loss of 2.6 molecules of water. However the anhydrous substance was so hygroscopic that it was impossible to weight it properly.

On the thermobalance the loss of weight commenced at 30°C, 2.8 molecules being lost at 80°C, 2.84 at 100°C. Decomposition set in at 130°C, but the residue was still soluble in dilute HCl, ThO_2 did not appear below 200°C.

In view of the hygroscopic nature of the substance, the following experiment was attempted. The air drying tower of thermobalance air supply was replaced by a wash bottle contain- warm water. Air was passed at 2 litres/min with the heater off. After 90 minutes a 50 mg sample had regained 98% of its original weight, Fig. 1.3, a slackening off of hydration occurs at 25% and may indicate the existance of a monohydrate, but the dehydration curve was perfectly smooth.

- 1.23 Preparation -

1.23 Preparation of $M_2Th_2Ox_5.7H_2O$.

(a) Hydrolysis of $(NH_4)_4ThOx_4.7H_2O$.

When a solution of thorium oxalate in excess oxalate was added to a larger colume of water than previously, e.g. an unlimited amount, or if 0.1 g $(NH_4)_4ThOx_47H_2O$ was added to 750 ml water, a product of different appearance was formed. It settled out in two hours and appeared to consist of irregular fluffy particles, which when viewed under the microscope consisted of aggregates of hair shaped particles. The products formed by adding the solid M_4ThOx_4 compounds or a solution of thorium oxalate in the appropriate oxalate, to an unlimited amount of water were all very similar in appearance. All had the characteristic hair-like appearance under the microscope. The solids filtered easily and were dried on filter paper over silica gel. Composition (mean of five analyses) for the ammonium form was as follows :-

	Th	C_2O_4	NH_4	H_2O
Moles	2.00	4.90	1.91	7.12
%	43.88	40.84	3.28	12.06

The potassium and sodium forms, from solutions of thorium oxalate in potassium and sodium oxalates, gave thorium : oxalate ratios of 2 : 4.78 and 2 : 4.84 respectively.

(b) Hydrolysis of $(NH_4)_2ThOx_3$.

The same product is obtained by treating $(NH_4)_2ThOx_3$ with excess cold water. 2×10^{-4} moles of the air dried complex was treated with 500 ml cold water with mechanical stirring for four days. The suspension was then filtered and the filtrate was found to contain 0.8×10^{-4} moles oxalate and 0.85×10^{-4} moles ammonia with only 1.2×10^{-7} moles thorium.

This indicates the reaction :-

$$2ThOx_3^{2-} \longrightarrow Th_2Ox_5^{2-} + Ox^{2-}$$

If the hydrogen ion concentration of a solution containing $ThOx_4^{4-}$ or $ThOx_3^{2-}$ is lowered the forward reaction is favoured because the final end-product $ThOx_2$ is soluble in excess mineral acid.

Direct production of $M_2Th_2Ox_5.7H_2O$ from $Th(NO_3)_4$.

25 ml of thorium nitrate solution containing 100 mg Th was added to 500 ml water containing 50 ml conc. nitric acid and 4.0 g oxalic acid. The solution was slowly neutralised with 1 : 1 ammonia solution; after 30 ml had been added a fine suspension separated out. The pH at this point was 0.7. After 45 ml had been added the suspension coagulated into fluffy particles of the 2 : 5 complex. The pH of the solution was 1.0. Addition of 10% KOH or NaOH produced a similar suspension and a heavy precipitate at the same pH values.

Analysis of five samples of the dried final product gave the following composition :-

	Th	C_2O_4	NH_4	H_2O	NO_3
%	43.67	41.00	3.38	11.95	0.23
Moles	2.00	4.86	1.98	7.04	0.04

In the case of the addition of KOH and NaOH the corresponding thorium : oxalate ratios were 2 : 4.87 and 2 : 3.82 respectively. The number of water molecules was 6.8 and 5.7 respectively.

Another method of precipitation of the complex utilises the lower solubility of $M_2Th_2Ox_5.7H_2O$ as compared with the solubility of the corresponding acid.

500 ml of a solution containing 0.1 g Th as $Th(NO_3)_4$, 50 ml nitric acid, and 4 g oxalic acid, was carefully adjusted to a pH of 0.08 by the addition of 1 : 1 ammonia solution. 1 g ammonium nitrate in a concentrated solution was added in one aliquot and an immediate precipitate was formed. A similar result was obtained using 10% NaOH and $NaNO_3$, and KOH and KNO_3. The composition of the precipitate was :

	Th	C_2O_4	NH_4	H_2O	NO_3
%	43.68	42.05	3.35	11.92	0.25
Moles	2.00	4.82	1.97	7.02	0.05

The potassium and sodium compounds gave thorium : oxalate ratios of 2 : 4.81 and 2 : 4.73 respectively.

- Microscopic -

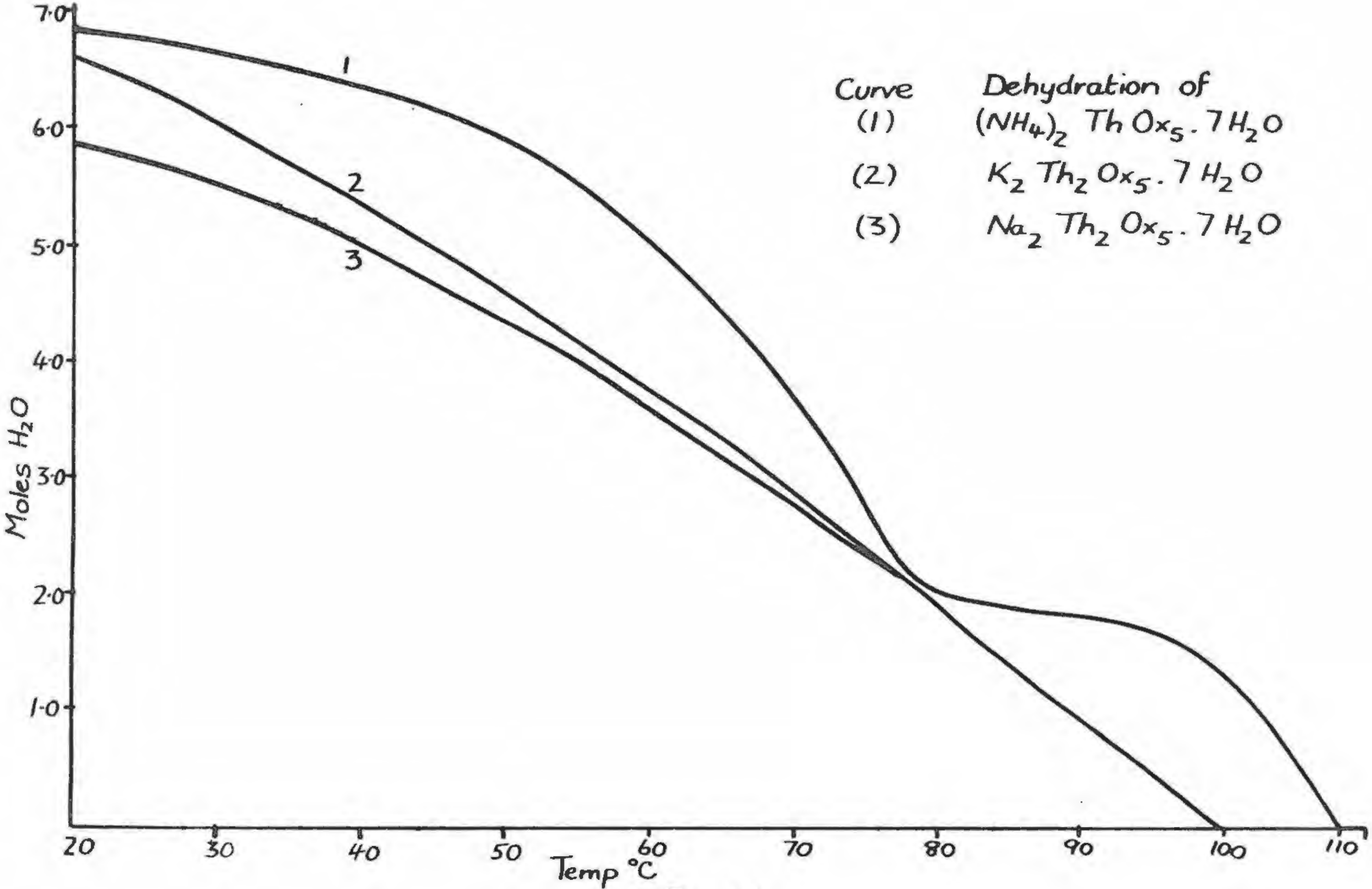

7·0
6·0
5·0
4·0
3·0
2·0
1·0
Moles H_2O
20
30
40
50
60
70
80
90
100
110
Temp °C
1
2
3
Curve
(1)
(2)
(3)
Dehydration of
$(NH_4)_2\ Th\,Ox_5 . 7H_2O$
$K_2\ Th_2\,Ox_5 . 7H_2O$
$Na_2\ Th_2\,Ox_5 . 7H_2O$

FIG 1.4

Microscopic examination.

The dry compound consisted of irregular shaped lumps of a very fine powder. The precipitate in its mother liquor consisted of hair-like crystals which disintegrated to a dust when dry. The visible fluffy particles in solution consisted of globular entanglements of the crystals which are raised by convection currents. They are destroyed by vigorous stirring or boiling. All three salts tend to do this.

Dehydration of $M_2Th_2Ox_5 7H_2O$.

The air-dried powder contained 6.9, 6.8 and 5.8 molecules water in the cases of NH_4, K and Na salts respectively. The specimans dried over silica gel contained 6.5, 6.4 and 5.8 molecules of water respectively. In the thermobalance, loss of water begins at $30^{\circ}C$, and at $75^{\circ}C$ about 4.5 molecules are lost in each case. A stable hydrate containing 2.2 molecules water appears in the case of the ammonium salt only (Fig. 1.4). Dehydration is complete at $110^{\circ}C$, but loss of weight above this is steady until $130^{\circ}C$ when decomposition is complete. The residue appears to be the carbonate. The anhydride, prepared by heating at $110^{\circ}C$, is also slightly hygroscopic.

1.24 Conversion of $(NH_4)_2ThOx_3.3H_2O$ to $(NH_4)_2Th_2Ox_5.7H_2O$.

If a solution of thorium oxalate in ammonium oxalate is added to a limited amount of hot water (in effect a solution of ammonium

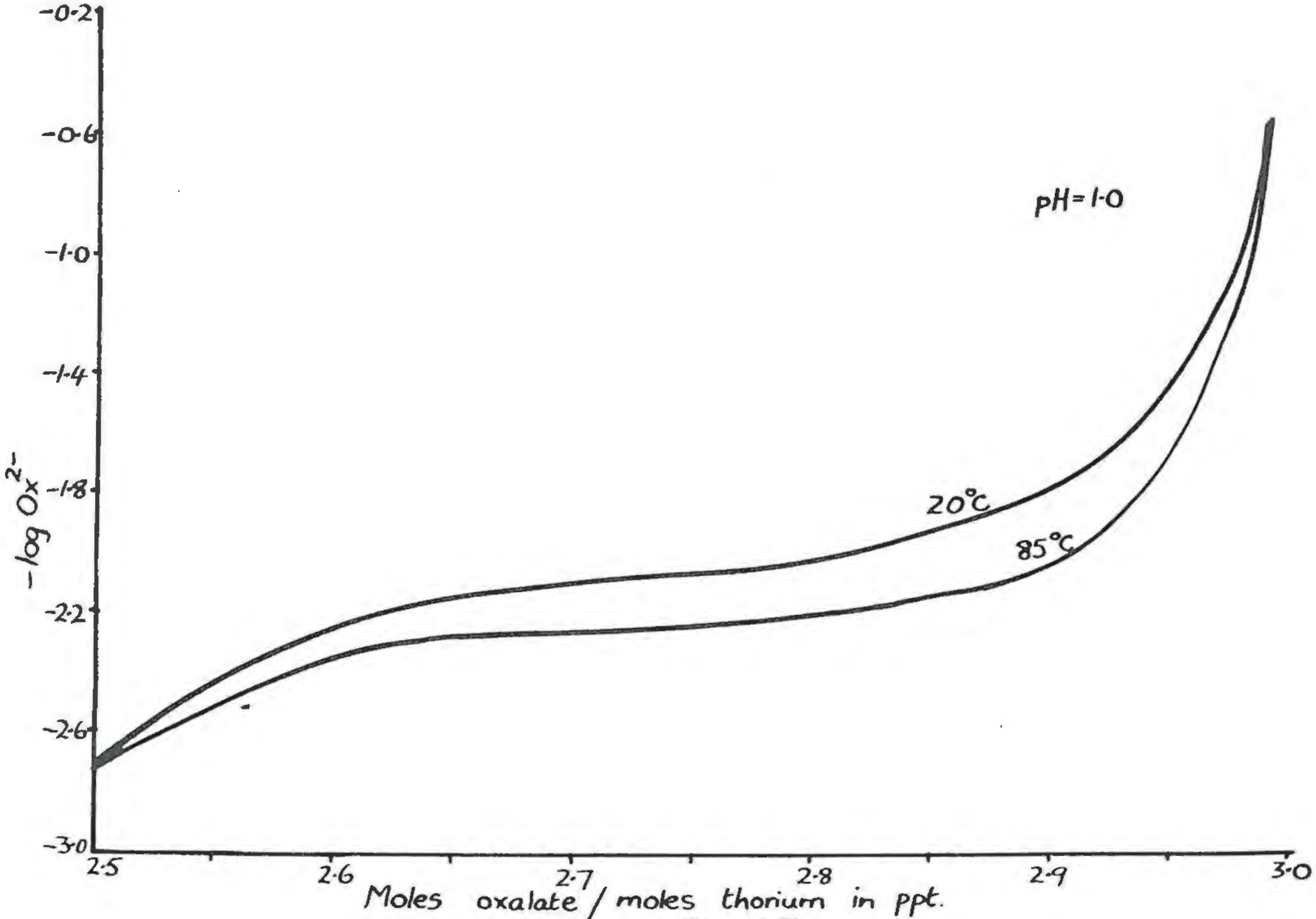

pH=1·0
20°C
85°C
-0·2
-0·6
-1·0
-1·4
-1·8
-2·2
-2·6
-3·0
$-\log Ox^{2-}$
2·5
2·6
2·7
2·8
2·9
3·0
Moles oxalate / moles thorium in ppt.

FIG 1.5

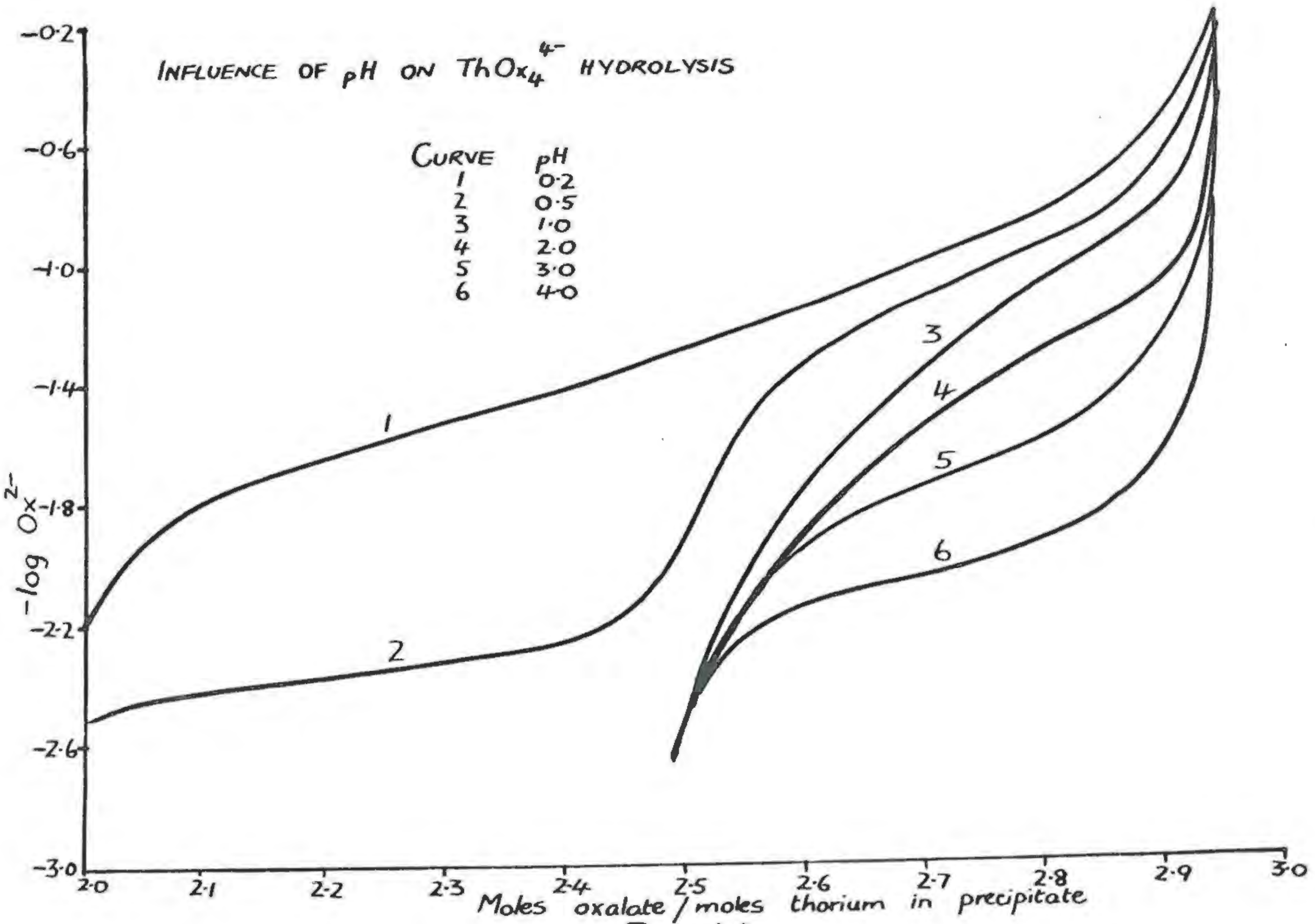

INFLUENCE OF pH ON ThOx$_4^{4-}$ HYDROLYSIS
CURVE pH
1 0·2
2 0·5
3 1·0
4 2·0
5 3·0
6 4·0
1
2
3
4
5
6
-0·2
-0·6
-1·0
-1·4
-1·8
-2·2
-2·6
-3·0
-log Ox^{2-}
2·0
2·1
2·2
2·3
2·4
2·5
2·6
2·7
2·8
2·9
3·0
Moles oxalate / moles thorium in precipitate

FIG 1.6

oxalate diluted by the addition of water), $(NH_4)_2ThOx_3.3H_2O$ forms. If the solution is added to a larger volume of hot or cold water $(NH_4)_2Th_2Ox_5.7H_2O$ forms.

Three factors affect the stability of $ThOx_3^{2-}$ solutions :-

(a) The concentration of the oxalate. See Fig. 1.5.

(b) The temperature. See Fig. 1.5 curve (2).

(c) The pH. Lowering the pH appears to favour the formation of lower oxalates, owing to the reduction in concentration of the oxalate ion due to the formation of unionised oxalic acid. See Fig. 1.6.

The curve in Fig. 1.5 was produced by measuring the oxalate concentrations of the supernatant liquids of a series of precipitations carried out by adding water to a solution of thorium oxalate in ammonium oxalate. The total oxalate content of this solution was known. Thus, from the oxalate content of the supernatant liquid and the thorium content of the precipitate (determined by titration and ignition) the thorium oxalate ratio of the precipitate could be determined. From Fig. 1.5 it is seen that at an oxalate concentration of 7×10^{-3}M $ThOx_3^{2-}$ is formed, and that at 85°C $ThOx_3^{2-}$ is more stable to hydrolysis. Also it can be seen that $ThOx_4^{4-}$ is not stable at oxalate concentrations below 0.35 M.

The curves in Fig. 1.6 were produced in the same way except that water adjusted to pH's of 0.2 to 4.0 by the addition of nitric acid, was used. From Fig. 1.6 it is seen that below pH 0.8 the precipitate consists of $ThOx_2$, or a mixture of $ThOx_2$ and $(NH_4)_2Th_2Ox$.

1.3 QUALITATIVE PRECIPITATION OF THORIUM AS $(NH_4)_2Th_2Ox_5 7H_2O$.

Because of the insolubility and ease of filtration of the above salt, it was decided to compare its precipitation with the precipitation of thorium oxalate as a means of determining thorium in the presence of rare earths. Thorium oxalate is normally precipitated in fairly strong mineral acid, pH 0.5 to 0.8, in the absence of ammonium salts.

The relative solubilities of thorium and the rare earth oxalates in saturated oxalate solutions is as follows: La 1.0, Pr 1.13, Nd 1.44, Ce 1.8, Y 10.99, Yb 104, and Th 2663(33). These differences in solubility have been made use of in the separation of thorium from the rare earths. However, the more weakly basic yttrium earths are appreciably soluble, and they are reprecipitated as the normal oxalate on addition of acid under the same conditions that thorium is precipitated. Hence a precipitation in the presence of excess ammonium oxalate, followed by a precipitation of thorium at higher acidity, will not free thorium from the yttrium earths. Furthermore the high acidity necessary to precipitate the thorium oxalate from the oxalate complex causes losses due to increased solubility. If the thorium is precipitated as a complex oxalate at a higher pH there is less possibility of co-precipitation of yttrium earths or losses due to increased solubility.

- 1.31 PREPARATION OF REAGENTS: -

1.31 PREPARATION OF REAGENTS.

Preparation of a standard thorium nitrate solution (1.0 mg ThO_2/ml).

1 g of reactor grade thoria (Thorium Ltd.) was heated to constant weight at 750°C in a platinum crucible. It was dissolved in 10 ml of concentrated nitric acid, containing 1 drop of 0.1% hydrofluoric acid, by gentle heating. The solution was made up to 1 litre by the addition of water and standardised according to the weight of thoria dissolved. The pH of the solution was 0.8.

Preparation of yttrium earth solution.

10 g of a sample of Y_2O_3 (Thorium Ltd.) heated to constant weight at 750°C was dissolved in 25 ml of concentrated nitric acid and evaporated down to near dryness and made up to a litre by the addition of water. Although the yttria contained traces of rare earths, the amount of thoria, as determined by the arsenazo - tartaric acid method(66), was only 24 p.p.m. Both solutions were stored in polythene aspirators.

1.32 PROCEDURE I.

The solution containing the thorium was acidified using 10 ml concentrated nitric acid, and then diluted to 400 ml by the addition of water; 20 ml of 8% oxalic acid solution was added and the solution heated to 90°C. The solution was adjusted to the required pH as soon as possible. The precipitate was heated on a water bath for 4 hours and filtered through a Whatman No. 40 paper, and washed

- twice with 1% -

twice with 1% ammonium nitrate solution. The following table illustrates typical results which were obtained.

Conditions: Weight ThO_2 = 50.21 mg; Volume conc. HNO_3 = 10 ml; Volume 8% oxalic acid = 20 ml.

Wt. R_2O_3	Vol. of 1:1 NH_4OH	pH	Gain or loss in wt. ThO_2 mg.	Ratio moles oxalate/thorium.
0	125 ml	2.1	-1.3	2.62
	100	1.7	-0.7	2.58
	92	1.5	-0.5	2.54
	83	1.3	-0.3	2.55
	71	1.0	-0.1	2.54
	62	0.8	-0.3	2.48
	42	0.6	-0.8	2.36
50 mg	125	2.0	+0.5	
	100	1.7	+0.4	
	90	1.4	+0.3	
	80	1.2	+0.3	
	70	1.0	+0.3	
	60	0.8	+0.6	
	40	0.4	+1.1	
100 mg	125	2.1	+1.2	
	100	1.7	+0.8	
	90	1.4	+0.6	
	80	1.2	+0.6	
	70	1.0	+0.5	
	60	0.8	+0.9	

Addition of 4 g solid oxalic acid to 400 ml boiling solution containing thorium and 4 ml concentrated HCl gave the following results :-

R_2O_3	pH	Gain or loss ThO_2	Ratio oxalate/thorium.
100 mg	0.5	+1.9	2.22
50	0.5	+0.8	2.30
10	0.5	+0.3	2.21
0	0.5	-0.2	2.12

The final procedure was as follows :-

10 ml concentrated HNO_3 was added to the thorium solution contained in 100 ml water at 90°C. To this was added 20 ml of 8% oxalic acid. Immediately thereafter 85 ml of 1 : 1 ammonia was added (otherwise a suspension of thorium oxalate appears after 2 mins.). The solution was diluted to 400 ml with boiling water (if the amount of rare earths is less than that of thorium the volume may be reduced to 200 ml). The precipitate was placed on a water bath for 4 hours, and filtered through a Whatman No. 40 paper. The beaker was swabbed out with half another paper since the precipitate tended to adhere to the beaker. The precipitate was washed three times with 1% ammonium nitrate containing 1% nitric acid, (tests with oxalate wash liquors produced losses). Both papers were ignited at 750°C for 30 mins in a closed platinum crucible.

1.33 PROCEDURE II.

The sample was treated with ammonium nitrate and nitric acid, then

- ammonium oxalate -

ammonium oxalate solution was added to the heated solution. 50.21 mg ThO_2 dissolved in 100 ml of water containing 10 ml of 50% ammonium nitrate and 10 ml nitric acid. 20 ml 5% ammonium oxalate was then added. The following results were obtained :-

Wt.R_2O_3	Vol. conc. HNO_3 added.	pH.	Loss or gain of ThO_2.	Ratio moles oxalate/thorium.
0	0.5 ml	2.2	-0.9 mg	2.67
	1.5	1.8	-0.5	2.62
	2.0	1.6	-0.4	2.60
	3.0	1.3	-0.4	2.52
	4.0	1.1	-0.4	2.48
	4.5	0.9	+ 0.7	2.45
	6.0	0.5	-1.2	2.32
50 mg	0.5	2.1	+0.8	
	1.5	1.8	+0.6	
	2.0	1.5	+0.5	
	3.0	1.3	+0.4	
	4.0	1.1	+0.3	
	4.5	0.8	+0.5	
	6.0	0.5	+1.9	
100 mg	0.5	2.1	+1.4	
	1.5	1.8	+1.1	
	2.0	1.6	+0.4	
	3.0	1.2	+0.4	
	4.0	1.0	+0.4	
	4.5	0.8	+0.9	
	6.0	0.5	+1.7	

To detect the effect of changing the oxalate concentration a second series of precipitations was carried out. The following results were obtained under the conditions of 50.21 mg ThO_2, 10 ml 50% NH_4NO_3 and 4 ml concentrated HNO_3 being present in 100 ml.

Wt.R_2O_3.	Vol. 5% $(NH_4)_2Ox$.	pH.	Loss or gain in weight ThO_2.	Ratio moles oxalate/thorium.
0	10 ml	1.0	-0.2 mg	2.40
	15	1.1	-0.3	2.36
	20	1.1	-0.1	2.45
	25	1.1	-0.4	2.52
	30	1.3	-1.2	2.58
50 mg	10	1.0	+0.8	
	15	1.1	+0.6	
	20	1.1	+0.4	
	25	1.1	+0.6	
	30	1.2	+1.5	
100 mg	10	1.1	+0.9	
	15	1.1	+0.6	
	20	1.2	+0.4	
	25	1.2	+0.8	
	30	1.3	+1.9	
	4 g solid oxalic acid.	1.0	+0.6	

The final procedure was as follows :-

10 ml of 50% ammonium nitrate solution was added to the thorium

solution contained in 100 ml, followed by the dropwise addition of concentrated nitric acid until the pH dropped to 1.0 to 1.2 (as estimated using a pH meter). The solution was warmed to near boiling, and 20 ml of 5% ammonium oxalate solution added all at once. The precipitate was kept on a water bath for 4 hours and filtered through a Whatman No. 40 paper. The precipitate was washed three times with boiling 1% ammonium nitrate and 1% nitric acid solution. The beaker was swabbed out with half a filter paper. Both were ignited at 750°C in closed platinum crucible for 30 minutes.

1.34 COMPARISON OF METHODS I AND II.

Of the two, II gave more easily filterable precipitates which showed less tendency to adhere to the sides of the beaker. In the presence of 100 mg ZrO_2 (as $ZrO(NO_3)_2$), procedures I and II gave gains of +0.9 mg and +0.6 mg respectively.

The accuracy of the methods appears to involve the compensation of errors due to solubility and co-precipitation. Owing to solubility losses the lower limit is 50 mg ThO_2 and the maximum amount of rare earths about half that of the thorium.

2. pH TITRATIONS OF THORIUM OXALATE SOLUTIONS.

Attempts to investigate the equilibria :

$$Th^{4+} + 3H_2Ox \rightleftharpoons ThOx_3^{2-} + 6H^+,$$

$$Th^{4+} + 2\tfrac{1}{2}H_2Ox \rightleftharpoons \tfrac{1}{2}Th_2Ox_5^{2-} + 5H^+,$$

and $$Th^{4+} + 2H_2Ox \rightleftharpoons ThOx_2 + 4H^+.$$

by pH measurements were not successful owing to the strong hydrolysis of the Th^{4+} ion in dilute solution to form polymeric hydroxy complexes of the type $Th(O.OH.Th)_n^{4+n}$ (48) in equilibrium with hydrogen ions.

$$(n+1)Th^{4+} + 3nH_2O \longrightarrow Th((OH)_3Th)_n^{4+n} + 3nH^+$$

$$\longrightarrow Th(O.OH.Th)_n^{4+n} + nH_2O .$$

This accounts for the low pH of thorium nitrate solutions, i.e. 2.8. Upsetting this equilibrium by adding OH^- causes the precipitation of hydrous thorium oxide.

On titrating 0.01 M $Th(NO_3)_4$ with 0.01 M NaOH, using a Beckman model H mains titrimeter, 6 moles of hydrogen ion were indicated. This shows that at this concentration the predominate ionic species is n = 2. The extended flat portion of this curve, Fig. 2.1, and the sharpness of the end-point rule out the possibility of the formation of ions of other values of n at this concentration.

Fig. 2.2 shows the pH at which precipitation of the hydrous oxide

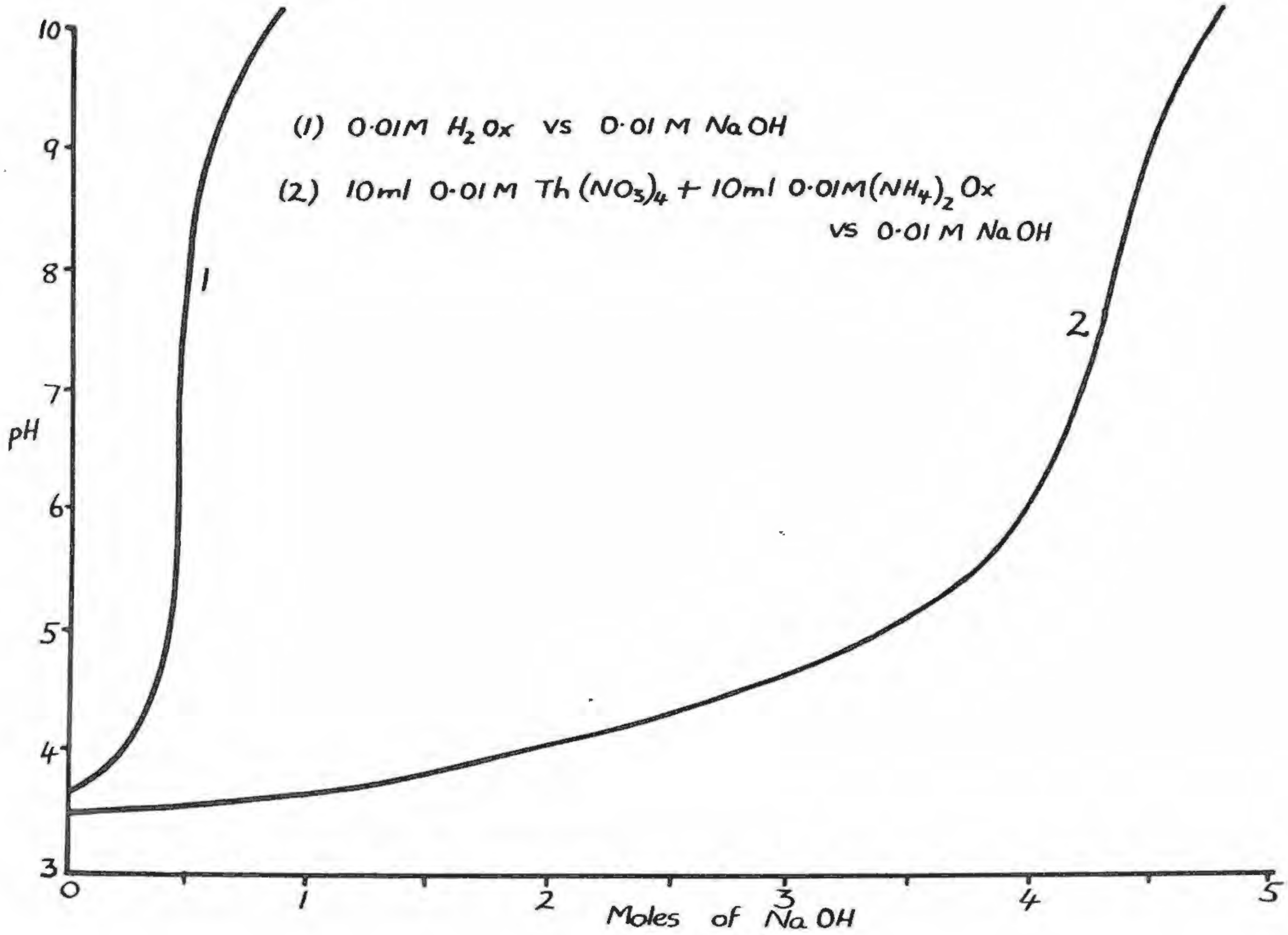

(1) 0·01M H_2Ox vs 0·01 M NaOH
(2) 10ml 0·01M $Th(NO_3)_4$ + 10ml 0·01M$(NH_4)_2Ox$ vs 0·01 M NaOH
1
2
pH
10
9
8
7
6
5
4
3
0
1
2
3
4
5
Moles of NaOH

FIG 2.1

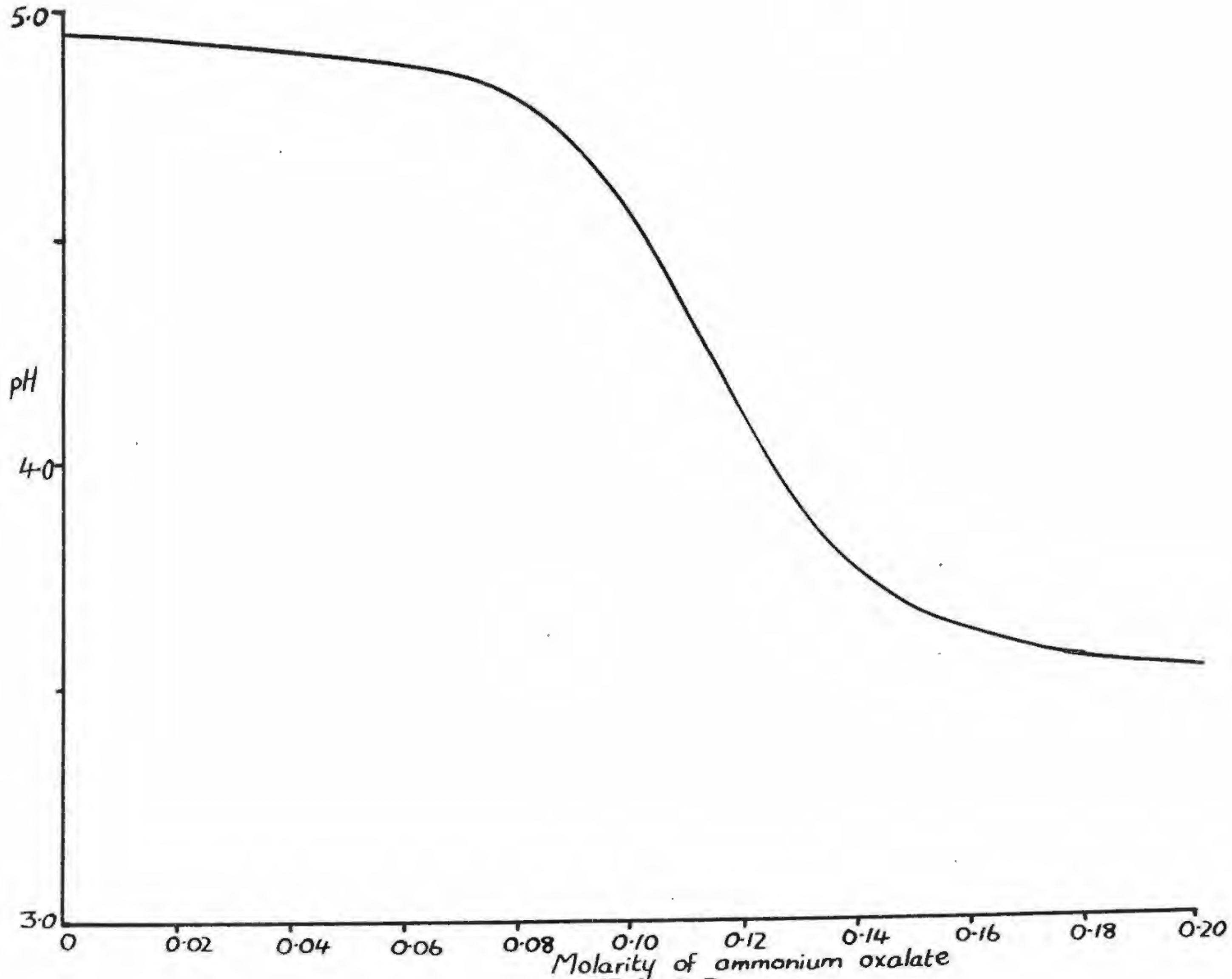

5·0
4·0
3·0
pH
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
0·18
0·20
Molarity of ammonium oxalate

FIG 2.2

begins, plotted against excess oxalate concentration, the thorium concentration being 0.01 M. The pH at the point when turbidity first appears on the addition of 0.01 M NaOH is lowered from 4.5 to 3.8 by the addition of from 0.08 to 0.1 M ammonium oxalate solution (i.e. 8 to 10 molecules oxalate per molecule thorium), this indicates that a change in ionic species occurs here, to one which is less stable with respect to the hydroxy thorium ion.

3. CONDUCTIVITY MEASUREMENTS.

3.1 APPARATUS.

Conductiometric titrations were carried out using a Doran transistorised conductance bridge. The cell used was of the dipping type designed for small volumes. The resistances measured were of the order of one ohm. The measurements were carried out in a thermostat at 20 ± 0.2°C or in a boiling water bath. The leads were totally enclosed. The solutions were shaken well before each reading.

3.2 REAGENTS USED.

(a) 2 M $Th(NO_3)_4$ solution.

96 g reactor grade $Th(NO_3)_4$ (Thorium Ltd.) were dissolved in 100 ml of water. The concentration of $Th(NO_3)_4$ was determined by evaporation of a 1 ml sample on a Whatman ashless tablet followed by ignition for 30 mins at 850°C. Owing to the viscous nature of the prepared solution the same burette was used for the standardisation as was used for the subsequent titrations.

(b) 0.1 M oxalate solutions.

These were prepared from their respective salts and standardised against 0.05 N ceric sulphate solution.

(c) Water.

Owing to the high conductivities consequent on the low pH's used, doubly distilled water condensed in tin and in equilibrium

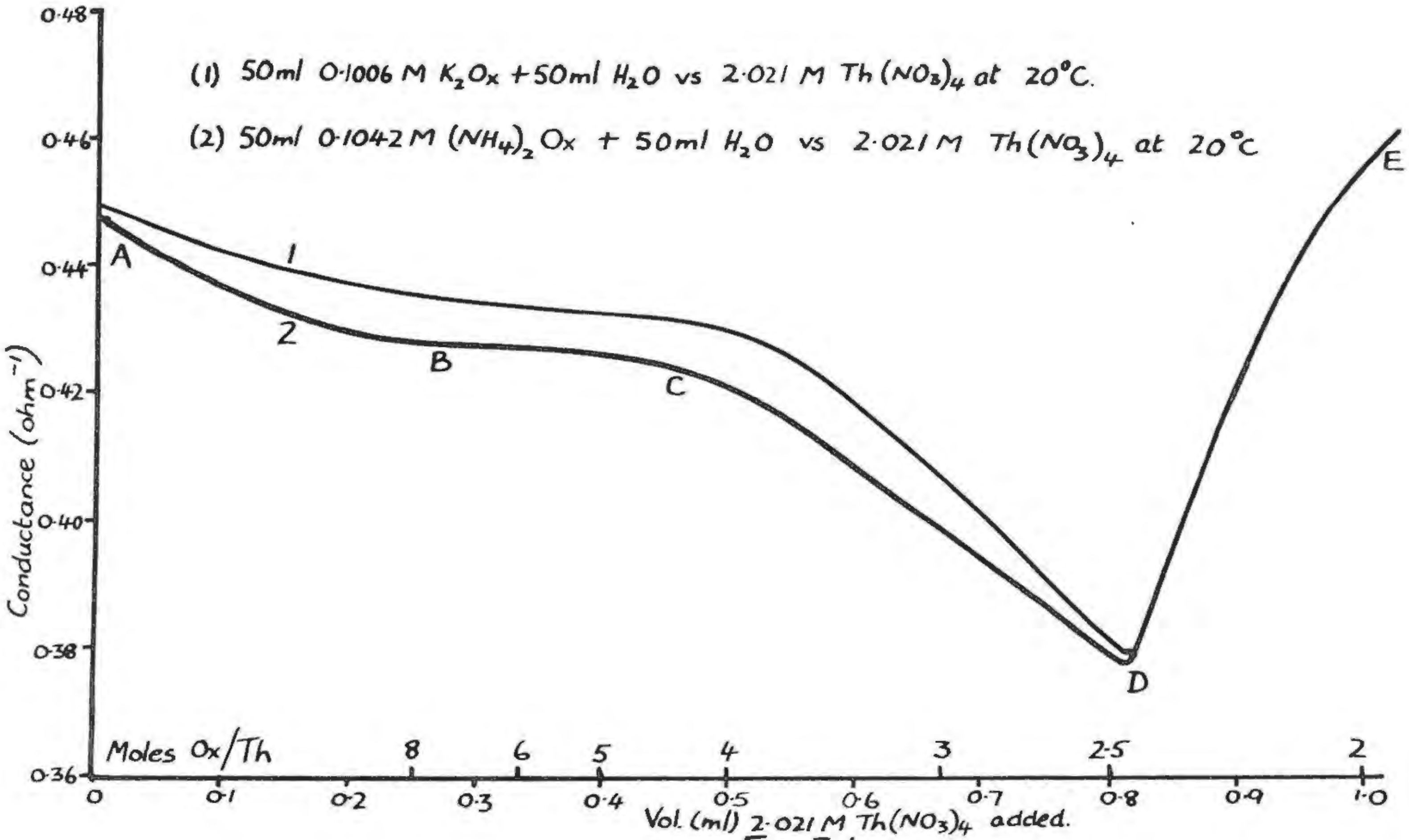

(1) 50ml 0·1006 M K_2Ox + 50ml H_2O vs 2·021 M $Th(NO_3)_4$ at 20°C.
(2) 50ml 0·1042 M $(NH_4)_2Ox$ + 50ml H_2O vs 2·021 M $Th(NO_3)_4$ at 20°C
Conductance (ohm⁻¹)
0·48
0·46
0·44
0·42
0·40
0·38
0·36
1
2
A
B
C
D
E
Moles Ox/Th
8
6
5
4
3
2·5
2
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
Vol. (ml) 2·021 M $Th(NO_3)_4$ added.

FIG 3.1

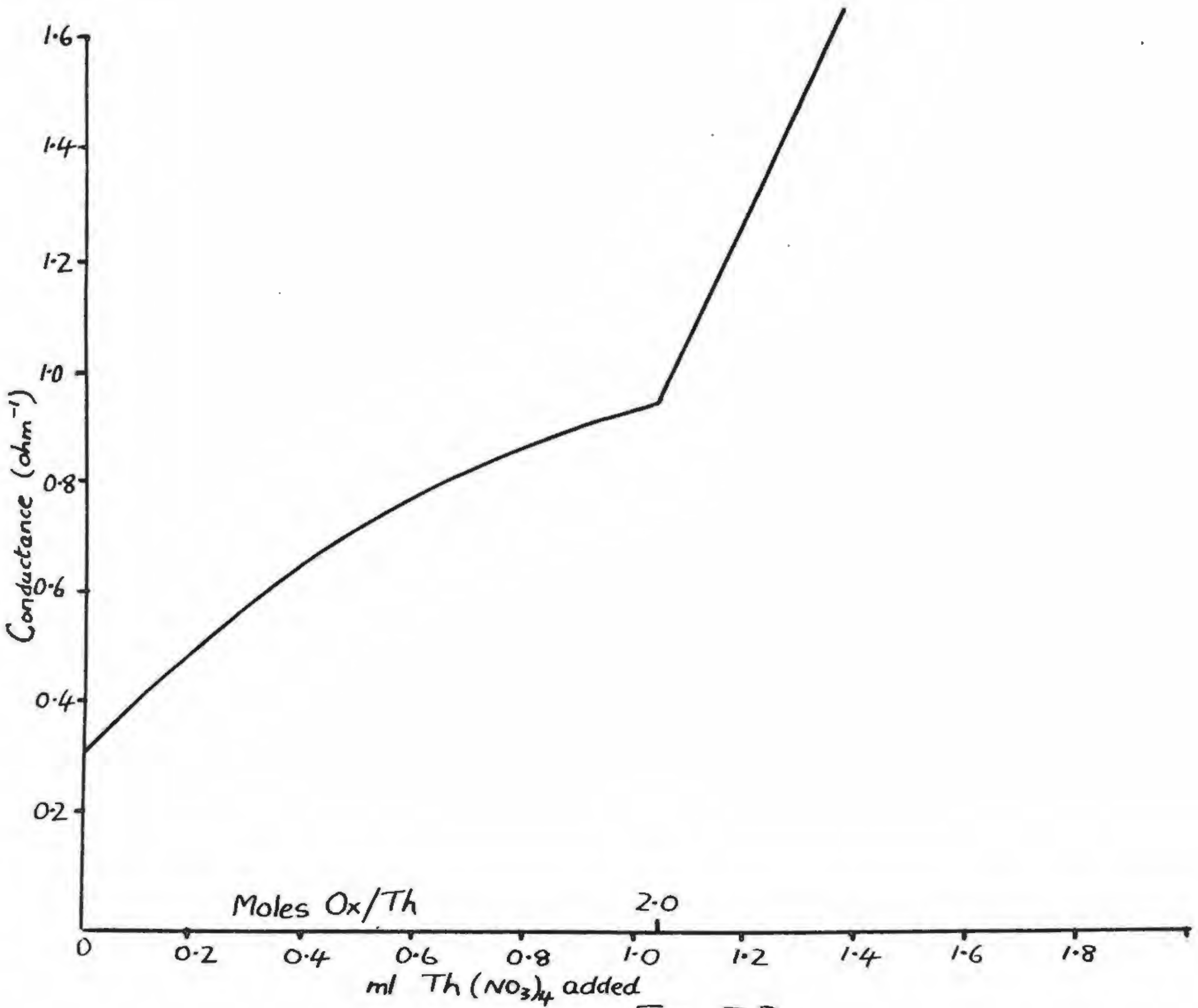

1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
Conductance (ohm^{-1})
Moles Ox/Th
2·0
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
ml Th$(NO_3)_4$ added

FIG 3.2

with air was used.

3.3 RESULTS.

3.31 Thorium added to oxalate.

Fig. 3.1, Curve (1): 50 ml of 0.1006 M K_2Ox plus 50 ml of water were titrated against 2.021 M $Th(NO_3)_4$. The pH at the beginning was 2.8 and at the end was 1.6. The temperature was 20^oC. Referring to the Fig., from A to B (10 drops) the conductivity drops gradually, levelling off at B (6.5 moles). No definite break can be detected. At C (3.8 moles) a definite change occurs, coinciding with the first appearance of turbidity. The conductivity drops more sharply to D (2.48 moles), where precipitation first occurs. It then rises steeply to E.

Fig. 3.1, Curve (2): As for Curve (1) but with 50 ml 0.1042 M $(NH_4)_2Ox$ in place of the K_2Ox solution. The curve is similar to (1) except that the break at B is a little more sharply defined, and occurs at 7.3 moles

Fig. 3.2: As for Curve (1) but with 50 ml 0.1010 M oxalic acid in place of the K_2Ox solution. Here the conductivity rises smoothly with no breaks until 2.03 moles, when the curve rises very steeply.

The hydrogen ions which are introduced with the thorium nitrate solution in equilibrium with hydrous thorium oxide must exert

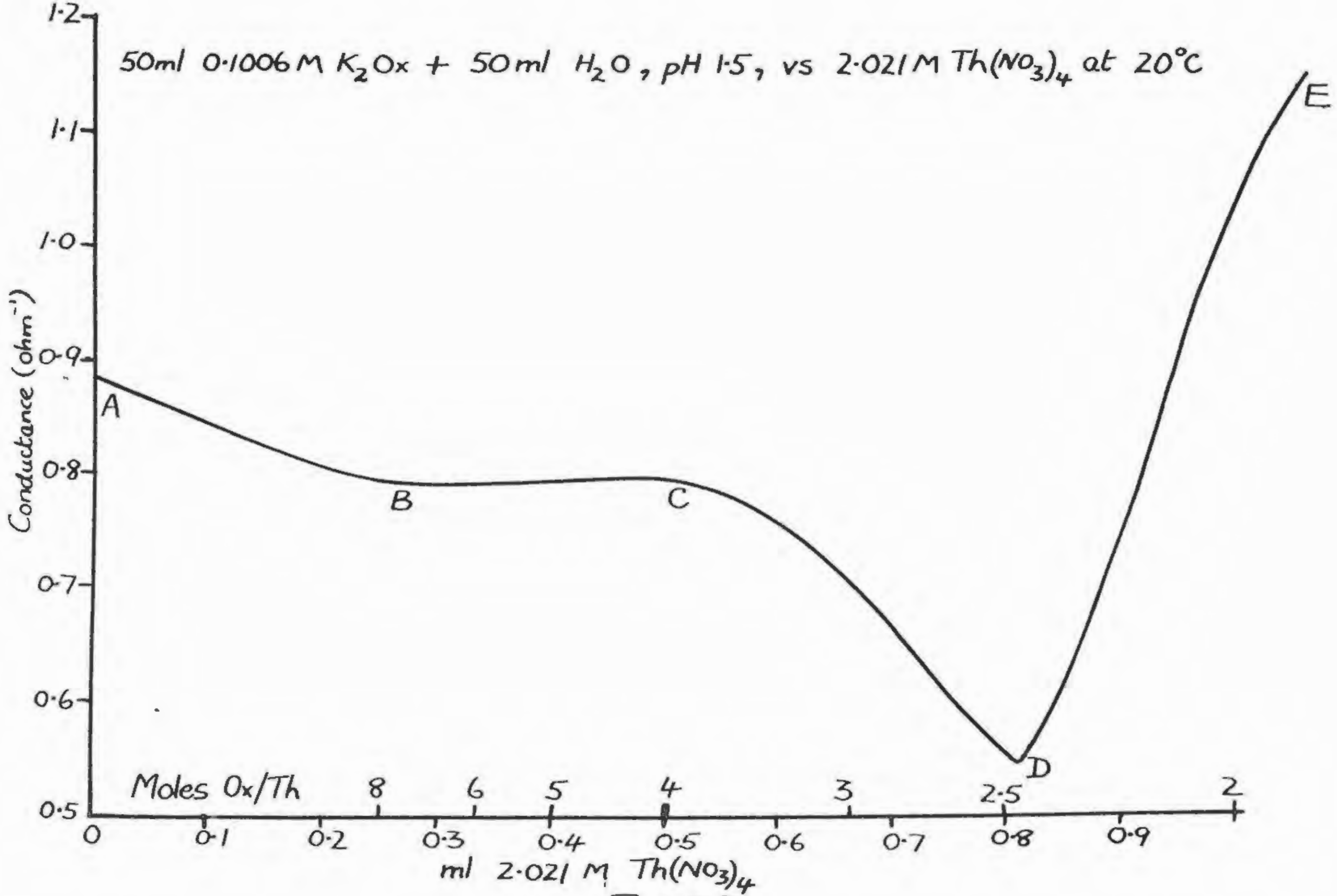

50ml 0·1006 M K_2Ox + 50ml H_2O, pH 1·5, vs 2·021 M $Th(NO_3)_4$ at 20°C
Conductance (ohm⁻¹)
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
A
B
C
D
E
Moles Ox/Th
8
6
5
4
3
2·5
2
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
ml 2·021 M $Th(NO_3)_4$

FIG 3.3

a disturbing influence causing the pH to drop to 1.6. Consequently nitric acid was added to the oxalate solution until the pH had dropped to 1.5, so that the added hydrogen ions would exert a comparatively smaller effect. The effect of this is shown in Fig. 3.3

Fig. 3.3: To obtain this plot 50 ml of 0.1006 M K_2Ox and 50 ml water were taken, and HNO_3 was added until the pH reached 1.5. The solution was titrated against 2.021 M $Th(NO_3)_4$ at 20°C. The pH at the end was 1.2. In this case the initially descending portion AB is steeper, a definite break occurs at B (7.5 moles), the portion BC descends somewhat to C (3.8 moles), and CD descends less steeply to D (2.42 moles). The curve is similar to curve (1) of Fig. 3.1 but the break at B is more clearly indicated.

3.23 Oxalate added to thorium.

Fig. 3.4: In this case 1.00 ml of 2.021 M $Th(NO_3)_4$ in 100 ml water and at a pH of 2.7 were titrated against 0.4140 M $(NH_4)_2Ox$. The curve ascends with increasing gradient with breaks at 0.4 and 1.9 moles oxalate per thorium. Turbidity appeared at 0.5 moles. At 95°C the conductivity ascended in a smooth curve, no breaks occurring and turbidity appearing at 1.22 moles.

- 3.3 CONCLUSION. -

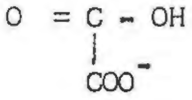
3.3 CONCLUSION.

3.31 Thorium added to oxalate.

In order to account for the above the following mechanism is proposed.

Portion AB.

Oxalic acid acts as an α-hydroxy anion,



$$O = \underset{\displaystyle COO^-}{\underset{|}{C}} - OH$$

and as soon as the thorium is added this reacts with it to give a monodentate complex, $Th(OCOCOO^-)_8{}^{4-}$. This reaction continues until B is reached at 7 to 8 moles of oxalate, i.e. when all the oxalate has been used up.

Portion BC.

At B all the oxalate has been complexed, and this portion represents the reaction between the above soluble complex and Th^{4+} as follows :

$$Th(OCOCOO^-)_8{}^{4-} + Th^{4+} \longrightarrow Th_2Ox_8{}^{8-}.$$

This corresponds to the solid compound $K_4ThOx_4.7H_2O$. The dimeric formular agrees with the findings of Brintzinger and Eckardt(24) and B. Frank(24a) from dialysis coefficient measurements.

Portion CD.

At C the thorium is all in the $Th_2Ox_8{}^{8-}$ form, this reacts further with Th^{4+} as follows :-

$$Th_2Ox_8{}^{8-} + Th^{4+} \longrightarrow Th_2Ox_6{}^{4-} + ThOx_2.$$

- At C, -

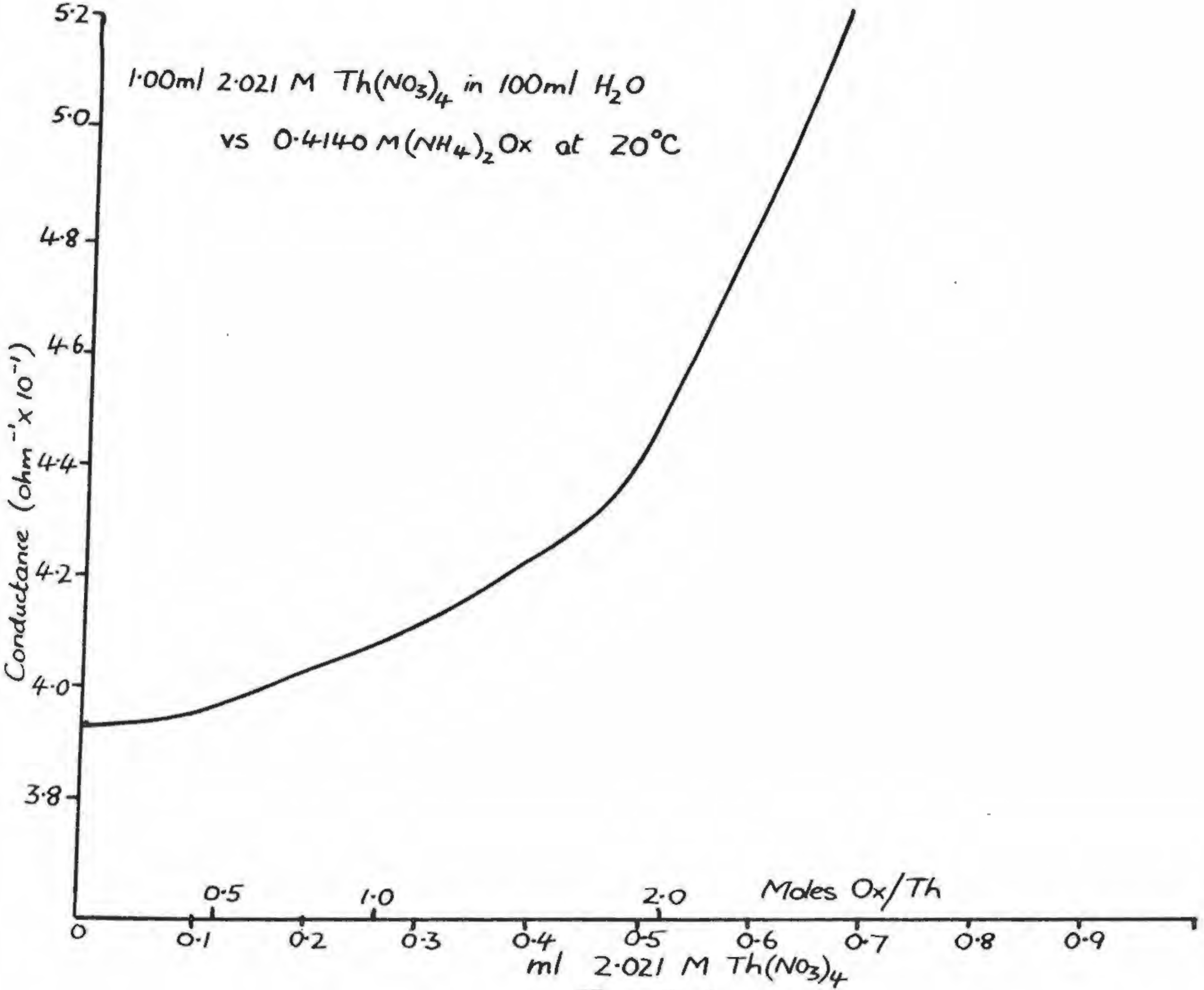

1·00ml 2·021 M Th(NO$_3$)$_4$ in 100ml H$_2$O
vs 0·4140 M(NH$_4$)$_2$Ox at 20°C
Conductance (ohm^{-1} x 10^{-1})
5·2
5·0
4·8
4·6
4·4
4·2
4·0
3·8
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
ml 2·021 M Th(NO$_3$)$_4$
0·5
1·0
2·0
Moles Ox/Th

FIG 3.4

At C, also, turbidity first appears. The conductivity would drop sharply, for the nett ionic charge is lowered by the precipitation of $ThOx_2$.

Another possibility is :

$$Th_2Ox_8^{8-} + 2Th^{4+} \longrightarrow 2Th_2Ox_5^{2-} + 2ThOx_2.$$

Since both $K_2Th_2Ox_5 7H_2O$ and $(NH_4)_2Th_2Ox_5 7H_2O$ are sparingly soluble, l of these substances and $ThOx_2$ may be precipitated together.

It is noted that the point D corresponds more closely to 2.5 than 2.0 moles oxalate and that the conductivity rises thereafter. Hence D represents the point at which all the oxalate is precipitated. It is possible that $Th_2Ox_6^{4-}$ may react with the $ThOx_2$ formed at the same time according to the equation,

$$Th_2Ox_6^{4-} + 2ThOx_2 \longrightarrow Th_4Ox_{10}^{4-}.$$

This agrees with the thermometric studies of Bose and Chowdhury(34), of the reaction between 0.1 M K_2Ox and 0.3 M $Th(NO_3)_4$. They postulated an ion $Th_2Ox_5^{2-}$ as a double compound $ThOx_2.ThOx_3^{2-}$.

Portion DE.

Here the conductivity rises sharply due to an excess of Th^{4+}.

3.24 Oxalate added to thorium.

Fig. 3.4.

The first break occurs at 0.5 moles oxalate, i.e. Th_2Ox^{6+}, and coinsides with the appearance of turbidity at 20°C. Since turbidity occurs at much higher ratios at higher temperatures, e.g. 90°C, and no break occurs at 0.5 moles at this temperature, it seems more likely that this point corresponds to the point at which $ThOx_2$ first begins to form. The curve rises until all the thorium is precipitated at 1.2 moles. At 5.2 molecules the precipitate redissolves but no breaks are shown.

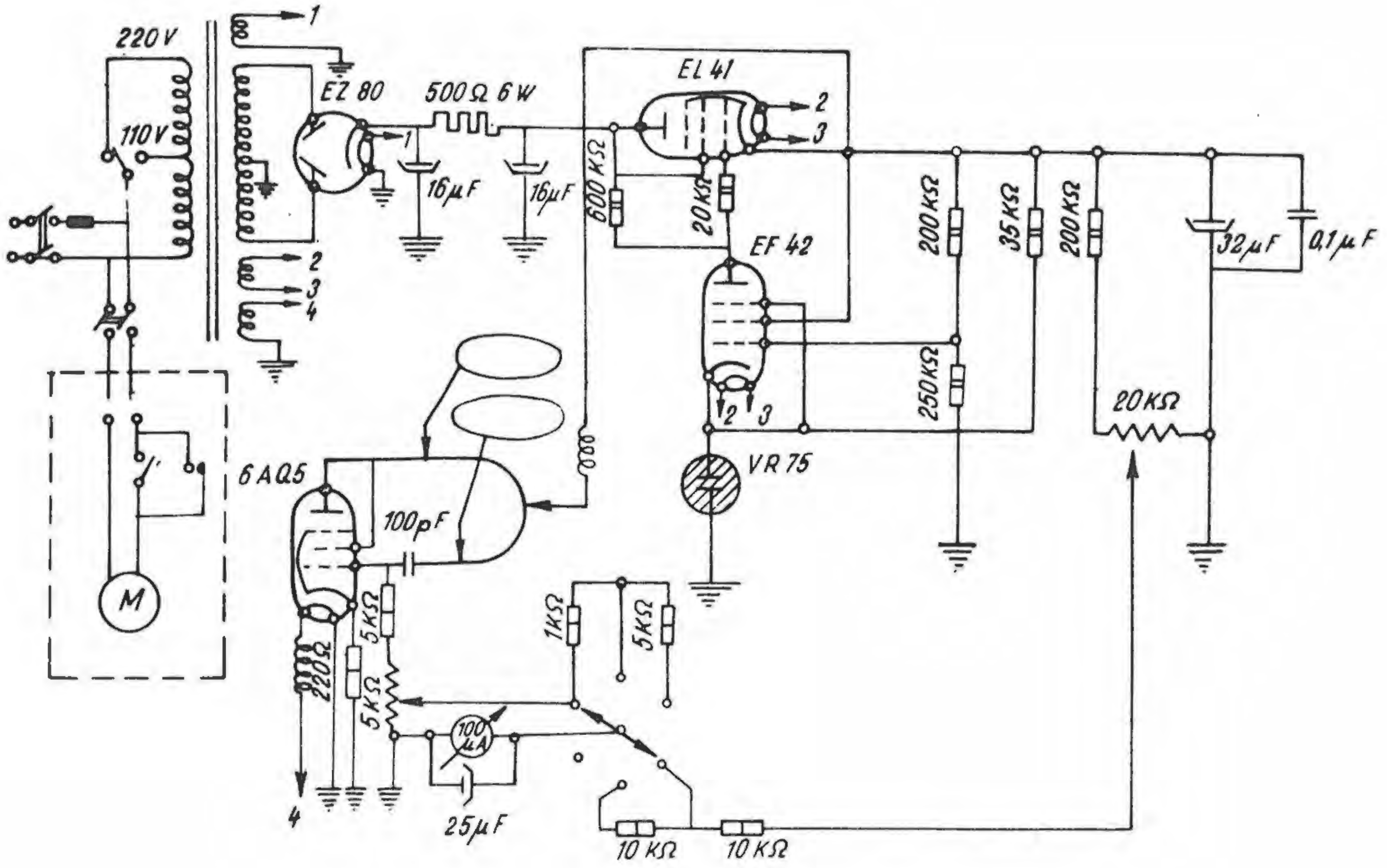

220V
110V
1
EZ 80
500Ω 6W
1
16μF
16μF
2
3
4
EL 41
2
3
600 KΩ
20 KΩ
EF 42
200 KΩ
35 KΩ
200 KΩ
32μF
0,1μF
250 KΩ
20 KΩ
2
3
VR 75
6 AQ5
100pF
M
220Ω
5 KΩ
5 KΩ
1KΩ
5 KΩ
100 μA
25μF
4
10 KΩ
10 KΩ

FIG 4.1

4. HIGH FREQUENCY CONDUCTIVITY.

The principle of this method lies in the change in dielectric constant and conductivity associated with a change in ionic species in a solution.

In the frequency range 10-100 Mc/s, there is no absorption of energy by the functional groups of the molecule. Thus the measurement of the dielectric constant is sensitive only to molecular polarity, and the measurement of conductivity sensitive only to ionic mobility.

4.1 APPARATUS USED.

A high frequency titrimeter after the design of Pungor, made by Meovill Budapest was used. The instrument circuit consists of a 100 Mc/s oscillator, valve 6AQ5 (Fig. 4.1), supplied by a voltage stabilising circuit. The oscillator coil consists of 2 loops of metal imbedded in a polystrene former. Inside this is a cylindrical hole in which a 50 ml beaker can be placed.

The grid current of the oscillator depends on the mutual inductance of the coil, which in turn depends on the resistance and dielectric constant of the core, the sample holder. The grid current is measured by a 100μA meter, with its sensitivity adjusted by the 5 kilohm potentiometer. Zero adjustment is supplied by passing a small current, from the high tension through the meter in the reverse direction. A small integral magnetic stirrer and a circular metal shield for the top of sample beaker are provided.

4.11 Performance.

Stability.

No variation of meter reading was obtained by varying the mains voltage ± 10% by means of a Variac. Zero drift over only one division was noted after 4 hours running. It was essential to properly earth the instrument. When the sample vessel was filled to over 5 mm above the upper electrode ring no change in reading was produced on adding water. The motor of the magnetic stirrer produced no change of reading on switching it on or off.

Small metal objects, e.g. a watch, produced large increases in the reading if placed near the oscillator coils even with the top shield ring in place. Hence all conducting objects were kept well away from the titrimeter.

Sensitivity.

The meter is graduated from 0 to 100μ A in unit divisions. These units are purely arbitrary, since in operation the sensitivity is adjusted to a maximum, and the zero to a convenient level. However they correspond to conductivity. In the smallest volume available, 40 ml, 0.05 mg Th as $Th(NO_3)_4$ was detectable. The sensitivity is greater with highly conducting ions such as H^+, OH^- and Th^{4+}.

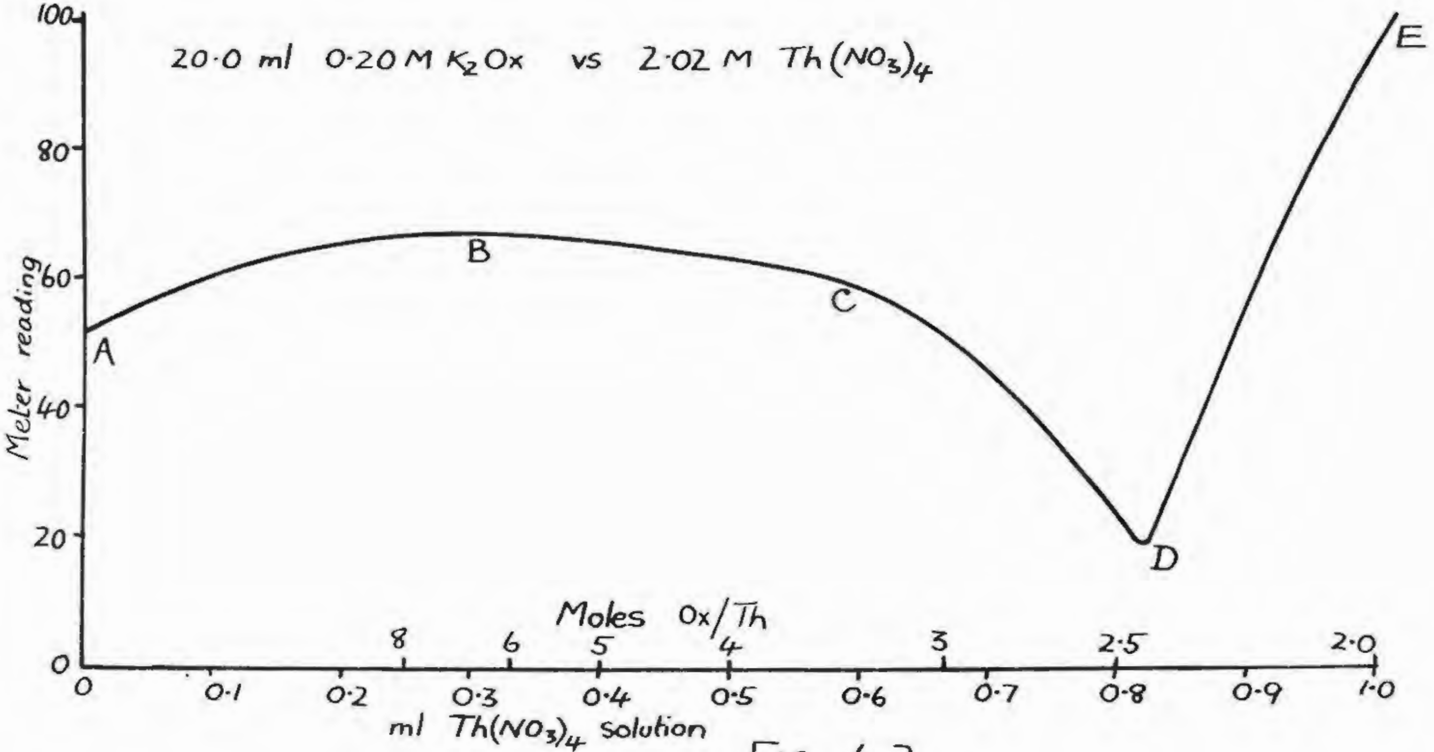
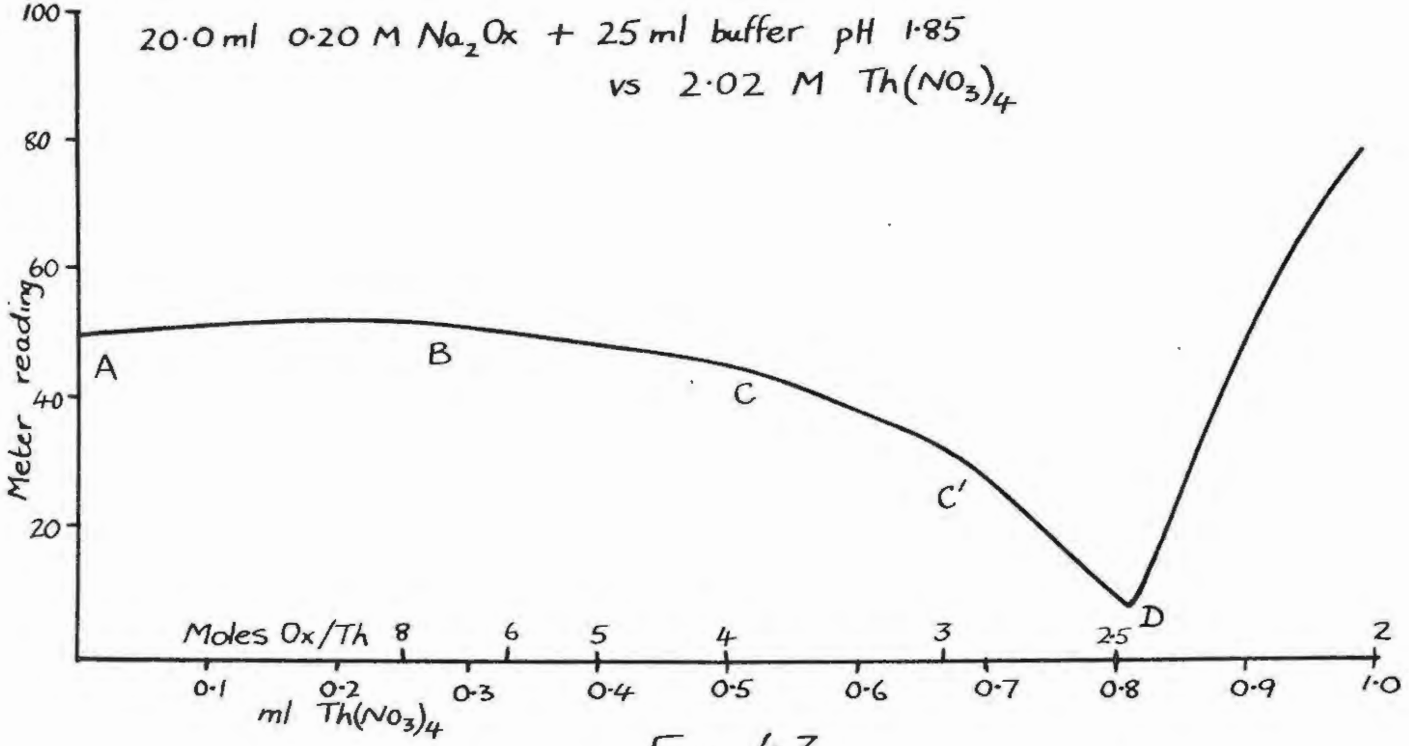

20·0 ml 0·20 M K_2Ox vs 2·02 M $Th(NO_3)_4$
Meter reading
100
80
60
40
20
0
A
B
C
D
E
Moles Ox/Th
8
6
5
4
3
2·5
2·0
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
ml $Th(NO_3)_4$ solution

FIG 4.2



20·0 ml 0·20 M Na_2Ox + 25 ml buffer pH 1·85
vs 2·02 M $Th(NO_3)_4$

FIG 4.3

4.12 Operation.

The instrument was allowed to warm up for at least 5 mins. The solution was placed in a 50 ml beaker and placed in the coil holder and the metal shield put in place. The zero was adjusted to a convenient figure, usually 50, and the sensitivity adjusted to a maximum as tested by placing a thin piece of wire near the coils.

4.2 RESULTS.

Fig. 4.2: This shows the results obtained on titrating 50 ml of 0.1 M K_2Ox with 2 M $Th(NO_3)_4$ solution. The curve rises from A to B, continues horizontally to C, and dips to a minimum at D (2.4 moles). The curve is smooth with no breaks.

Owing to the strong effect exerted by the presence of hydrogen ions both on conductivity and dielectric, interference caused by varying pH is even more serious than in low frequency measurements. The titration was therefore repeated in the presence of a sodium acetate - hydrochloric acid buffer at pH 1.8.

Buffer solution: This was made up of 50 ml N sodium acetate solution plus 53.0 ml of N HCl, diluted to 250 ml. The pH could be adjusted between pH 0.7 and 3.5 by varying the volume of N HCl solution.

Fig. 4.3: The plot was obtained by titrating 20 ml of 0.2 M K_2Ox plus 25 ml pH 1.8 buffer solution against a 2.02 M $Th(NO_3)_4$ solution. This curve resembles the low frequency curves. From A to B the

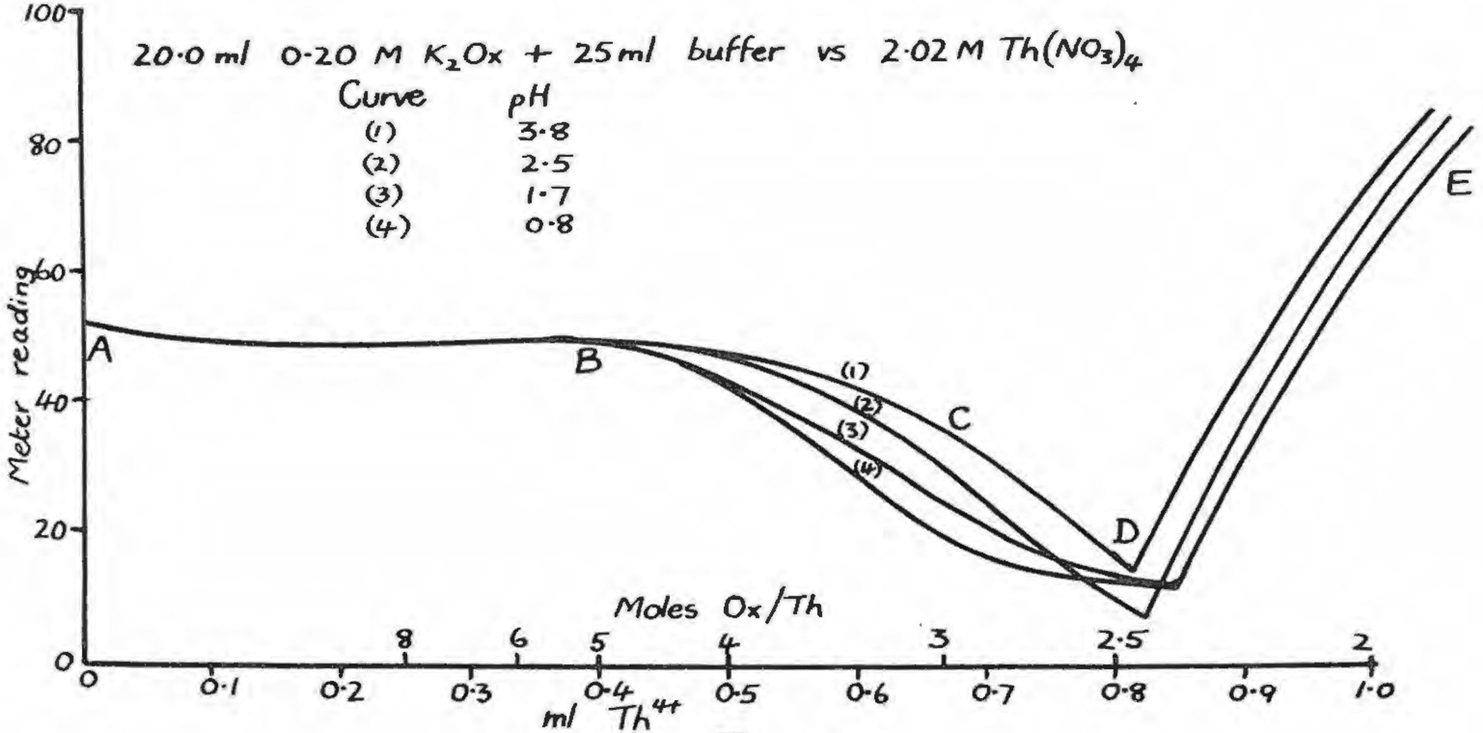

20·0 ml 0·20 M K_2Ox + 25 ml buffer vs 2·02 M $Th(NO_3)_4$
Curve pH
(1) 3·8
(2) 2·5
(3) 1·7
(4) 0·8
Meter reading
100
80
60
40
20
0
A
B
C
D
E
(1)
(2)
(3)
(4)
Moles Ox/Th
8
6
5
4
3
2·5
2
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
ml Th^{4+}

FIG 4.4

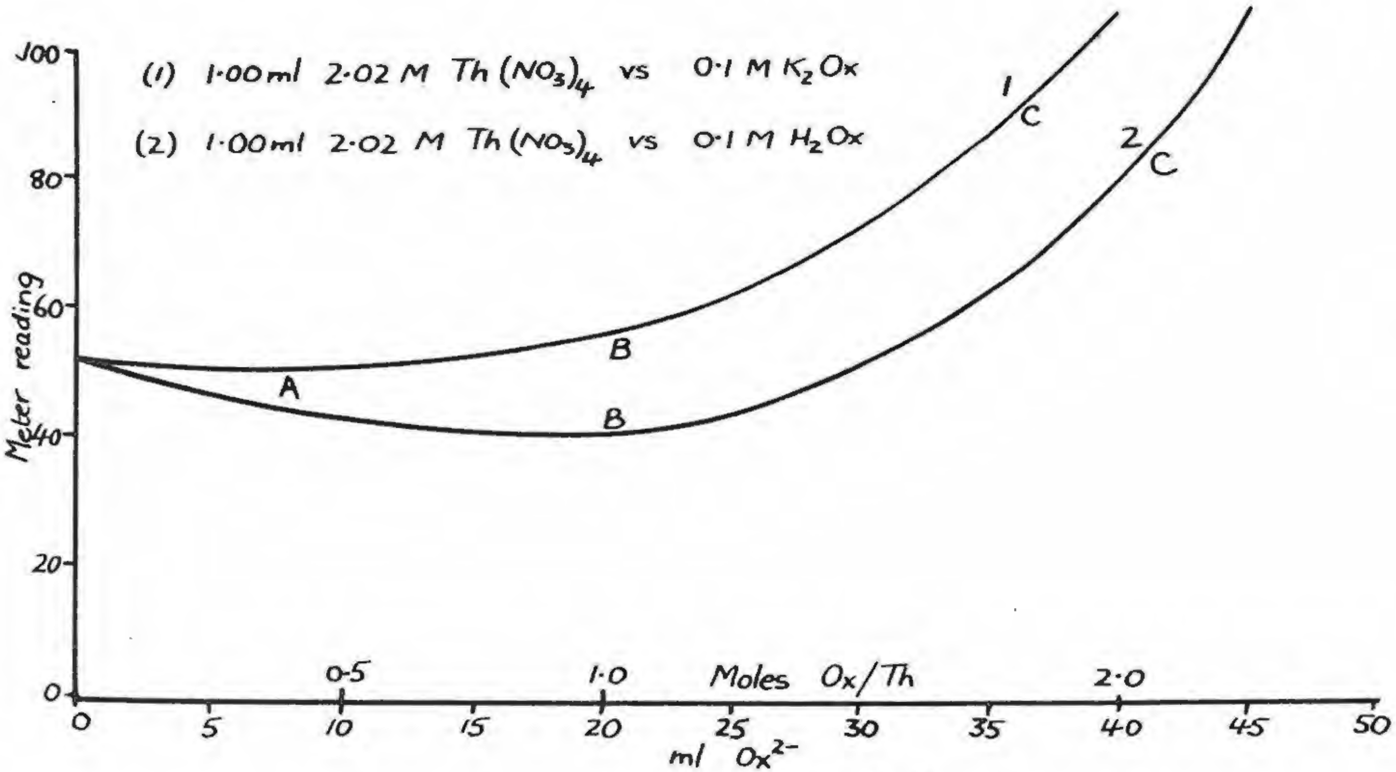

(1) 1·00ml 2·02 M Th $(NO_3)_4$ vs 0·1 M K_2Ox
(2) 1·00ml 2·02 M Th $(NO_3)_4$ vs 0·1 M H_2Ox
Meter reading
100
80
60
40
20
0
A
B
B
1
C
2
C
Moles Ox/Th
0·5
1·0
2·0
0
5
10
15
20
25
30
35
40
45
50
ml Ox^{2-}

FIG 4.5

curve runs almost horizontally, B is well defined at 7.6 moles. The curve then drops gently to C, 3.8 moles, and then more sharply to C' (about 3.0 moles). A minimum occurs at D (2.48 moles), the curve then rises sharply with a slight change of gradient at E (1.8 moles). Owing to the impossibility of obtaining more than 2½ figures from the readings, i.e. 0.5 on a 1 to 100 scale, it is difficult to say if, in fact, definite breaks occur at C' and E. (3 and 2 moles).

Fig. 4.4.

The graphs show the results for a series of the above titrations carried out at pH values from 0.8 to 3.8. The pH was altered by varying the amount of hydrochloric acid in the buffer solution. The zero was adjusted to the same point each time.

Fig. 4.5.

In this case oxalate solution was added to a thorium solution. No buffer was needed but the pH was adjusted to 2.0 by the addition of a few drops of nitric acid solution.

Curve (1) represents 1.00 ml of 2 M $Th(NO_3)_4$ in 50 ml of water titrated against 0.1 M K_2Ox. The curve descends slightly to A, then rises gradually to B, more steeply to C, then sharply upwards. The minimum point A is at 0.5 moles oxalate, B at 1.1, and C at 1.95.

Curve (2). As above but with 0.1 M oxalic acid in place of 0.1 M K_2Ox. The curve descends to B (1.05 moles) then rises with a slight change in gradient at C (1.9 moles). There is no break at 0.5 moles.

4.3. CONCLUSIONS.

4.31 Addition of oxalate to thorium. (Fig. 4.3).

Portion AB.

The initial addition of oxalate produces no drop in reading. This indicates that the drop in conductivity is being compensated for by a rise in dielectric constant, i.e. the molecules become more polar.

Portion BC.

The drop indicates a less polar structure being formed.

Portion CC'.

Particularly at higher pH's, 2 to 4, the break at C', 3 moles, is more pronounced. Thus at pH greater than 2, the reaction

$$Th_2Ox_8^{8-} + Th^{4+} \longrightarrow Th_2Ox_6^{4-} + ThOx_2$$

is preferred to

$$Th_2Ox_8^{8-} + 2Th^{4+} \longrightarrow Th_2Ox_5^{2-} + 2ThOx_2.$$

This may be due to a conversion

$$Th_2Ox_6^{4-} \longrightarrow Th_2Ox_5^{2-} + Ox^{2-}$$

at higher acidity due to the removal of Ox^{2-} as oxalic acid.

- Portion C'D. -

Portion C'D.

Drops sharply to a break at 2.4, this portion represents the reactions:

$$Th_2Ox_6^{4-} + Th^{4+} \longrightarrow 3ThOx_2 \qquad (A)$$

and

$$Th_2Ox_6^{4-} + 2ThOx_2 \longrightarrow K_4Th_2Ox_{10} \qquad (B)$$

which occur simultaneously.

Portion DE.

The curves of Fig. 4.4 represent a slow rate of addition, 1 drop per 5 mins, and the slight change in gradient at E represents the solid phase reaction

$$K_4Th_4Ox_{10} + Th^{4+} \longrightarrow 5ThOx_2 + 4K^+.$$

The effect of lowering the pH in Fig. 4.4 is to reduce the influence of the $(ThOx_3)_2^{4-}$ ion. Below pH 1 the minimum point was displaced towards 2.0 molecules, due to the conversion:

$$Th_4Ox_{10}^{4-} \longrightarrow 4ThOx_2 + 2Ox^{2-}.$$

4.32. Addition of oxalate to thorium. (Fig. 4.5, Curve (1)).

Since the curve descends to A, whilst the low frequency curve rises, this must indicate a change in dielectric constant. This is propably due to the formation of $ThOx_2$, since turbidity first appears at A. The formation of Th_2Ox^{6+} could not account for turbidity at this point.

Portion AB.

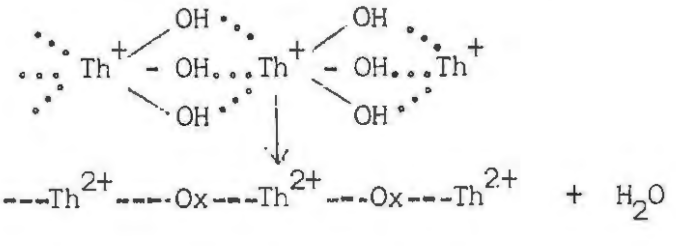
The very slight change in direction at B, not duplicated in low frequency measurements, may correspond to the formation of $ThOx^{2+}$ or a linear polymer $(ThOx)_n^{2n+}$ of the type mentioned by Bobtelsky and Ben-Bassat(44).

4.33 Addition of oxalic acid to thorium. (Fig. 4.5, Curve (2)).

The curve is similar with the break at B (1.2 moles) more pronounded. Analysis of the solid phases at points A, B and C, obtained by centrifuging the cell contents, all revealed 1.9 moles oxalate per thorium. The rising portion BC may represent the change,

$$(ThOx)_n^{2n+} + nOx^{2-} \longrightarrow nThOx_2.$$

If the reaction is carried out without the addition of nitric acid (p. 60) the break at B is clearer. At these pH values the thorium is in the form of $Th[(OH)_3TH]_n^{4+n}$, with n having values between 2 and 4. Point C may represent the end of the reaction



- 5. DETERMINATION -

5. DETERMINATION OF THE FORMATION CONSTANTS OF OXALATE COMPLEXES OF THORIUM.

The formation constants of $ThOx_4^{4-}$ and $ThOx_3^{2-}$ were determined by analysis of the liquid in equilibrium with the solid phase for hydrogen ion, total oxalate and total thorium.

From the plot of $-\log[Th]_{Total}$ vs. $-\log a_{Ox^{2-}}$, the nature and formation constants of the complexes can be deduced.

If we assume that the reactions taking place are :-

(i) $ThOx_4^{4-} \rightleftharpoons ThOx_3^{2-} + Ox^{2-}$,

(ii) $2ThOx_3^{2-} \rightleftharpoons Th_2Ox_5^{2-} + Ox^{2-}$,

(iii) $(NH_4)_2Th_2Ox_5 \rightleftharpoons Th_2Ox_5^{2-} + Ox^{2-} + 2NH_4^+$.

The corresponding formation constants being :-

$$K_I = \frac{[ThOx_3^{2-}]\, a_{Ox^{2-}}}{[ThOx_4^{4-}]} \qquad (1)$$

$$K_{II} = \frac{[Th_2Ox_5^{2-}]\, a_{Ox^{2-}}}{[ThOx_3^{2-}]^2} \qquad (2)$$

$$K_{SP} = [Th_2Ox_5^{2-}].a^2_{NH_{4+}} \qquad (3)$$

where $[ThOx_4^{4-}]$, $[ThOx_3^{2-}]$, and $[Th_2Ox_5^{2-}]$ represent the concentrations in moles per litre of the respective ions assuming the activity coefficients to be unity.

Neglecting the contribution of the Th^{4+} ion, the total thorium concentration is :-

$$Th_{Total} = [ThOx_4{}^{4-}] + [ThOx_3{}^{2-}] + 2[Th_2Ox_5{}^{2-}] \qquad (4)$$

$$= \frac{[ThOx_3{}^{2-}]\, a_{Ox^{2-}}}{K_I} + \frac{[Th_2Ox_5{}^{2-}]\, a^{\frac{1}{2}}_{Ox^{2-}}}{K_{II}} + \frac{2K_{SP}}{a^2_{NH_4^+}}$$

$$= \frac{a_{Ox^{2-}}}{K_I}\,\frac{[Th_2Ox_5{}^{2-}]\, a^{\frac{1}{2}}_{Ox^{2-}}}{K_{II}} + \frac{[Th_2Ox_5{}^{2-}]\, a_{Ox^{2-}}}{K_{II}} + 2K_{SP}/a^2_{NH_4^+}$$

$$= \frac{K^{\frac{1}{2}}_{SP} \cdot a^{1\frac{1}{2}}_{Ox^{2-}}}{a_{NH_4^+}\, K_I K^{\frac{1}{2}}_{II}} + \frac{K^{\frac{1}{2}}_{SP} \cdot a^{\frac{1}{2}}_{Ox^{2-}}}{a_{NH_4^+}\, K^{\frac{1}{2}}_{II}} + \frac{2K_{SP}}{a^2_{NH_4^+}}$$

$$= \frac{K^{\frac{1}{2}}_{SP}}{a_{NH_4^+}}\; \frac{a^{1\frac{1}{2}}_{Ox^{2-}}}{K_I K_{II}{}^{\frac{1}{2}}} + \frac{a^{\frac{1}{2}}_{Ox^{2-}}}{K_{II}{}^{\frac{1}{2}}} + \frac{2K^{\frac{1}{2}}_{SP}}{a_{NH_4^+}} \qquad (5)$$

If on the other hand the reactions taking place are assumed to be :-

$$Th_2Ox_8{}^{8-} \rightleftharpoons Th_2Ox_6{}^{4-} + 2Ox^{2-} \qquad IV$$

$$2Th_2Ox_6{}^{4-} \rightleftharpoons Th_4Ox_{10}{}^{4-} + 2Ox^{2-} \qquad V$$

$$(NH_4)_4Th_4Ox_{10} \rightleftharpoons Th_4Ox_{10}{}^{4-} + 4NH_4^+ \qquad VI$$

- Then -

Then,

$$[\mathrm{Th}]_{\mathrm{Total}} = 2[\mathrm{Th_2Ox_8}^{8-}] + 2[\mathrm{Th_2Ox_6}^{4-}] + 4[\mathrm{Th_4Ox_{10}}^{4-}]$$

$$= \frac{2a^2_{\mathrm{Ox}^{2-}}\,[\mathrm{Th_2Ox_6}^{4-}]}{K_{\mathrm{I}}} + 2\left(\frac{a^2_{\mathrm{Ox}^{2-}}\,[\mathrm{Th_4Ox_{10}}^{4-}]}{K_{\mathrm{II}}}\right)^{\frac{1}{2}} + \frac{4K_{\mathrm{SP}}}{a^4_{\mathrm{NH_4^+}}}$$

$$= \frac{4a^3_{\mathrm{Ox}^{2-}}\,[\mathrm{Th_4Ox_{10}}^{4-}]^{\frac{1}{2}}}{K_{\mathrm{I}}K^{\frac{1}{2}}_{\mathrm{II}}} + \frac{2a_{\mathrm{Ox}^{2-}}\,[\mathrm{Th_4Ox_{10}}^{4-}]^{\frac{1}{2}}}{K^{\frac{1}{2}}_{\mathrm{II}}} + \frac{4K_{\mathrm{SP}}}{a^4_{\mathrm{NH_4^+}}}$$

$$= \frac{2K^{\frac{1}{2}}_{\mathrm{SP}}}{a^2_{\mathrm{NH_4^+}}}\;\frac{4a^3_{\mathrm{Ox}}}{K_{\mathrm{I}}K^{\frac{1}{2}}_{\mathrm{II}}} + \frac{2a_{\mathrm{Ox}}}{K^{\frac{1}{2}}_{\mathrm{II}}} + \frac{2K^{\frac{1}{2}}_{\mathrm{SP}}}{a^2_{\mathrm{NH_4^+}}} \qquad (6)$$

By comparing (5) and (6), and the graph of log $\mathrm{Th}_{\mathrm{Total}}$ vs. log a_{Ox} conclusions as to the state of the complex ions may be reached. To do this it is necessary to determine the values of a_{Ox}, $[\mathrm{Th}]_{\mathrm{Total}}$ and $a_{\mathrm{NH_4^+}}$, and the hydrogen ion activity.

5.1 Calculation of a_{Ox}.

The total oxalate concentration, as determined by titration, is given by

$$[\mathrm{Ox}^{2-}]_{\mathrm{Total}} = [\mathrm{H_2Ox}] + [\mathrm{HOx}^-] + [\mathrm{Ox}^{2-}] \qquad (7)$$

The quantities are related by the relations

$$K_1 = f_1\,\frac{[\mathrm{HOx}^-]}{[\mathrm{H_2Ox}]}\,a_{\mathrm{H}^+} = 5.38 \times 10^{-2} \qquad (72)$$

- K_2 -

$$K_2 = \frac{f_2[Ox^{2-}]}{f_1[HOx^-]} a_{H^+} = 5.42 \times 10^{-5} \qquad (73)$$

Where

K_1 and K_2 are the first and second ionisation constants,

f_1 = the activity coefficient of HOx^-,

f_2 = the activity coefficient of Ox^{2-} .

The activity of H_2Ox may be taken as 1.0.

By solving the above equations we obtain :

$$a_{Ox} = \frac{K_2K_1}{a^2_{H^+} + \frac{a_{H^+}.K_1}{f_1} + \frac{K_1K_2}{f_2}}$$

f_1 was taken as equal to $f_\pm$ for hydrochloric acid in potassium chloride solutions of equal ionic strength$^{(73)}$. Values of $f_{Ox^{2-}}/f_{HOx^-}.f_{Cl^-}$ were obtained from the data in the determination of K_2 for oxalic acid$^{(73)}$. f_2 was obtained from these by multiplying the indicated value by f_1^2, assuming $f_{HOx^-} = f_{Cl^-} = f_1$.

5.2 Procedure.

The equilibrium was approached from two directions :

(1) A solution of $ThOx_4^{4-}$ in $(NH_4)_2Ox$ was diluted by adding ammonium oxalate-oxalic acid buffer.

(2) Wet, well washed $(NH_4)_2Th_2Ox_5.7H_2O$ was added to ammonium oxalate oxalic-acid buffer.

- 5.21 Sampling -

5.21 Sampling Procedure.

The pH of the solution was measured, then after the precipitate had settled, 50 ml of the solution was drawn into a 50 ml burette by a suction bulb. Of this 10 ml was used for thorium determination, and aliquots of 20 ml for oxalate and ammonium determinations.

5.22 Determination of a_{H^+}.

The pH of the solution was measured by a Beckman model H mains pH meter. The meter was standardised against a Beckman pH = 4 standard buffer, and a graph was prepared of actigity coefficients at various ionic strengths.

5.23 Determination of total oxalate.

If necessary, the 20 ml sample was diluted to a convenient volume and titrated against 0.05 N $Ce(SO_4)_2$ in the presence of N H_2SO_4 with OsO_4 as catalyst.

5.24 Determination of total thorium.

The Thorin colorimetric method was used. The sample was evaporated to dryness under an infra-red lamp and the excess oxalate removed by sublimation at 170°C. The residue was warmed gently with three 2.5 ml portions of fuming nitric acid. The nearly dry residue was dissolved in 1 ml of conc. HCl, transferred to a 50 ml flask and 5 ml

0.1% Thorin reagent followed by 20 ml absolute alcohol added. The transmittance was measured after 1 hour in 1 cm cells at 525 mμ.

5.25 Determination of $a_{NH_4^+}$.

The 20 ml sample was evaporated to about 10 ml under an infra-red lamp and transferred to the semi-micro distillation apparatus. The estimated concentration was multiplied by the activity coefficient obtained from graph of activity coefficient NH_4^+ vs. ionic strength(74).

5.26 Preparation of solutions.

1.0 M oxalic acid, 0.3 M ammonium oxalate, and 1.0 M ammonium chloride were mixed in various ratios to give the required oxalate and ammonium ion concentrations. The latter was kept constant at 1.10 M corresponding to an activity of 0.79. The solutions were diluted to 250 ml and pipetted into 500 ml flasks which were placed in a thermostat. When they had reached 25.0°C thorium was added as (i) a very concentrated solution of $(NH_4)_4ThOx_4$, (ii) solid well-washed $(NH_4)_2Th_2Ox_5$, and (iii) a concentrated $Th(NO_3)_4$ solution, until a definite precipitate had appeared. The solutions were shaken vigorously for 10 mins. at first, then for 1 min. intervals every 3 to 6 hours for 3 days.

5.3 RESULTS.

The following results were obtained :-

5.31 Thorium added as $(NH_4)_4ThOx_4 7H_2O$ solution.

pH	$-\log[Ox]_{tot}$	$-\log a_{Ox^{2-}}$	$[NH_4^+]$	$-\log[Th]_{tot}$ observed	$-\log[Th]_{tot}$ calculated.
0.35	1.64	6.90	1.10	5.65	5.80
0.70	2.04	6.30	1.10	5.10	5.35
1.11	2.29	5.86	1.10	4.65	4.95
1.22	1.78	5.20	1.09	4.20	4.31
1.40	1.74	4.90	1.09	3.78	4.01
1.05	0.77	4.45	1.09	3.41	3.56
1.56	1.32	4.28	1.09	3.08	3.39
1.62	0.22	4.02	1.08	3.06	3.28
2.15	1.56	3.88	1.08	2.81	2.99
2.20	1.40	3.60	1.08	2.46	2.71
2.05	0.99	3.42	1.08	1.83	2.52
2.32	1.85	3.15	1.09	1.78	2.25
2.30	0.94	3.02	1.09	1.75	2.11
2.48	1.89	2.78	1.09	1.76	1.82
2.52	0.76	2.52	1.10	1.82	1.62
2.44	0.55	2.44	1.10	1.40	1.27
2.28	1.09	2.28	1.11	0.96	0.96
3.06	0.65	1.99	1.13	0.17	0.22
3.15	0.91	2.05	1.12	0.36	0.42
3.40	1.25	2.20	1.11	0.5	0.65
4.25	1.49	1.91	1.25	-0.17	-0.08

- 5.32 -

5.32 Thorium added as solid $(NH_4)_2Th_2Ox_5 7H_2O$.

pH	$-\log[Ox]_{tot}$	$-\log a_{Ox^{2-}}$	$[NH_4^+]$	$-\log[Th]_{tot}$ observed	$-\log[Th]_{tot}$ calculated.
0.35	1.92	6.81	1.10	5.81	5.76
0.62	2.08	6.47	1.09	5.50	5.10
0.98	2.29	6.05	1.09	5.18	5.10
1.25	1.44	5.82	1.08	4.85	4.85
1.34	2.26	5.50	1.08	4.71	4.60
1.31	1.94	5.21	1.08	4.38	4.30
1.35	1.73	4.96	1.08	4.05	4.03
1.28	1.24	4.61	1.07	3.27	3.59
1.46	1.14	4.22	1.07	3.14	3.28
1.52	0.98	3.92	1.07	2.78	2.97
1.89	1.27	3.70	1.07	2.63	2.72
2.30	1.20	3.27	1.07	2.12	2.37
2.52	1.13	2.98	1.08	1.94	2.00
2.48	0.85	2.75	1.08	1.70	1.78
2.69	0.85	2.52	1.08	1.47	1.45
2.73	0.90	2.40	1.09	1.28	1.16
2.37	0.16	2.18	1.09	0.73	0.60
2.94	0.63	2.07	1.09	0.57	0.49
2.97	0.56	1.98	1.10	0.25	0.21
3.18	0.88	1.89	1.14	-0.04	-0.11

- 5.33 -

5.33 Thorium added as $Th(NO_3)_4$ solution.

pH	$-\log[Ox]_{tot}$	$-\log a_{Ox^{2-}}$	$[NH_4^+]$	$-\log[Th]_{tot}$ observed	$-\log[Th]_{tot}$ calculated.
0.35	2.06	6.89	1.09	5.92	5.80
0.75	2.07	6.24	1.09	5.32	5.24
1.18	1.14	5.89	1.08	5.03	4.95
1.20	1.66	5.64	1.08	4.90	4.72
1.28	1.96	5.28	1.08	4.41	4.37
1.37	1.80	5.00	1.07	4.27	4.10
1.41	1.62	4.87	1.07	4.08	3.97
1.27	1.19	4.52	1.08	3.73	3.66
1.33	1.06	3.88	1.08	3.42	3.31
2.15	1.57	3.63	1.08	3.10	2.98
2.15	1.91	3.58	1.08	2.69	2.64
2.06	1.11	3.36	1.09	2.51	2.40
2.30	1.03	3.11	1.09	2.20	2.19
2.42	1.64	2.82	1.09	1.80	1.83
2.48	0.86	2.75	1.09	1.70	1.77
2.51	0.83	2.60	1.09	1.60	1.61
2.43	0.66	2.49	1.09	1.47	1.38
2.30	0.25	2.33	1.09	1.12	0.94
2.51	0.49	2.20	1.10	0.72	0.65
3.17	0.92	2.12	1.10	0.57	0.45
3.15	0.91	2.05	1.11	0.38	0.32

- 5.4 CONCLUSION -

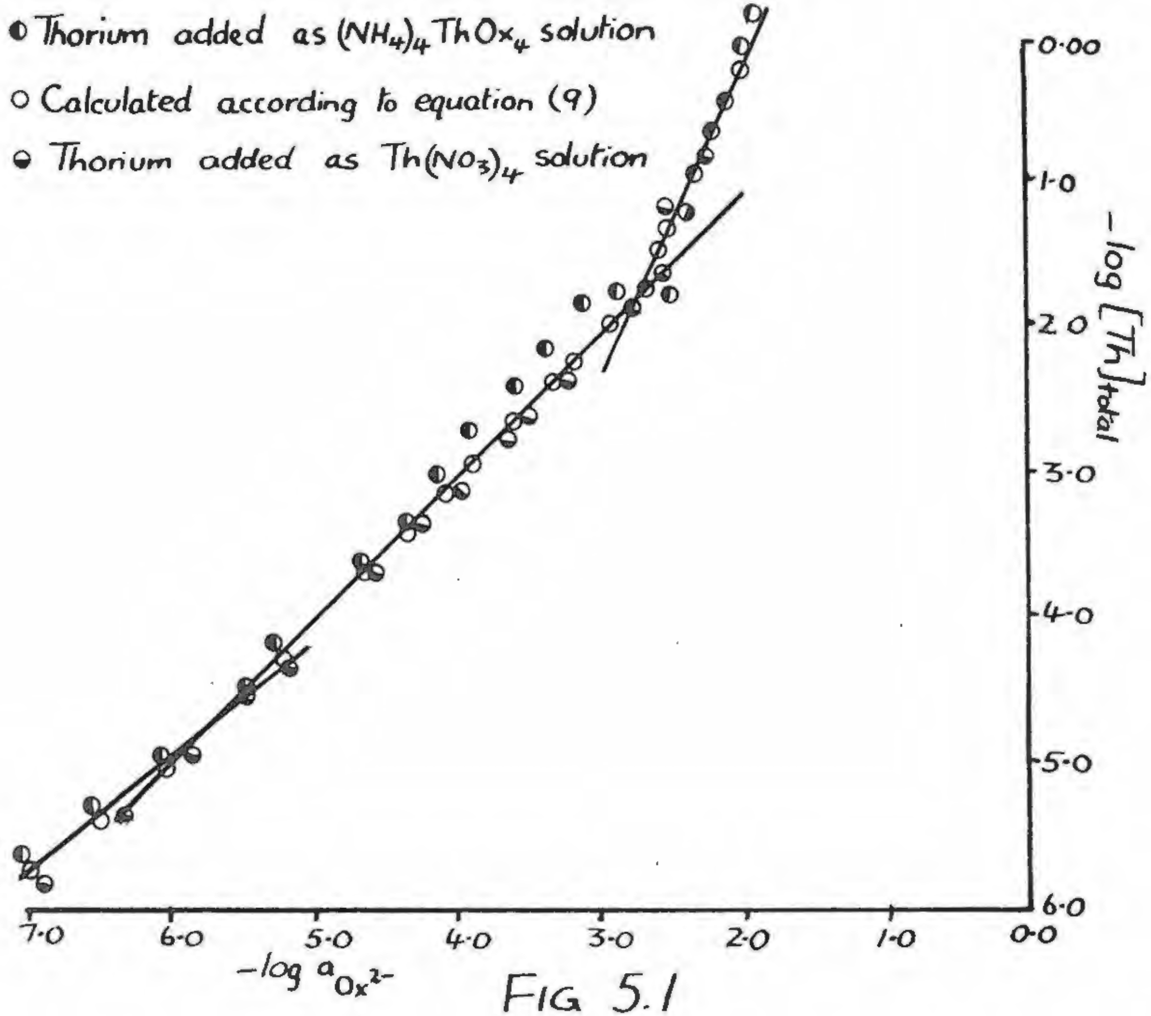

● Thorium added as (NH4)4 ThOx4 solution
○ Calculated according to equation (9)
◒ Thorium added as Th(NO3)4 solution
0·00
1·0
2.0
3·0
4·0
5·0
6·0
- log [Th]total
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
-log a0x2-

FIG 5.1

5.4 CONCLUSION.

The calculated figures in the last column of the tables were based on the following figures :-

$$K_I = 3.2 \times 10^{-5} ,$$

$$K_{II} = 4.0 \times 10^{-10} ,$$

and $$K_{SP} = 6.2 \times 10^{-8} .$$

In the cases referred to in 5.31 to 5.33 the agreement with the observed figures as given by $s = \frac{(E_{calc} - E_{obs})^2}{N}$,

where E_{calc} is the calculated value and E_{obs} is the observed value of $-\log[Th]$. In the cases referred to, the values of s are 0.19, 0.17 and 0.18 respectively, which represents a fair agreement with equation (6), and the above values for the constants.

From Fig. 5.1 the gradient of the curve, $d \log[Th]/d \log a_{Ox}$ indicates that equation (6) is operative, since the gradients of the two sections are approximately 3 and 1. The point of change corresponds with the change from $ThOx_4^{4-}$ to $ThOx_3^{2-}$ and agrees with that found in Fig. 1.6.

BIBLIOGRAPHY.

1. Bahr. Annalen, 132, 231 (1864).

2. Bunsen. Ann. Phys. Chem., 155, 375 (1875).

3. B. Brauner. J. Chem. Soc., 73, 951 (1898).

4. Glaser. Zeit. Anal. Chem., 36, 231 (1897).
   37, 25 (1898).

5. A. Rosenheim, V. Samter and I. Davidsohn. Zeit. Anorg. Chem., 35, 424 (1903).

6. P. Cleve. Bull. Soc. Chim., France., 21, 116 (1902).

7. A. Rosenheim, V. Samter and I. Davidsohn. Ber. D. Chem. Ges., 35, 402 (1902).

8. O. Hauser and F. Wirth. Zeit. Anal. Chem., 47, 389 (1908).

9. Wyrouboff and Verneuil. Comptes Rend., 128, 1573 (1899).

10. O. Hauser and F. Wirth. Zeit. Anorg. Chem., 78, 75 (1912).

11. R. Meyer and O Hauser. Die Analyse der seltenen Erde und der Erdsäuren. Die chemische Analyse. XIV/XV Band. Ferdinand Enke, Stuttgard, 1912.

12. C. James, C. F. Whittemore and H. C. Holden. J. Am. Chem. Soc., 30, 1853 (1915)

13. H. T. Britton and M. E. Jarrett. J. Chem. Soc., 111, 1494 (1936).

14. P. Cleve. Bih. Svenska Akad. Handl., 2 , 24 (1874).

15. A. Rosenheim, B. Raibman and G. Schendl. Z. Znorg. Chem. 196, 161 (1931).

16. Colani. Comptes Rend., 156, 1075 (1912).

17. F. Wirth. Z. Anorg. Chem., 76, 174 (1912).

18. E. Benz. Z. Angew. Chem., 15, 297 (1902).

19. J. Bonardi. Bull. U.S. Bur. Mines., 212, 19 (1923).

- 20. -

20. H. Little. A Textbook of Inorganic Chemistry, Edited by J. Friend. Vol. IV pp. 319-322.

21. J. Spencer. The Metals of the Rare Earths. Longmans, Green & Co., London 1919. p. 159.

22. T. Möeller, G. K Sweitzer and B.D. Stow. Chem. Reviews, 42, 63 (1948).

23. C. J. Rodden and J. C. Warf. Analytical aspects of the Chemistry of the Manhattan Project, McGraw-Hill Book Co., pp.160-207

24. H. Brintzinger and W. Eckardt. Z. Anorg. Chem., 224, 93 (1935).

24a. Frank.B. Ann. Univ. Mariae Curie Sklodowska, Lubin - Polonia, Sect. AA 11, 47 (1956). Ex. Chem. Abstracts, 53, 13754 (1959).

25. T. C. Ingles. Canadian Chem. Proc., 35, 397 (1951).

26. M. Carron, D. Skinner and R. Stevens. Anal. Chem., 27, 1061 (1955).

27. H. Willard and L. Fordon. Anal. Chem., 20, 165 (1948).

28. H. Kall and L. Gordon. Ibid., 25, 1256 (1953).

29. B. Rider and M G. Mellon. Anal. Chim. Acta., 2, 370 (1948).

30. V. Kuznetsov. Dokl. Akad. Nauk. SSSR., 31, 895 (1941).

31. H. Matsuyana, T. Hara and K. Kayama. J. Chem. Soc., Japan. 79, 958 (1958).

32. R. Prîbil. Magyar Kem. Folyoirat. 64, 54 (1958).

33. Vickery. "The Chemistry of the Lanthanons".

34. M. Bose and D. M. Chowdhury. J. Ind. Chem. Soc., 32, 673 (1955).

35. S. K. Siddhanta. Ibid., 25, 579 (1948).

36. M. Bose and D.M. Chowdhury. Ibid., 31, 111 (1954).

37. Magareta Dyrssen. Receuil., 75, 748 (1956).

38. David Dyrssen. Svensk. Kem. Tidskr., 68, 212 (1956).

39. David Dyrssen. Ibid., 65, 43 (1953).

40. M. Bobtelsky. "Heterometry", Elsevier Publishing Co., 1960.

41. M. Bobtelsky and B. Graus. J. Am. Chem. Soc., 77, 1990 (1955).

42. M. Bobtelsky and I. Bar-Gadda. Bull. Soc. Chim., France, 382 (1953)

43. M. Bobtelsky and B. Graus. Bull. Research Council Israel, 3, 82 (1953).

44. M. Bobtelsky and H. Ben-Bassat. Bull. Soc. Chim., France, 180 (1958).

45. " " Ibid. 1138 (1958).

46. Komatsu, Taki and Takoda. J. Chem. Soc., Japan, 80, 1090 (1959)

47. K. Kraus and R. Hommberg. J. Phys. Chem., 58, 1325 (1954).

48. Sirkka Hietanen. Receuil, 75, 711 (1956).

49. A. K. Dey. Kolloid Zeit., 174, 15 (1961).

50. P. G. Menon and D. Singh. Z. Anal. Chem., 176, 264 (1960).

51. R. Hara and P. West. Anal. Chim. Acta., 12, 285 (1955).

52. E. Pungor and E. Zapp. Acta Chim. Acad. Sci. Hung., 25, 133 (1960).

53. A. Zielen. J. Am. Chem. Soc., 81, 5022 (1959).

54. Y. Tolmacher. Bull. Acad. Sci. SSR., 320 (1944).

55. L. E. Marchi and J. P. McReynold. J. Am. Chem. Soc., 65, 333 (1945).

56. G. T. Seaborg and J. J. Katz. "The Actinide Elements". (1955).

57. V. Kuznetsov, S. Savvin and V. Mikhailov. Russian Chemical Reviews, 29, 243 (1960).

58. V. Krishnamurty and G. Harris. Chem. Reviews, 61, 213 (1961).

59. D. Dyrrsen. Svensk. Kemisk. Tidsk., 7, 153 (1950).

60. Not in text.

61. Not in text.

62. R. Thomson, M. Perry and W. Byerly. Anal. Chem., 21, 1239 (1949).

63. C. Banks and H. Byrd. Ibid., 25, 417 (1953).

64. J. Clinch. Anal. Chim. Acta., 14, 162 (1956).

65. F. Grimaldi and M. Fletcher. Anal. Chem., 28, 812 (1956).

66. V. Kuznetsov and V. Nikol'skaya. Zhur. Anal. Khim., 15, 299 (1960).

67. V. Kuznetsov and S. B. Savvin. Ibid., 15, 175 (1960).

68. S. K. Datta. Z. Anal. Chem., 153, 89 (1956).

69. G. Owens II and Yoe. Anal. Chim. Acta., 23, 321 (1960).

70. R. Delhez. J. Chem. Ed., 37, 151 (1960).

71. Not in text.

72. L. S. Parker. J. Am. Chem. Soc., 63, 1007 (1941).

73. G. Pinching and R. Bates. J. Research U.S. Nat. Bur. Standards, 40, 405 (1948).

74. H. S. Harned and B. B. Owen. "The Physical Chemistry of Electrolytic Solutions", 3rd Ed., Appendix A, p.731.

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