

On the Complex Formation Between Thorium and Acetylacetonone

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It was once believed that complex compounds are formed directly in one step like $\text{Me} + m\text{X} \rightarrow \text{MeX}_m$, where Me is a metal ion and X is an uncharged molecule or a negative ion (ligand). Accordingly no other complexes would be formed in appreciable amounts.

During the last few decades a number of complex systems have been thoroughly studied; in all cases not only the complex with maximum number m of ligands appears to be formed, but also, to some extent, all intermediate steps MeX_n , where $n = 1, 2, \dots, m-1$. This is true both for systems with inorganic ions like $\text{Cr}^{3+} - \text{SCN}^-$ ⁽¹⁾ and $\text{Hg}^{2+} - \text{Cl}^-$ ⁽²⁾, for systems where the ligand is uncharged, like metal-ammine systems⁽³⁾, and for systems involving organic ions like $\text{Cu}^{2+} - \text{CH}_3\text{COO}^-$ ⁽⁴⁾.

Organic molecules with two coordinating groups (*e. g.* salicylaldehyde, oxine, cupferron, acetylacetonone) combine with metals to form so-called chelates, or inner complexes. One might suspect that these chelates will be formed in the same stepwise manner. Recently Calvin and Wilson⁵ have calculated equilibrium constants for the formation of a great number of copper(II) chelates, CuX_2 and the intermediate step CuX^- , in a mixture of dioxane and water; in most cases the accuracy was rather low. However there is still a widespread opinion that in the formation of chelates only the uncharged complex is obtained. Hückel⁶, when discussing the formation of acetylacetonone chelates, states that "Die Zahl der innerkomplex gebundenen Acetylacetonreste entspricht fast durchweg der Wertigkeit der als Zentralatom fungierenden Metalles, so dass sich die allgemeine Formel für die Acetylacetonate $\text{Me}(\text{CH}_3\text{COCH}:\text{COCH}_3)_m$ in der m die Wertigkeit des Metalles bedeutet, aufstellen lässt."

In this paper the results are given of an investigation of the complex formation between Th^{4+} and acetylacetonone (HAA). The data could be explained well *only* by assuming that *all* complexes ThAa^{3+} , ThAa_2^{2+} , ThAa_3^+ and ThAa_4 are formed; with this assumption the mass action constants for the reaction steps could be calculated.

METHOD OF INVESTIGATION

To be able to calculate the constants for a complex equilibrium one has to know the total amount of central atom and ligand and the free concentration of at least one definite species. Sometimes emf measurements have been used to find the concentration of central ion or ligand. This was not possible in the present case, as no reproducible thorium or acetylacetonate electrode had been constructed. Nor could optical methods be used, at least not with visible light, since the thorium-acetylacetonone complexes are uncoloured.

In his classical investigation on the complex formation between Hg^{2+} and X^- ($\text{X} = \text{Cl}^-$, Br^- , I^-) Morse⁷ made use of the fact that HgX_2 molecules, but not ions, are soluble in toluene. From the distribution of mercury between toluene and water as a function of $[\text{X}^-]$ he could calculate the concentration of HgX^+ and HgX_2 .

An analogous method has been used here; the distribution of thorium between benzene and water has been measured as a function of the concentration of free Aa^- in the aqueous phase. The radioactive isotope Th^{234} (UX_1) was used in tracer amounts, never exceeding 10^{-10} mol/l.

By the use of radioactive tracers instead of macro amounts several advantages are gained: a) the ligand concentration can be increased without exceeding the solubility product of the uncharged complex, b) the concentrations of other substances in solution are not affected by the addition of tracer amounts of the central atom; this will simplify the mathematical treatment, and c) in general the radiometric method of analysis is much simpler than other analytical methods. Grahame and Seaborg⁸ have shown that the distribution ratio of tracer isotopes between two phases is equal to that for macro amounts of the same element.

Zirconium gives a complex with thenoyltrifluoroacetone (TTA) soluble in benzene. Connick and McVey⁽²⁰⁾ have investigated the distribution of radioactive Zr^{95} between benzene and water, in which some TTA had been dissolved, as a function of the concentration of different organic and inorganic anions. From these measurements they could calculate some complex formation constants. This method is an extension of that used by Morse, and

may in the future be of great value for determining complexes where emf and optical methods fail. However the constants obtained by these authors should not be regarded as definite until some of the assumptions made concerning the system zirconium-TTA-water have proved to be true.

DEPENDENCE OF THE DISTRIBUTION COEFFICIENT ON THE HAa CONCENTRATION

Many authors have given general mathematical treatments of the formation of mononuclear *e.g.* 3, 9 and polynuclear *e.g.* 4, 9, 10 complexes. The discussion will treat only the special case of thorium complexes in aqueous solution.

It is presumed that no ions exist in the benzene phase. In the following the index *aq* and the charges of ions are omitted for the sake of simplicity (*E.g.* [ThAa₂] means the concentration of the ion ThAa₂²⁺ in the aqueous phase). Since all solutions have an approximately constant ionic strength of 0.01, all activity coefficients are constant, and by using concentrations in the law of mass action, stoichiometric constants are obtained.

In an aqueous solution of thorium and acetylacetonate mononuclear complexes ThAa_{*n*} and polynuclear complexes Th_{*m*}Aa_{*n*} might occur. Moreover we have products of hydrolysis, which can be written as Th(OH)_{*n*}, Th_{*m*}(OH)_{*n*}, and mixed complexes Th_{*m*}Aa_{*n*}(OH)_{*p*}. If hydrolysis can be neglected, mixed complexes can probably also be neglected. Indeed, no evidence for their existence was obtained, and no mathematical treatment for mixed complexes will be made here. The following section I will deal with the simplest case, when only mononuclear complexes are formed. In II the general case is treated.

I. Mononuclear complexes are formed

We define the complex product κ_n by

$$\kappa_n = [\text{ThAa}_n] [\text{Th}]^{-1} [\text{Aa}]^{-n} \quad (1)$$

If the hydrolysis product, β_n , is defined analogous to the complex product, we have

$$\beta_n = [\text{Th(OH)}_n] [\text{Th}]^{-1} [\text{OH}]^{-n} \quad (2)$$

The total concentration of thorium in the aqueous phase $[\text{Th}]_{\text{aq, tot}}$ must then be

$$[\text{Th}]_{\text{aq, tot}} = [\text{Th}] + \sum_{n=1}^{n=N} [\text{ThAa}_n] + \sum_{n=1}^{n=P} [\text{Th}(\text{OH})_n] \quad (3)$$

ThAa_N and $\text{Th}(\text{OH})_P$ are the complexes with maximum number ligands respectively. Now the measurements are made on the radioactive Th^{234} in solution. The radioactivity in the aqueous phase, I_{aq} disintegrations/minute, under defined conditions must be proportional to $[\text{Th}]_{\text{aq, tot}}$:

$$[\text{Th}]_{\text{aq, tot}} = A_{\text{aq}} \cdot I_{\text{aq}} \quad (4a)$$

The only existing form of thorium in the benzene phase at these low concentrations is ThAa_4 . At macro concentrations some association between ThAa_4 molecules takes place; the evidence for this is apparent from the studies of Biltz and Clinch¹¹. Using the subscript be for the benzene phase, we have

$$[\text{Th}]_{\text{be, tot}} = [\text{ThAa}_4]_{\text{be}} \quad (5)$$

If the distribution factor of ThAa_4 is λ_4 ,

$$\lambda_4 = [\text{ThAa}_4]_{\text{be}} / [\text{ThAa}_4]_{\text{aq}} \quad (6)$$

we get

$$[\text{Th}]_{\text{be, tot}} = \lambda_4 [\text{ThAa}_4]_{\text{aq}} \quad (7)$$

If the measurements on the benzene phase are also made under defined conditions we obtain

$$[\text{Th}]_{\text{be, tot}} = A_{\text{be}} \cdot I_{\text{be}} \quad (4b)$$

Now we may define the apparent distribution coefficient q :

$$q = I_{\text{be}} / I_{\text{aq}} = [\text{Th}]_{\text{be, tot}} \cdot A_{\text{aq}} / [\text{Th}]_{\text{aq, tot}} \cdot A_{\text{be}} \quad (8)$$

We define λ'_4 by

$$\lambda'_4 = \lambda_4 \cdot A_{\text{aq}} / A_{\text{be}} \quad (9)$$

It will be shown later that $A_{\text{be}} / A_{\text{aq}}$ is approximately 1 in the present case. With Equations (1) — (9) we get

$$q = \frac{\lambda'_4 \kappa_4 [\text{Aa}]^4}{1 + \sum \kappa_n [\text{Aa}]^n + \sum \beta_n [\text{OH}]^n} \quad (10a)$$

This equation shows that different curves $q = f [\text{Aa}]$ will be obtained for different pH, if $\sum \beta_n [\text{OH}]^n$ cannot be neglected when compared with $1 + \sum \kappa_n [\text{Aa}]^n$. If the hydrolysis is negligible, Equation (10a) will take the form (note that $\kappa_0 = 1$)

$$q = \frac{\lambda'_4 \cdot \kappa_4 [\text{Aa}]^4}{\sum_{n=0}^{n=N} \kappa_n [\text{Aa}]^n} \quad (10b)$$

If we introduce a set of new constants φ_n , where

$$\varphi_{4-n} = [\text{ThAa}_n] [\text{ThAa}_4]^{-1} [\text{Aa}]^{4-n} = \kappa_n \cdot \kappa_4^{-1} \quad (11)$$

Equation (10b) can be simplified to

$$q = \lambda'_4 (\sum \varphi_{4-n} [\text{Aa}]^{n-4})^{-1} \quad (12a)$$

We have $\varphi_0 = \kappa_0 = 1$. If no negatively charged complexes are formed, then

$$q = \frac{\lambda'_4}{\varphi_4 [\text{Aa}]^{-4} + \varphi_3 [\text{Aa}]^{-3} + \varphi_2 [\text{Aa}]^{-2} + \varphi_1 [\text{Aa}]^{-1} + 1} \quad (12b)$$

In case negative complexes ThAa_5^- , ThAa_6^{2-} , etc., are formed additional terms $\varphi_{-1} [\text{Aa}]$, $\varphi_{-2} [\text{Aa}]^2$, etc., occur in the denominator of Equation (12b).

Acetylacetone is a weak acid with the dissociation constant $K_a = 1.17 \cdot 10^{-9}$ at 25°C ⁽¹²⁾. If V_{be}° ml benzene with an acetylacetone concentration of $[\text{HAA}]_{\text{be}}^\circ$ is shaken with V_{aq}° ml water containing no acetylacetone, we find after equilibrium that

$$[\text{HAA}]_{\text{aq}} = [\text{HAA}]_{\text{be}}^\circ (1 + K_a [\text{H}^+]^{-1} + D V_{\text{be}} / V_{\text{aq}}) \cdot V_{\text{aq}} / V_{\text{be}} \quad (13)$$

where D is the distribution coefficient of acetylacetone between the two liquids. D is practically constant for pH between 1 and 7, and an ionic strength less than 0.02 mol/l; D was found to be 5.95⁽¹³⁾. V_{aq} and V_{be} are the equilibrium volumes of the two phases; in this case we have assumed $V_{\text{aq}}^\circ = V_{\text{aq}}$ and $V_{\text{be}}^\circ = V_{\text{be}}$, which is true for low acetylacetone concentrations. If $\text{pAa} = -\log[\text{Aa}^-]$ and $V_{\text{aq}} = V_{\text{be}}$ we have

$$\text{pAa} = \text{p}K_a - \text{pH} - \log [\text{HAA}]_{\text{be}}^\circ / (D + 1 + [\text{H}^+]^{-1} K_a) \quad (14)$$

For $1 < \text{pH} < 7$ we can in the case of acetylacetone neglect $[\text{H}^+].K_a$ when compared to $D + 1$. Introducing the values of the constants we get

$$\text{pAa} = 9.77 - \text{pH} - \log[\text{HAa}]_{\text{be}}^{\circ} \quad (15)$$

The addition of tracer amounts of thorium to the acetylacetone solution will bind some Aa^- , but this amount is negligible when compared to the amount of acetylacetone in the two phases.

II. Polynuclear complexes are formed

If complexes with two or more central atoms are formed the complex product must be defined by

$$\kappa_{m,n} = [\text{Th}_m \text{Aa}_n] [\text{Th}]^{-m} [\text{Aa}]^{-n} \quad (16)$$

in which $\kappa_{1,n} = \kappa_n$ from Equation (1). For the analogous hydrolysis constants $\beta_{m,n}$ can be defined. Since Equations (4) — (9) are still valid, we get

$$q = \frac{\lambda'_4 \kappa_4 [\text{Aa}]^4}{1 + \sum \sum m \beta_{m,n} [\text{Th}]^{m-1} [\text{OH}]^n + \sum \sum m \kappa_{m,n} [\text{Th}]^{m-1} [\text{Aa}]^n} \quad (17)$$

In this equation the apparent distribution coefficient q is a function of not only pH and $[\text{Aa}]$ but also of the thorium concentration $[\text{Th}]$. It would be a difficult task to determine the constants $\kappa_{m,n}$ and $\beta_{m,n}$ in this general case; however under the experimental conditions of the present work, case I seems to be realised, as might have been expected because of the very low thorium concentration.

EXPERIMENTAL

Chemicals used

Except for thorium and acetylacetone all chemicals employed were of analytical grade and were used without further purification or analysis.

Pure acetylacetone was prepared according to a method described elsewhere¹³. It was kept in benzene solution.

The thorium isotope Th^{234} (UX_1) is a natural disintegration product of U^{238} (UI), the most common uranium isotope. The uranium now produced for use in reactors contains no other beta active thorium isotope than Th^{234} and Th^{231} (UY), which is a disintegration product of U^{235} , and disintegrates by soft β -emission. When radioactive equilibrium exists between UI and UX_1 , 1 mg of uranium will give 738 beta particles per minute from UX_1 . The energy of these beta particles is too low (0.12 MeV) to be mea-

sured by common glass-wall GM-counters. However the next member in the disintegration series UX_2 (Pa^{234}) has a beta energy of 2.32 MeV, and this high energy makes it easily detectable. Radioactive equilibrium between UX_1 and UX_2 will be practically reached within 10 minutes; after this time the radioactivity of UX_2 indicates where UX_1 is to be found. The half-life of UX_1 is 24.1 days²¹.

Dyrssen¹⁴ has given a fairly simple method for preparing carrier-free UX_1 . A few grams of uranyl nitrate are shaken with some 10 ml of ether, previously saturated with water. In the small aqueous layer formed, practically all UX_1 is to be found. This aqueous phase is diluted with a few ml of 0.1 M HCl and run through an ion exchanger column (Wofatit KS): Th^{4+} (UX_1) and UO_2^{2+} are adsorbed. The uranyl ions are washed out with 2 M HCl. UX_1 is desorbed by 0.5 M oxalic acid, and the eluate is evaporated. The oxalic acid then sublimes, leaving carrier free UX_1 , which is dissolved in a small amount of strong $HClO_4$.

Distribution experiments

The two phases were prepared in a 60 ml separatory funnel in the following way:

To 0.03 ml of UX_1 solution, calculated amounts of water, $HClO_4$ and NaOH were added so as to give 15 ml solution of ionic strength 0.01 and the acidity desired. Finally 15 ml of benzene of a known acetylacetone concentration, $[HAA]_{be}^0$, was added.

The separatory funnels were sealed with glass stoppers and shaken for about 20 hours at $25.0 \pm 0.2^\circ C$. The loss of solution due to possible leakage was less than 0.1 %. The phases were allowed to separate in the thermostat, definite volumes of both phases were taken out, and their radioactivity I_{aq} and I_{be} was measured in a reproducible manner (see next section).

The pH of the aqueous phase was measured with a glass electrode and a standard pH-meter; the accuracy was ± 0.02 pH-units. From the amount of $HClO_4$ and NaOH added, and $[HAA]_{be}^0$, the pH could be roughly predicted for $pH \leq 4$, but not for higher pH. No buffer solutions were added since these might give complexes with Th^{4+} and thus compete with the acetylacetone; no complexes are formed between sodium and acetylacetone^{15, 16}.

The radioactive measurements

The radioactivity of UX_1 (or actually UX_2) could be measured either in the solution directly or after evaporation to dryness. The first method was found to be the most convenient.

The radioactive liquid to be measured is contained in a special "immersion cup". The arrangement with the GM-tube (Type B6, 20th Century Electronics, London; wall thickness about 30 mg/cm²) is shown in Fig. 1. When inserting the GM-tube in the immersion cup, liquid is pressed up and surrounds the sensitive part of the counter tube. The GM-tube is well centered in the cup, but separate experiments have shown that this is not too important. This is also to be expected since the mean range of beta particles from UX_2 is 3 mm in water, while the thickness of the liquid layer is about 1 mm.

On each cup a line has been etched. When liquid is filled to this line and the GM-tube is inserted, the liquid surface will reach the same height for different cups. As these cups are not exactly of the same internal diameter (± 0.2 mm) different cups will contain different volumes of liquid. In the experiment recorded in Fig. 2, different volumes of a solution of constant specific radioactivity were brought into a certain immersion cup, and the number of counts per minute, I , measured. On this cup the line was etched

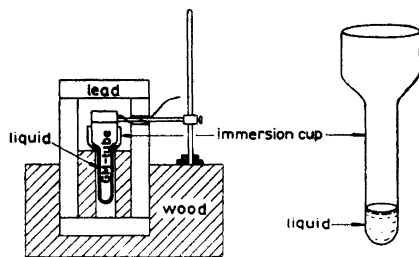


Fig. 1. The experimental arrangement with the GM-tube inserted in the immersion cup.

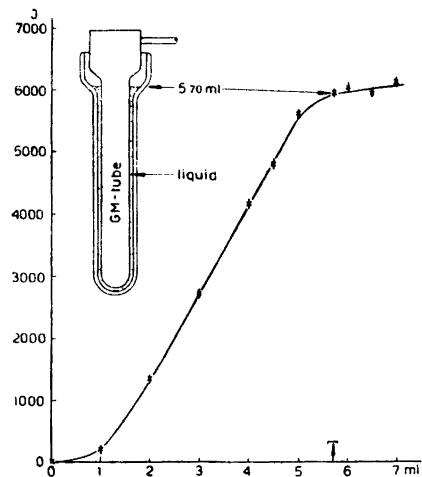


Fig. 2. The variation of radioactivity measured (I counts/minute) as a function of the volume in ml of an UX_1 -solution of constant specific activity.

at 5.7 ml, where a variation of ± 0.1 ml will change I by less than 1%. Due to the different volumes of liquid in the cups these have been calibrated against each other with a standard UX_1 -solution; this introduces the calibration factor, ψ . The ψ -scale was arbitrarily chosen by making $\psi = 1$ for one cup, the "standard immersion cup".

Before the measurements on UX_1 the cup is filled with pure water and the zero effect I_0 is determined. If the following measurement on the aqueous UX_1 -solution gives I_m , we have the corrected activity I_{aq} :

$$I_{aq} = \psi (I_m - I_0) \quad (18)$$

For the activity in the benzene phase an analogous equation is obtained; in this case the zero effect is taken on pure benzene. The radioactivity adsorbed on the glass wall of the GM-tube is desorbed by washing with $H_2SO_4 \cdot K_2Cr_2O_7$.

The deviations given in Table 1 are standard errors (the square root of the total number of counts divided by the time of measurement). Only in one case the activity was so high, that corrections for the resolving time of the counter had to be made.

To determine the efficiency of the counting arrangement an immersion cup was filled with a known amount of uranyl nitrate solution, and the radioactivity was measured; this gave 131 ± 1 counts/min. mg U. It is known that 1 mg U in equilibrium with UX_1 and UX_2 gives 738 beta UX_2 /min. From these two values we calculate that $131/738 = 17.8\%$ of all betas from UX_2 in the solution are counted by the electronic circuit.

From 1 g uranium, which was completely freed from thorium one year ago, there will now be about $7.2 \cdot 10^{-13}$ mol Th^{230} (I_0) + Th^{234} . This amount of Th will give approximately $7.4 \cdot 10^5$ β disintegrations/minute. We can now find for the standard immersion

cup, which has a $\psi = 1$ and a volume of 5.20 ml, that 1 count/min corresponds to $7.2 \cdot 10^{-13}/7.4 \cdot 10^5 \cdot 5.20 \cdot 10^{-3} \cdot 0.178 = 1.05 \cdot 10^{-15}$ mol Th/l. According to Equation (4a) this value must be A_{aq} ; thus we have

$$[\text{Th}]_{\text{aq, tot}} = 1.05 \cdot 10^{-15} \cdot I_{\text{aq}} \quad \text{mol/l} \quad (19)$$

The absorption of beta particles varies with the density of the absorber *e.g.* (17). The exponential relationship $I = I_0 \cdot e^{-ux}$, where x is the thickness in cm of the absorbing layer and u is the absorption coefficient, is roughly valid for beta particles. The mass absorption coefficient u/d , where d is the density, is nearly independent of the atomic number of the absorber. If E_m is the maximum energy of the betas, one can use the empirical relationship $E_m^{1.33} \cdot u = 22 \cdot d$ to find u . For $E_m = 2.32$ MeV and $d_{\text{be}} = 0.897$ we can calculate $I/I_0 = 0.697$ for a water layer of 0.5 mm, and 0.729 for a benzene layer of the same thickness. This means that the absorption of beta particles from UX_2 in 0.5 mm of water is 0.729/0.697 times that in benzene. If the experimental conditions are the same for the measurements on the benzene solution to those for the aqueous solution, we have $A_{\text{be}} = A_{\text{aq}} \cdot 0.697/0.729$, or $A_{\text{be}} = 1.00 \cdot 10^{-15}$ mol. min/l. counts. Thus we have

$$[\text{Th}]_{\text{be, tot}} = 1.00 \cdot 10^{-15} \cdot I_{\text{be}} \quad \text{mol/l} \quad (20)$$

ANALYSIS OF THE DISTRIBUTION CURVE

In Table 1 the experimental data ($[\text{HAa}]_{\text{be}}^\circ$, pH, I_{be} , I_{aq}) are tabulated. From pH and $[\text{HAa}]_{\text{be}}^\circ$ we can calculate $[\text{HAa}]_{\text{aq}}$ and pAa by means of Equation (15). With Equation (8) I_{be} and I_{aq} gives q . The symbols in the last column of Table 1 are the same as shown in Fig. 3, where $\log q$ is given as a function of pAa (this curve will be referred to as the "distribution curve"). Table 1 is divided in five sections, each representing a definite pH-range.

In Fig. 3 almost all points are on one continuous curve. For the five symbols $\#$ and \blacktriangle the concentration of acetylacetone in the benzene phase is 5-molar; *i. e.* the benzene solution consists of 50% acetylacetone. The q measured for these points is not the distribution of UX_1 between benzene and water, but the distribution between 50% benzene + 50% acetylacetone and water. Thus the low values of q obtained here are either due to that ThAa_4 is more soluble in benzene than in acetylacetone, which seems improbable, or that ThAa_4 is less soluble in pure water than in water containing much acetylacetone. These five q values have not been used in the calculation of the complex constants.

In the deduction of Equation (10a) it was pointed out that if the thorium hydrolysis influences the equilibrium between thorium and acetylacetone, different curves $q = f[\text{Aa}]$ should be obtained for different pH. At pH > 3 the thorium hydrolysis is considerable¹⁸. As the pH was widely different

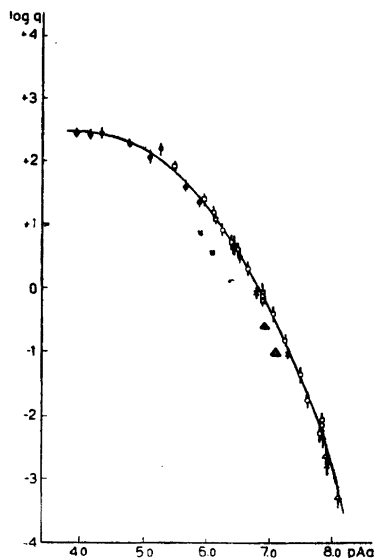


Fig. 3. The distribution of UX_1 between benzene and water (q) as a function of the concentration of acetylacetonate ions ($pAa = -\log[Aa^-]$). The different signs relate to pH-values according to Table 1: Δ pH \approx 2; \times pH \approx 3; \circ pH \approx 4; \square pH \approx 5; \bullet pH \approx 6. The curve was drawn to fit the experimental points; it was used for calculating κ_n by method A.

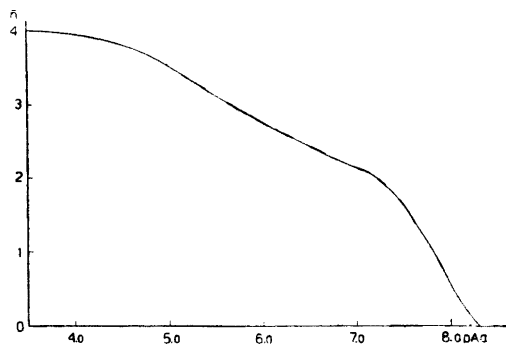


Fig. 4. The average number of ligands per central atom (\bar{n}) as a function of the concentration of free ligand ($pAa = -\log[Aa^-]$), calculated from the smooth curve in Figure 3.

in the five series of measurement (see Table 1) the curvature in Fig. 3 can not be due to the thorium hydrolysis, but solely to the complex formation between thorium and acetylacetone.

It is shown in Equation (17) that at constant pH and pAa, q will be a function of $[Th]$ if polynuclear complexes are formed. A separate investigation at pH 3 and pAa 6.9 showed that a variation of I_{aq} from 10 to over 1,000 counts/min had no influence on q , which was about 1. It is thus concluded that no polynuclear complexes are formed at these low concentrations.

THE CALCULATION OF COMPLEX CONSTANTS FROM THE DISTRIBUTION CURVE

It is clear from the considerations in the preceding section that hydrolysis and polynuclear complexes can be neglected; then Equation (10b) is valid. There are many ways to evaluate the constants in this equation; here two independent methods will be used.

A. The ligand number \bar{n} is generally defined as the mean number of ligands per central atom. In our case we have

$$\bar{n} = \sum n[\text{ThAa}_n]_{\text{aq}} / [\text{Th}]_{\text{aq, tot}} \quad (21)$$

The fraction of Th present in form of the n^{th} complex is

$$\alpha_n = [\text{ThAa}_n]_{\text{aq}} / [\text{Th}]_{\text{aq, tot}} \quad (22)$$

Comparing this with Equations (6) — (9) we find that

$$q = \alpha_n \cdot \lambda'_4 \quad (23)$$

From Equations (21) and (22) we can deduce

$$\bar{n} = n + d(\log \alpha_n) / d(\text{pAa}) \quad (24)$$

which gives together with (23)

$$\bar{n} = 4 + d(\log q) / (d\text{pAa}) \quad (25)$$

Fig. 3 shows $\log q$ as a function of pAa . By graphical derivation of this curve using Equation (25) we can obtain $\bar{n} = f(\text{pAa})$, the complex formation curve, which is shown in Fig. 4. We transform Equation (21) to a form more suitable for mathematical treatment⁽³⁾:

$$\bar{n} + (\bar{n} - 1) \kappa_1 [\text{Aa}] + (\bar{n} - 2) \kappa_2 [\text{Aa}]^2 + (\bar{n} - 3) \kappa_3 [\text{Aa}]^3 + (\bar{n} - 4) \kappa_4 [\text{Aa}]^4 = 0 \quad (26)$$

Each point on the curve in Fig. 4 will give an equation of this kind. Four points on the curve will suffice for the determination of all the constants; we take $\bar{n} = 0.5, 1.5, 2.5$ and 3.5 . The solution of the set of equations thus obtained is achieved by using determinants. From these values of κ_n we use Equation (11) to calculate φ_n , and thus obtain the following values:

$$\varphi_1 = 1.13 \cdot 10^{-5}, \quad \varphi_2 = 4.38 \cdot 10^{-12}, \quad \varphi_3 = 1.63 \cdot 10^{-19}, \quad \varphi_4 = 1.15 \cdot 10^{-27}.$$

The values $\bar{n} = n - 0.5$ are taken because at each of these points two complexes dominate, and the errors from the presence of the other complexes are negligible. Consequently we find

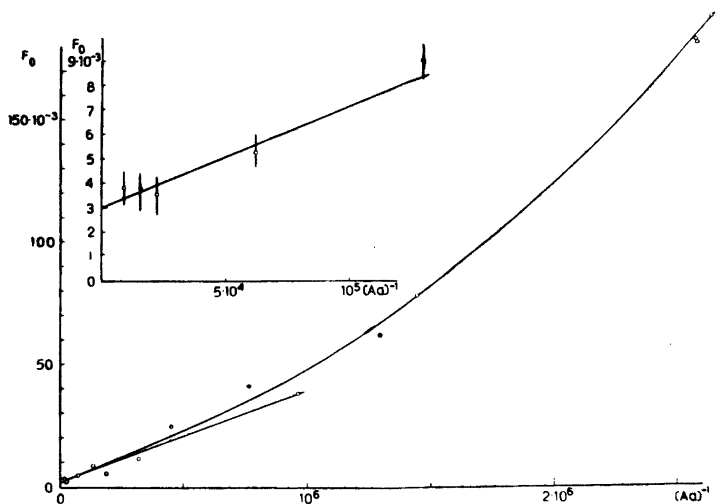


Fig. 5. The variation of $F_0 = 1/q$ with $[Aa]^{-1}$ calculated from the experimental points in Figure 3. The intercept on the F_0 -axis gives $1/\lambda'_4$ and the slope of the curve at this point is φ_1/λ'_4 .

$$[Aa]_n^{-1} = n - 0.5 \approx \kappa_n \kappa_{n-1}^{-1} = k_n \quad (27)$$

where k_n is called the complex formation constant:

$$k_n = [\text{ThAa}_n] [\text{ThAa}_{n-1}]^{-1} [Aa]^{-1} \quad (28)$$

B. Before proceeding to calculate the complex formation constants, we will see what values of φ_n will be obtained by the second method, which is analogous to that used by Leden⁹; with this method the influence of the experimental errors is more clearly seen, and the uncertain procedure of taking derivatives on a smoothed curve is avoided.

Equation (12b) is transformed to

$$F_0 = 1/q = (1 + \varphi_1 [Aa]^{-1} + \varphi_2 [Aa]^{-2} + \varphi_3 [Aa]^{-3} + \varphi_4 [Aa]^{-4}) \lambda'_4{}^{-1} \quad (29)$$

In Table 2 F_0 and $[Aa]^{-1}$ are calculated from the data in Table 1 (not from the smooth curve in Fig. 3). In Fig. 5 F_0 is given as a function of $[Aa]^{-1}$. The intercept on the F_0 -axis gives $1/\lambda'_4$ and the slope of the curve at this point gives φ_1/λ'_4 according to Equation (29). We then get $\lambda'_4 = 330 \pm 30$ and $\varphi_1 = (1.2 \pm 0.2)10^{-5}$.

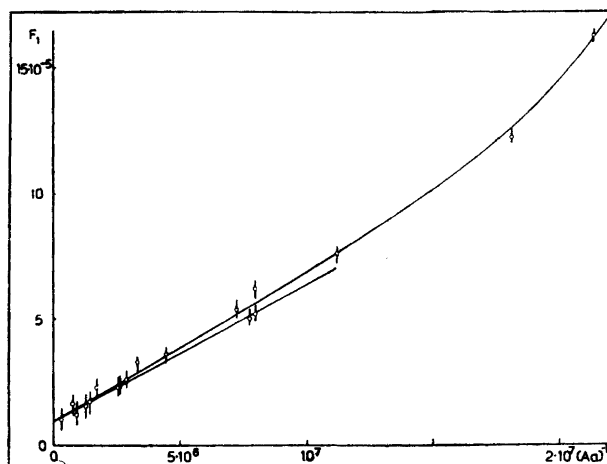


Fig. 6. F_1 calculated according to Equation (30) as a function of $[Aa]^{-1}$. The intercept on the F_1 -axis gives φ_1 and the slope of the curve at this point φ_2 .

In an analogous manner we derive functions $F_1, F_2, etc.$,

$$F_1 = \left(\frac{\lambda'_4}{q} - 1\right) [Aa] = \varphi_1 + \varphi_2 [Aa]^{-1} + \varphi_3 [Aa]^{-2} + \varphi_4 [Aa]^{-3} \quad (30)$$

$$F_2 = (F_1 - \varphi_1) [Aa] = \varphi_2 + \varphi_3 [Aa]^{-1} + \varphi_4 [Aa]^{-2} \quad (31)$$

The values of F_1 and F_2 are found in Table 2. In Figs. 6 and 7 they are given as functions of $[Aa]^{-1}$. From Fig. 6 we obtain $\varphi_1 = (1.0 \pm 0.1) 10^{-5}$ and $\varphi_2 = (5.4 \pm 0.3) 10^{-12}$. This φ_1 is somewhat lower than the φ_1 obtained from Fig. 5, but as it is more accurate it has been used for the calculation of F_2 . From Fig. 7 we have $\varphi_2 = (5 \pm 1) 10^{-12}$; no calculation of F_3 has been done because the errors will be too great. As the value of φ_2 from Fig. 6 is more exact than that from Fig. 7, the value $\varphi_2 = (5.4 \pm 0.3) 10^{-12}$ has been accepted.

As the errors in the calculation of F_2 are considerable, no attempt to find F_3 and F_4 has been done. To obtain φ_3 and φ_4 we deduce

$$F_5 = \left(\frac{\lambda'_4}{q} - 1\right) [Aa]^4 = \varphi_4 + \varphi_3 [Aa] + \varphi_2 [Aa]^2 + \varphi_1 [Aa]^3 \quad (32)$$

F_5 is calculated in Table 2 and given as a function of $[Aa]$ in Fig. 8. From this curve we find $\varphi_4 = (1.5 \pm 0.5) 10^{-27}$ and $\varphi_3 = (1.0 \pm 0.2) 10^{-19}$.

Table 1. Calculation of the distribution curve from experimental data.

pH	[HAA] _{bc} ⁰	[HAA] _{aq}	pAa	I_{bc}	I_{aq}	q	$\log q$	
1.90	0.605	0.087	8.10	10 ± 1	18200	0.00055	- 3.26	△
1.98	6.73	0.967	6.97	282	1179	0.240	- 0.62	▲
1.98	5.38	0.775	7.07	81	826	0.098	- 1.01	▲
2.00	0.865	0.124	7.85	6.7 ± 3	1510	0.0044	- 2.30	△
1.94	0.865	0.124	7.89	2.7 ± 1	1106	0.0024	- 2.70	△
3.06	6.73	0.967	5.89	1030	143	7.20	+ 0.86	#
2.88	6.73	0.967	6.07	1290	359	3.59	+ 0.56	#
2.66	5.38	0.775	6.39	750	595	1.26	+ 0.10	#
2.99	0.865	0.124	6.86	429	511	0.84	- 0.08	×
2.98	0.288	0.0415	7.33	81 ± 5	856	0.095	- 1.02	×
3.20	0.0450	0.0065	7.93	1.6 ± 1.2	974	0.0016	- 2.70	×
3.74	0.865	0.124	6.11	1238	78 ± 1	16.0	+ 1.20	○
3.72	0.806	0.116	6.16	1253	99 ± 8	12.7	+ 1.10	○
3.90	0.450	0.0645	6.23	474	59 ± 3	8.03	+ 0.90	○
4.02	0.225	0.0323	6.41	468	86	5.45	+ 0.74	○
3.85	0.323	0.0465	6.42	1047	203	5.16	+ 0.71	○
3.86	0.288	0.0465	6.46	996	223	4.33	+ 0.64	○
4.00	0.134	0.0193	6.65	1120	560	2.00	+ 0.30	○
4.05	0.0673	0.0097	6.90	339	430	0.79	- 0.10	○
3.90	0.0673	0.0097	7.05	290	752	0.386	- 0.41	○
3.75	0.0578	0.0083	7.26	92 ± 5	617	0.149	- 0.82	○
3.93	0.0225	0.00323	7.50	35 ± 2	814	0.043	- 1.37	○
3.70	0.0278	0.00397	7.63	11 ± 3	635	0.0173	- 1.76	○
4.00	0.0090	0.00129	7.83	4.3 ± 2.0	867	0.0050	- 2.30	○
3.88	0.0092	0.00133	7.85	4.0 ± 2.0	471	0.0084	- 2.10	○
3.98	0.0090	0.00129	7.85	5.7 ± 2.0	791	0.0072	- 2.15	○
4.93	0.225	0.0323	5.50	1100	14 ± 2	79.0	+ 1.90	□
4.97	0.0673	0.0097	5.98	790	31 ± 2	25.7	+ 1.41	□
4.54	0.0673	0.0097	6.41	668	120	5.57	+ 0.75	□
4.54	0.0225	0.00323	6.89	282	333	0.848	- 0.07	□
4.75	0.0134	0.00194	6.90	228	342	0.667	- 0.18	□
5.92	0.865	0.124	3.93	2210	8.5 ± 0.9	260	+ 2.42	●
5.69	0.806	0.116	4.18	1432	5.4 ± 2.0	265	+ 2.42	●
6.62	0.0673	0.0097	4.33	915	3.2 ± 1.8	285	+ 2.45	●
6.64	0.0225	0.00323	4.79	689	3.6 ± 1.5	190	+ 2.28	●
5.84	0.0673	0.0097	5.11	720	6.7 ± 3.0	110	+ 2.04	●
5.68	0.0673	0.0097	5.27	1190	7.2 ± 2	165	+ 2.18	●
6.00	0.0134	0.00193	5.65	247	6.4 ± 2	38.6	+ 1.59	●
5.55	0.0225	0.00323	5.88	562	23 ± 2	24.4	+ 1.38	●
5.61	0.0045	0.00065	6.52	720	241	3.0	+ 0.48	●

Table 2. Calculation of F_n from the data in Table 1 according to Equations (29)–(32).
 In Figures 5 to 8 these F_n are used for the determination of φ_n .

[Aa]	1/[Aa]	F_0	F_1	F_2	F_5
$11.8 \cdot 10^{-5}$	$8.5 \cdot 10^3$	0.00385			
6.62	15.1	0.00377			
4.67	21.4	0.00351			
1.62	61.6	0.00526			
$78.0 \cdot 10^{-7}$	$1.29 \cdot 10^5$	0.00909			
53.8	1.86	0.00606			
31.6	3.16	0.01266	$10.04 \cdot 10^{-6}$		
22.4	4.47	0.02564	16.71		
13.2	7.59	0.04167	16.83		
10.46	9.56	0.03846	12.23	$2.33 \cdot 10^{-12}$	
7.75	12.9	0.06250	15.21	4.04	
6.94	14.4	0.07874	17.34	5.09	
5.88	17.0	0.1245	23.6	8.00	
3.89	25.7	0.1828	23.1	5.10	
3.89	25.7	0.1835	23.2	5.13	
3.80	26.3	0.1938	23.9	5.28	
3.47	28.8	0.2309	26.1	5.59	
3.02	33.1	0.333	32.9	6.92	
2.24	44.6	0.500	36.7	5.98	$41.2 \cdot 10^{-26}$
1.38	72.4	1.190	54.1	6.09	14.3
$12.89 \cdot 10^{-8}$	77.5	1.179	50.0	5.16	10.7
12.59	79.4	1.250	51.9	5.28	10.34
12.59	79.4	1.50	62.2	6.57	12.4
8.93	$1.12 \cdot 10^7$	2.59	76.3	5.92	5.39
5.49	1.82	6.71	$1.215 \cdot 10^{-4}$	6.12	2.02
4.67	2.14	10.5	1.616	6.61	1.65
3.16	3.16	23.3	2.43	7.36	0.77 ± 0.05
2.34	4.27	57.8	4.46	10.20	0.58 ± 0.14
1.48	6.76	200	9.77	14.31	0.32 ± 0.15
1.41	7.07	227	10.56	14.75	0.30 ± 0.10
1.41	7.07	118	5.48	7.59	0.16 ± 0.06
1.41	7.07	140	6.51	9.04	0.18 ± 0.07
1.29	7.75	417	17.75	22.77	0.38 ± 0.12
1.27	7.85	625	26.20	33.1	0.54 ± 0.40
0.79	12.6	1820	47.4	37.4	0.24 ± 0.02

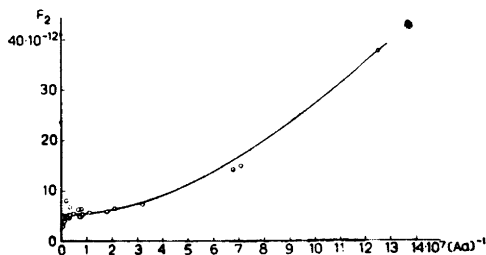


Fig. 7. F_2 calculated according to Equation (31) as a function of $[Aa^-]^{-1}$. The intercept on the F_2 -axis gives an approximate value of φ_2 ; the scattering of the points is too great to make any calculation of φ_3 possible from the slope of the line at $F_2 = 0$.

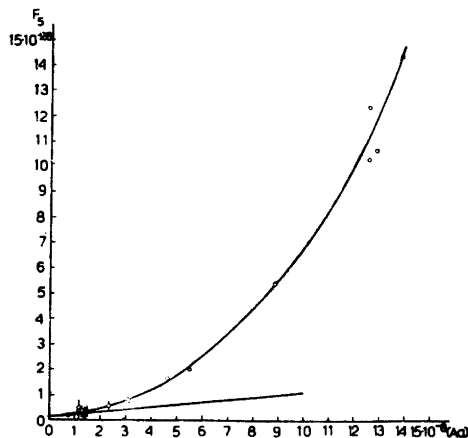


Fig. 8. F_5 calculated with Equation (32) as a function of $[Aa^-]$. The intercept on the F_5 -axis gives φ_4 and the slope of the line φ_3 . The values of F_5 are given in Table 2.

Table 3. Comparison of φ_n obtained by method A and B.

	Method A	Method B
φ_1	$1.13 \cdot 10^{-5}$	$(1.0 \pm 0.1) 10^{-5}$
φ_2	$4.38 \cdot 10^{-12}$	$(5.4 \pm 0.3) 10^{-12}$
φ_3	$1.63 \cdot 10^{-19}$	$(1.0 \pm 0.2) 10^{-19}$
φ_4	$1.15 \cdot 10^{-27}$	$(1.5 \pm 0.5) 10^{-27}$

In Table 3 the values of φ obtained by the two methods are compared. These values have been used in Equation (12b) to calculate q as a function of $[Aa]$. The two resultant curves, q_A and q_B , are shown in Fig. 9, where the symbols are taken from Table 1. The difference between the two curves is very small; the closest agreement to the measured points is given by q_B . With the values from Method B k_n is calculated:

$$\begin{aligned}
 k_1 &= (0.7 \pm 0.3) 10^8 && 1/\text{mol} \\
 k_2 &= (5.4 \pm 1.7) 10^7 && \text{»} \\
 k_3 &= (1.9 \pm 0.3) 10^6 && \text{»} \\
 k_4 &= (1.0 \pm 0.1) 10^5 && \text{»}
 \end{aligned}$$

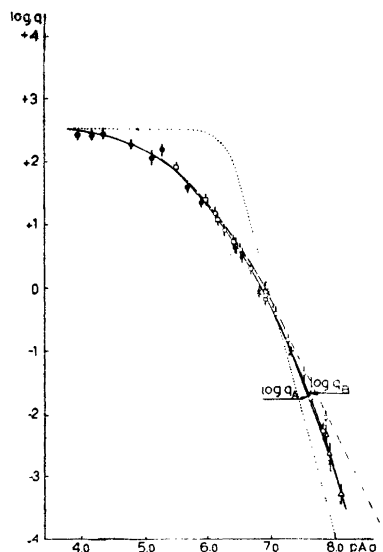


Fig. 9. $\log q$ is calculated as a function of pAa under the following assumptions: The only thorium species existing in the aqueous phase are a) Th^{4+} and $ThAa_4$ (.....); b) $ThAa_4$, $ThAa_3^+$, $ThAa_2^{2+}$ (---); c) all species $ThAa_n^{4-n}$ for $0 \leq n \leq 4$ (—). The experimental points are the same as in Figure 3.

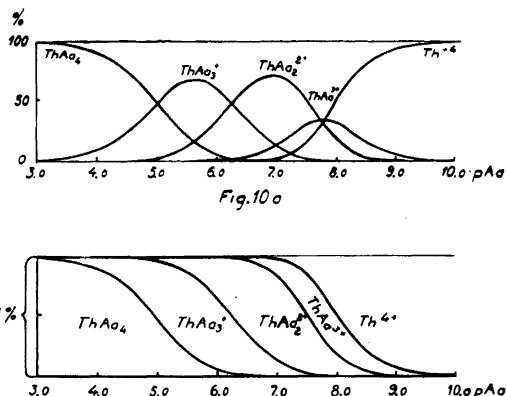


Fig. 10 a and Fig. 10 b. The percentage of the different complexes as a function of the concentration of acetylacetonate ions ($pAa = -\log [Aa^-]$) in two different graphical representations: in a) the percentage of a complex for a certain pAa is the height of the curve over the zero line; in b) the percentage is the length of the vertical line at this pAa which falls in the area of that complex.

Equation (22) is transformed to

$$\alpha_n = \frac{\varphi_{4-n} [Aa]^{n-4}}{\varphi_4 [Aa]^{-4} + \varphi_3 [Aa]^{-3} + \varphi_2 [Aa]^{-2} + \varphi_1 [Aa]^{-1} + 1} \quad (33)$$

α_n is calculated with φ from method B. Fig. 10a gives directly the percentage of the n^{th} complex ($= 100\alpha_n$) at a certain pAa . The same result is given in an other graphical representation in Fig. 10b; the percentage of a complex is here given by the height of the vertical line which falls in the region of that complex for a certain pAa . Thus the areas in Fig. 10b gives the ranges of existence of the individual complexes.

The true distribution factor of $ThAa_4$ between benzene and water is given by Equation (9), where $A_{bc}/A_{aq} = 0.96$ and $\lambda'_4 = 330 \pm 30$. We then have $\lambda_4 = 315 \pm 30$. This may be compared with the value of 80 for the distri-

bution of PuAa_4 between benzene and water, found by Harvey *et al.*¹⁹ However they report no data on the concentration of acetylacetone.

DISCUSSION

In the calculations made here it has been presumed from the beginning that all complexes ThAa_n^{4-n} should exist. Attempts have been made to find if any complexes could be eliminated.

If we assume that the equilibrium between thorium and acetylacetone in water is completely described by



we can deduce the equation

$$\left(\frac{\lambda'_4}{q} - 1\right) [\text{Aa}]^4 = \kappa_4^{-1} \quad (34)$$

Comparing Equations (32) and (34) it is seen that $F_5 = \kappa_4^{-1}$, if Equation (34) is valid. In Table 2 the values for F_5 are given; as no constant value is obtained, it may be concluded that the assumption for the deduction of Equation (34) is certainly wrong. The dotted line in Fig. 9 gives q as a function of $[\text{Aa}]$ according to Equation (34); κ_4^{-1} was chosen $3.3 \cdot 10^{-26}$. If the κ_4^{-1} value is varied the curve will be displaced along the pAa-axis retaining its form constant. It is easily seen that a good agreement with the measured q cannot be obtained.

If we assume that $[\text{Th}] = [\text{ThAa}] = 0$, we can obtain a curve, which fits the upper part of the experimental distribution curve very well; this gives the dashed line in Fig. 9. However the agreement with the experimental points is bad for $\log q < 0$. Thus it may be concluded that all species Th^{4+} , ThAa^{3+} , ThAa_2^{2+} , ThAa_3^+ and ThAa_4 exist in the aqueous solution.

If negatively charged complexes like ThAa_5^- , ThAa_6^{2-} , *etc.*, were formed, q should reach a maximum at a certain pAa, and then decrease for higher concentrations of Aa^- . From Fig. 3 it is seen that q approaches to a maximum. It has not been possible to make measurements on higher $[\text{Aa}]$ than $\approx 10^{-4}$, and negative complexes may exist at still higher $[\text{Aa}]$. It is unlikely on steric grounds, however, that negative complexes are formed. The present results give no evidence of higher complexes than ThAa_4 .

SUMMARY

The complexes of Th^{4+} and acetylacetonone (HAA) in aqueous solution have been investigated by measuring the distribution of tracer amounts of Th^{234} (UX_1) between benzene and aqueous solutions of various $[\text{Aa}^-]$. The measurements have been performed at 25°C and at an approximately constant ionic strength of 0.01 mol/l , which was brought about by adding HClO_4 and NaOH . The hydrolysis of Th^{4+} was found to be negligible, and no polynuclear complexes seemed to be formed at these low concentrations. The results could be explained only by assuming that all complexes ThAa^{3+} , ThAa_2^{2+} , ThAa_3^+ and ThAa_4 exist. The constants for the stepwise addition of Aa^- to Th^{4+} (k_1, k_2, \dots) and those for the over all addition ($\kappa_1, \kappa_2, \dots$) were calculated by two independent methods, and consistent results were obtained;

$$\begin{array}{ll} k_1 = (0.7 \pm 0.3) 10^8 & \kappa_1 = 0.7 \cdot 10^8 \\ k_2 = (5.4 \pm 1.7) 10^7 & \kappa_2 = 3.8 \cdot 10^{15} \\ k_3 = (1.9 \pm 0.3) 10^6 & \kappa_3 = 7.2 \cdot 10^{21} \\ k_4 = (1.0 \pm 0.1) 10^5 & \kappa_4 = 7.2 \cdot 10^{26} \end{array}$$

The distribution constant of ThAa_4 between benzene and water was found to be $\lambda_4 = 315 \pm 30$.

I wish to thank the head of FOA 1, Professor Gustav Ljunggren, for helping me in many ways, and Professor Arne Ölander for the interest he has shown in this work. I am greatly indebted to Professor Lars Gunnar Sillén for the many valuable suggestions, which have proved so helpful to me. With my friends Laborator Roland Rynninger and Fil.mag. David Dyrssen I have had many fruitful discussions.

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