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NITRATO NITROSYLRUTHENIUM COMPLEXES AND THEIR EXTRACTION FROM NITRIC ACID SYSTEMS BY TRIBUTYL PHOSPHATE

PART I. LABORATORY STUDIES

by

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ABSTRACT

A separation of the individual nitrato nitrosylruthenium complexes which exist in aqueous nitric acid solutions has been achieved by paper chromatography, and the technique has also been applied to solutions of the complexes in TBP-HNO_3-H_2O systems. It has been possible to determine the equilibrium compositions of solutions of these complexes, the partition coefficients, with TBP, of the individual complexes under certain specified conditions, and the rates of the reactions by which there is interchange between the complexes. This knowledge has been used to interpret the overall ruthenium distribution coefficients which are obtained when solutions of these complexes, under a wide variety of concentrations of aqueous nitric acid and of TBP, are intimately mixed.

The conditions investigated are related to acid systems for the extraction by TBP of fissile material from nitric acid solutions of irradiated fuels: in such solutions, fission product ruthenium can occur, to a greater or lesser extent, as these nitrato (RuNO) complexes.

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1. INTRODUCTION

Over the past few years, several laboratories have investigated the problem of ruthenium decontamination in a Primary Separation Process by solvent extraction for the treatment of irradiated uranium fuels. Apart from work on "head-end" or pre-treatments to improve ruthenium decontamination, studies on fuel solutions, some synthetic, some actual, have been reported by Aikin and Bruce at Chalk River(1), by Martin(2) and by Sangster(3) at A.E.R.E., by Woodward and Jamrack(4) and by Naylor(5) at Windscale as well as by a number of research workers in the U.S.A. Each piece of work has added knowledge to the ruthenium problem, but a complete understanding of the effect of dissolving and feed adjustment conditions on the species of ruthenium, and of the role in the extractor of such factors as concentration, residence time, temperature, on the ruthenium decontamination factors, has not emerged.

The work presented in this report is confined

(a) To studies with nitrato nitrosylruthenium complexes. Other ruthenium species, RuIV and nitro complexes of nitrosylruthenium, can be found as a result of the dissolution of irradiated metal fuels in nitric acid, but it is likely that batch or continuous dissolution in boiling nitric acid will produce feed solutions containing a substantial fraction of the ruthenium in the form of nitrato nitrosylruthenium complexes.

(b) To acid systems. Acid deficient systems have not been covered. When the pH of the solution is >1, ruthenium presents little or no problem since the nitrosylruthenium nitrato complexes are then almost completely hydrolysed to solvent inextractable polynuclear species.

(c) To tributyl phosphate (diluted with an inert paraffinic hydrocarbon) as the solvent.

(d) To ruthenium concentrations in the range 10^{-4} to 10^{-2} M. Concentrations of the order of 10^{-4}M apply to natural or near-natural uranium fuel irradiated under conditions which might prevail in power reactors: thus, with an irradiation of 3000 MWD/T, such a fuel gives, for a solution containing 200-300 gms U/1, a ruthenium concentration of 1 to 2 x 10^{-4}M. Ruthenium concentrations of the order of 10^{-3}M may occur from enriched fuels after high burn-up.

In this part, Part I, the characteristics of the various individual nitrato nitrosylruthenium complexes which have been recognised in aqueous and TBP solutions are given, together with the compositions of certain solutions at equilibrium, partition coefficients for the individual complexes, and the rates at which these complexes change into one another. These results refer to typical solutions containing nitric acid and in some cases uranium. The manner in which these complexes, and the reactions in which they are concerned, influence the overall distribution of ruthenium after aqueous and TBP phases are intimately mixed for various times is explained and illustrated.

Although the object of this study has been primarily directed towards an understanding of the behaviour of ruthenium in the first extractor of a TBP solvent extraction separation process, the data given on the various complexes and their properties are relevant to other conditions (e.g. second and subsequent TBP cycles, the treatment of fission product raffinates) in which nitrato nitrosylruthenium complexes exist.

In Part II, which will appear as a separate report, the behaviour of ruthenium (present as nitrato complexes of nitrosylruthenium in nitric acid - uranyl nitrate solutions) in miniature extractor runs carried out under a variety of Extractor I conditions will be reported and correlated with the properties of these complexes as set out in this Part.

2. THE NITROSYLRUTHENIUM NITRATO COMPLEXES FOUND IN SOLUTION

Previous work has indicated the existence in aqueous solution of a discrete number of complexes with characteristic solvent extraction properties(6). By techniques which involve solvent extraction either from two stirred phases or by elution on cellulose paper (paper partition-chromatography), quantitative data concerning certain properties of the complexes and of the amounts present under various conditions have now been obtained.

2.1 Experimental.

(a) Stock solutions of nitrosylruthenium nitrato complexes in nitric acid.

Various Ru^{106} labelled stock solutions in ~12M HNO_3, supplied by R.C.C. Amersham and used in miniature extractor runs (Part II), were the initial source of these complexes. For much of the work a single well-aged (> 3 months) stock solution, Solution X, of ruthenium concentration 1.33×10^{-2}M, in 11.3M HNO_3 was used: this was made by evaporation under atmospheric pressure of a mixture of several solutions, mainly in 1-3M HNO_3, in order to have a large bulk of a solution of fixed composition.

Although the formation and preservation of these nitrato complexes in nitric acid solution is relatively simple, there are conditions in which side reactions affect their purity and composition: thus exposure to atmospheric oxygen of solutions in >12M HNO_3 has been found to lead by way of a purple complex to ruthenium which is no longer nitrosylruthenium but is in a higher oxidation state. This side-reaction can be avoided by keeping such stock solutions in stoppered bottles protected from light. Also, a high temperature stage (e.g. by boiling) is necessary in the preparation of these solutions from nitrosylruthenium hydroxide in order to ensure decomposition of any polynuclear (RuNO) species. On the other hand, when solutions in 1-5M nitric acid are boiled, we have found a tendency for the nitrato (RuNO) complexes to be converted to nitro (RuNO) complexes owing to the unavoidable presence of traces of nitrous acid formed under such conditions: this reaction is prevented when the nitric acid concentration is sufficiently high. It follows that suitable stock solutions are those which contain 7-12M nitric acid and for which the final stage in their preparation has involved a heating stage in this acidity range. Such stock solutions are most conveniently made from other ruthenium compounds by way of RuO_4 which can be separated from an aqueous phase either by extraction with carbon tetrachloride or by distillation before being brought into contact with 7-12M nitric acid in the presence of oxides of nitrogen. The resulting solution should be heated for a few minutes to complete the conversion of ruthenium to the (RuNO) state. RuIV, which is the most likely contaminant, when present to an extent $>2 \times 10^{-4}$M, can be noticed visibly by its prominant brown colour: a more refined method for testing for freedom from RuIV is based on an examination of the absorption spectrum(7) of the solution.

The formation of nitro from the nitrato complexes was avoided in the experimental investigations by keeping stock solutions in darkness and by the use of reagents (nitric acid and organic solvents) of low nitrous acid content.

(b) Paper Chromatography.

The technique previously described(8) was employed: it has in some cases been slightly modified in that only 0.001 ml of the sample was applied to the Whatman CRL/1 paper strip. This gives a much better resolution of the complexes than that obtained when 0.01 ml samples are taken (Fig. 1). In all cases, methyl isopropyl ketone conditioned with 3M HNO_3 was used as the eluting solvent, and the time taken for elution was about 30 mins. The chromatograms were analysed for ruthenium by dividing the paper strip, in which the distance between the starting line and the solvent front was 8 cm, into 17 sections and β or γ counting each section for Ru^{106}. For reference purposes, the section to which the drop of liquid was applied is called Section 1, and the other sections are numbered consecutively up to the solvent front (Section 17).

2.2 Identification of Complexes.

An examination of typical paper chromatograms of solutions, derived from Solution X,

(i) In aqueous nitric acid (Figs. 1 and 2),

(ii) In tributyl phosphate solutions containing H_2O, HNO_3 and kerosene as a diluent (Fig. 3),

clearly indicates the existence of a limited number of forms with characteristic R_F values: it will be noticed that the resolution is better for TBP solutions than for aqueous solutions: in the latter, some interchange of species during the time of elution probably occurs. From the chromatograms of aqueous and TBP solutions it appears that there are four species, A, B, C and D (Table 1), which occur in both types of solution. The characterisation of these species, in terms of the particular nitrosylruthenium complexes given in Table 1, is based on the following supporting information:-

(a) When the solid trinitrato complex, $[RuNO(NO_3)_3(H_2O)_2]\ 2H_2O$, is dissolved in dry methyl isopropyl ketone, and this solution is applied to a paper strip and eluted by the standard method, ruthenium appears only on the solvent front ($R_F \sim 1$): this characterises Complex A.

(b) The proportions, at equilibrium, of species with high R_F values increases as the aqueous concentration of nitric acid increases (cf. Figs. 1 and 2).

(c) The existence of a mononuclear dinitrato complex can be deduced from the work of Jenkins and Wain(9).

(d) Observations, by paper chromatographic analysis, on the kinetics of decomposition and formation of the trinitrato species in dilute and concentrated nitric acid respectively, indicate that Complexes B and C are formed as intermediates in these reactions.

(e) The equilibrium between the complexes in 3M nitric acid is found, both by distribution measurement and by paper chromatography, to be independent of the total ruthenium concentration from $10^{-6}M$ to $3 \times 10^{-3}M$, e.g. values of the ruthenium distribution coefficient, for standard conditions of extraction (30 sec. stirring at 0°C, which is long enough

TABLE I

NITROSYLRUTHENIUM NITRATO COMPLEXES FOUND IN HNO_3-H_2O AND IN TBP-HNO_3-H_2O SOLUTIONS

Species	Complex	R_F Value[(a)] Applied in Aqueous	TBP Solution	Remarks
A	Trinitrato-aquo, $[RuNO(NO_3)_3(H_2O)_2]$	1.0	0.8 (b)	Occurs in aqueous and TBP phases with secondary solvation by H_2O or TBP respectively.
A'	Trinitrato-TBP, $[RuNO(NO_3)_3(TBP)_2]$	-	0.95	Slowly produced in TBP phases from A.
B	Dinitrato, $RuNO(NO_3)_2{}^+$ or $[RuNO(NO_3)_2OH(H_2O)_2]$	0.5 to 0.9 (c)	0.6	Occur in aqueous and TBP phases.
C	Mononitrato, $RuNO.NO_3{}^{2+}$ or $[RuNONO_3(OH)_2(H_2O)_2]$	0.2	0.2	
D	Non-nitrato or Trihydroxo, $RuNO^{3+}$ or $[RuNO(OH)_3(H_2O)_2]$	0 to 0.1	0 to 0.1	
E	Polynuclear	0	-	A range of complexes is likely in aqueous solutions.

Notes:

(a) The R_F values listed are for aliquots of either aqueous or 30% TBP/kerosene solutions applied to the paper and eluted with methyl isopropyl ketone under standard conditions at room temperature. Merely on account of the method of dividing the paper, values are subject to an error of ± 0.04.

(b) The lower R_F value from a TBP solution is due to the preferential extraction of TBP and kerosene which appear at the solvent front.

(c) A sharp peak is never found with the dinitrato complex in aqueous solution; it appears on a number of adjacent strips (Figs. 1 and 2).

(d) The Complexes B, C and D are represented both as charged cations (with the maximum charge possible) and as uncharged molecules. Charged forms predominate in aqueous nitric acid solutions, uncharged forms in TBP solutions.

to reach equilibrium between the phases for each complex but not long enough to allow significant interchange between the complexes within each phase), between 3M HNO_3 and 30% TBP are

Total Ru (M)	D_{Ru}
10^{-6}	0.120
10^{-5}	0.125, 0.128
10^{-4}	0.128
3×10^{-3}	0.120

The existence of appreciable quantities of species with different numbers of ruthenium atoms per molecule is therefore under these conditions thermodynamically excluded.

Except for low acid conditions (<0.1M HNO_3) when polynuclear complexes may be present, we are therefore mainly concerned with four discrete (RuNO) complexes which form a regular sequence from the non-nitrato complex to the trinitrato complex. Further points which concern these complexes in aqueous or in organic phases are discussed below.

2.3 Complexes in Aqueous Nitric Acid.

There is evidence from partition coefficients that in relatively concentrated nitric acid (>12M) there may be further nitration of the trinitrato complex with the replacement of one or both of the aquo groups to form the tetra- or pentanitrato complex. These would appear in paper chromatography with Complex A.

The non-nitrato complex, Complex D, is represented in Table I as being mononuclear. We have no positive evidence for this formulation: in view of the tendency of ruthenium as (RuNO) in organic media, and as RuIV in aqueous media, to form binuclear oxygen-bridged compounds, -Ru-O-Ru-, Complex D might equally well possess this structure, i.e. exist as aquo-cations, $[RuNO{-}O{-}RuNO]^{n+}$ where n is 6 or less, or as the unionised molecule $[RuNO(OH)_2(H_2O)_2.O.RuNO(OH)_2(H_2O)_2]$.

The polynuclear complexes (E of Table I) can be a mixture of complexes of various molecular weights all relatively inextractable from aqueous solution by organic solvents. Rather stable polymers occur with PuIV in solutions below 0.1M in HNO_3 and with ZrIV in solutions below 1M in HNO_3: comparable polymers have not been found during this work though they may exist in solutions of nitrosylruthenium hydroxide in cold dilute nitric acid. However, condensation, e.g. by (OH) bridging, to simple polynuclear forms has been postulated for a number of partially hydrolysed cations, and we suggest that the same phenomenon occurs with the non-nitrato complex. These polymers, unlike "colloidal" PuIV, are depolymerised at a finite rate by cold 7-12M nitric acid (para. 5).

2.4 Complexes in TBP Solutions.

(a) Aquo-complexes.

When solid (RuNO) nitrato complexes are freshly dissolved in TBP solutions, or when the nitrato complexes have just been extracted from an aqueous phase, the complexes appear to enter the organic phase in the first place as solvated aquo-complexes, e.g. as TBP solvated $[RuNO(NO_3)_3(H_2O)_2]$.

Ligand substitution in nitrosylruthenium complexes is a relatively slow process: when aqueous phases containing nitrato nitrosylruthenium complexes are vigorously stirred with immiscible organic solvents such as TBP, they are extracted in a few seconds and there is no significant variation in the ruthenium distribution coefficient at 0° for stirring times from 10-60 secs., i.e. the individual complexes are at equilibrium across the phase boundary, but they are not at equilibrium with each other within the phases and secondary changes occur for more prolonged stirring times. The complexes first extracted into the organic phase are therefore regarded as containing the original aquo groups around the central ruthenium atom. When subjected to paper chromatography, it is natural that such aquo-complexes give almost identical R_F values irrespective of whether they are applied in an aqueous or TBP phase (cf. Figs. 1 and 2 with Fig. 3). The main evidence for the presence of an average of two solvating TBP molecules is derived from the work of Martin(2) who found that the ruthenium distribution coefficients between 6M sodium nitrate and 2 to 30% TBP were approximately proportional to the square of the TBP concentration (extraction of mixtures of the mono-, di- and trinitrato complexes occurred). While partition coefficients obtained in this work for the di- and trinitrato complexes would support this view (para. 4.1), it must be realised that our measurements were made with rather higher concentrations of TBP than are desirable for the strict derivation of the degree of TBP complexing by this method.

(b) Non-Aquo-Complexes.

On ageing in a separated TBP phase, the above-mentioned aquo-complexes undergo a slow change. It is found that the new complex (or complexes) formed has an increased tendency to remain in an organic phase: the ruthenium distribution coefficient for standard conditions increases and, in paper chromatography, a new peak, even closer to the solvent front than that for the trinitrato-diaquo complex, appears, and grows with time (Fig. 4): the proportions of the lower nitrato complexes correspondingly decrease with time. Martin(2) suggested that the changes on ageing in TBP solutions are related to changes in TBP complexing, and postulated that a 2 TBP complex is converted to a 4 TBP complex. While accepting the principle that TBP complexing is involved, we view this reaction as a further example of slow ligand substitution around the central ruthenium atom, in this case the displacement of aquo by TBP groups giving Complex A', the non-aquo TBP complex $[RuNO(NO_3)_3(TBP)_2]$. This hypothesis is supported

(i) by the evidence of Sangster(3) who found that the equilibrium in this reaction is proportional to the square of the free* TBP concentration;

(ii) by the formation in some cases of a separate aqueous phase during ageing (para. 3.6); and

(iii) by the reaction being slowly reversed when the water concentration in the TBP phase is artificially increased.

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* Throughout this paper, "free TBP" is defined as the TBP uncomplexed by nitric acid or by uranyl nitrate.

Theoretically, mono- and dinitrato TBP complexes may also exist in such aged solutions. Histograms derived from paper chromatography of aged TBP solutions do not provide any clear evidence on this point and such complexes have therefore been excluded from Table I.

It must be remembered that the TBP solutions under consideration contain substantial amounts of nitric acid and water as well as any diluent such as kerosene. Aquo-complexes freshly extracted into the solvent phase are unlikely to be present in the proportions appropriate to equilibrium in the solvent phase. Relatively slow nitration and denitration reactions between the mono-, di- and trinitrato aquo-complexes occur in a TBP phase as in an aqueous phase, and it is found that the slow formation of the trinitrato TBP complex is linked with a decrease in the proportions of the lower nitrato complexes, i.e.,

$$\begin{tikzcd} \text{Mononitrato aquo-complex)} & \\ \text{Di- " " ")} \arrow[r, "HNO_3"] & \text{Trinitrato aquo-complex} \arrow[d, "TBP"] \\ & \text{Trinitrato TBP complex.} \end{tikzcd}$$

The presence of uranyl nitrate, or other nitrates which reduce the water concentration in the TBP phase, favours these reactions, but the conditions which obtain when the TBP phase is washed (or stripped) with water or dilute nitric acid lead to their slow reversal.

It will be noted that we have rejected the possibility that on ageing there is the formation of tetra- or pentanitrato complexes in a TBP phase by a reaction such as

$$HNO_3 + [RuNO(NO_3)_3(H_2O)_2].\ 2\ TBP \longrightarrow H[RuNO(NO_3)_4H_2O].\ 2\ TBP + H_2O.$$

In the analogous case of uranyl nitrate, pseudo-anionic metal complexes such as $H[UO_2(NO_3)_3]$ exist in some organic solvents, but are absent in TBP solutions in which $[UO_2(NO_3)_2(TBP)_2]$ only is found.(19)

We have attempted to prepare Complex A' by saturating dry 100% TBP with the trinitrato complex, $[RuNO(NO_3)_3(H_2O)_2].2H_2O$. The product, after centrifugation from the aqueous slurry formed was found to contain RuNO : NO_3 : : 1 : 2 and is thought to contain the binuclear structure $(NO_3)_2NO.Ru.O.RuNO(NO_3)_2$; this resembles the binuclear structure in other (RuNO) complexes, e.g. $Ru_2N_6O_{15}$ (6), prepared in organic media. It is therefore possible that Complex A' is itself binuclear or is slowly converted to a binuclear form.

3. EQUILIBRIUM CONDITIONS FOR (RuNO) NITRATO COMPLEXES

Equilibrium between uranyl nitrato complexes is established extremely rapidly in solution; in solvent extraction processes, the residence time per stage is at least of the order of seconds and therefore equilibrium conditions for uranyl nitrate are reached in each stage. With nitrosylruthenium complexes the rates of nitration and denitration are relatively slow (para. 5): with mixing and settling times per stage of the order of a few minutes, equilibrium conditions are unlikely to be established at room temperature. With these "inert" complexes, we are dealing with a case which is intermediate between that of mixtures of uranyl nitrato complexes (and similar "labile" complexes) and that of mixtures of stable organic compounds.

3.1 Experimental and Techniques.

Ruthenium distribution measurements and paper chromatography have been used to obtain the proportions of the various (RuNO) nitrato complexes at equilibrium in solution.

(a) Solutions Used.

Equilibria have been studied in detail for solutions made by the addition of water or concentrated nitric acid to Solution X; these were subsequently aged at least 24 hours at room temperature. Solution X (11.3M HNO_3) after long ageing contained about 4% of "inextractable" material (Table II A); this is attributed to the presence of RuIV, firstly because the amount present was found to be invarient with acidity over the range 9 to 15M HNO_3, and secondly because the cherry-red colour of the trinitrato complex in solution was visibly masked by the characteristic brown colour of RuIV nitrates which have a high molar extinction coefficient.(7)

(b) Distribution Measurements.

The information obtainable from a simple distribution measurement between two phases of say equal volume is, in this case, limited, because numerous discrete complexes are involved. It has therefore been necessary to employ a method (Martin's method(6,10), subsequently used by Sangster(3)) in which the ruthenium concentrations in the aqueous and organic phases are measured at various values of the ratio V, where

V = (volume of solvent phase) / (volume of aqueous phase);

Fig. 5 shows a typical example in which V has been varied from 0.2 to 8. It is possible, with two species of widely different extractability, to calculate from the results their separate partition coefficients and relative proportions for the given conditions, and to assess the total proportion of "inextractable" species present (see Appendix).

(c) Paper Chromatography.

The technique is described in para. 2.1 (b).

It is possible to obtain approximate compositions of solutions from the histograms alone: but factors such as incomplete resolution (which applies particularly to the dinitrato complex) and tailing back of the trinitrato complex (this is accentuated for samples of high acid concentration because of the decrease of acidity attendant on elution) introduce an appreciable uncertainty. For example, for 7.5 and 9.2M HNO_3 solutions, the values of 42% and 55.5% respectively given in Table II A for the trinitrato complex are based on Martin's method. Histograms for these solutions have on different occasions shown the following percentages of ruthenium on the three (of the 17) sections of the paper strip nearest to the solvent front:

Section	7.5M HNO_3			9.2M HNO_3		
17	33.0	41.9	39.2	49.1	36.6	42.0
16	6.5	6.0	7.3	13.9	18.0	7.4
15	6.3	4.9	2.5	2.6	3.1	6.5
Total	45.8	52.8	49.0	65.6	57.7	55.9

Since the dinitrato complex is found distributed over Sections 9 onwards, it is likely that it contributes slightly to the ruthenium on Sections 16 and 17. With these solutions paper chromatography is most suited to the determination of the percentage of ruthenium present either as highly extractable species ($R_F > 0.95$) in dilute acid or as weakly extractable species ($R_F < 0.1$) in concentrated acid.

3.2 Equilibria in Aqueous Nitric Acid Solutions.

3.2.1 At Room Temperature (20°C)

Previous information on equilibria in aqueous nitric acid solutions (ref. 6, p. 392; **ref. 8; and ref. 20, Table 6) has been considerably extended and in certain cases modified.**

Results are given in Table II A and Fig. 6: that 24 hours is sufficient time for equilibrium between the mononuclear complexes to be reached has been demonstrated by the application of paper chromatography to solutions ageing over a period of 4 weeks:-

Time of Ageing	% Ruthenium in			
	3M HNO_3 on sections		7.5M HNO_3 on sections	
	1 and 2	16 and 17	1 and 2	16 and 17
24 hours	35.7	9.6	11.4	45.8
88 "	33.2	9.2	11.6	45.6
2 weeks	34.7	9.8	12.0	46.5
4 "	34.4	9.1	11.6	44.0

Both techniques, paper chromatography and Martin's method, employed to obtain these results have their limitations, but together they have enabled the whole range of nitric acid concentrations to be covered.

(a) Below 3M HNO_3.

The percentage of extractable ruthenium is so low at these acidities that Martin's method becomes inapplicable: in this acidity range results have been

TABLE II

A. PERCENTAGES OF RUTHENIUM AS VARIOUS (RuNO) NITRATO COMPLEXES AT EQUILIBRIUM IN 0.1 TO 14.5M HNO_3 SOLUTIONS AT 20°C.

C_{HNO_3} (M)	C_{Ru} (M)	Percentage Ruthenium as Trinitrato	Dinitrato	Mononitrato	Non-nitrato* Complex
0.1	1.18×10^{-4}	0	0	5	95‡
1.0	1.18×10^{-3}	3.5	3	23.5	70
3.0	3.53 "	7	15	46	32
4.6	5.41 "	18	20	44	18
7.5	8.83 "	42	19	31.5φ	7.5
8.7	1.02×10^{-2}	50.5	21.5	23 φ	5
9.2	1.08 "	55.5	20	19.5 φ	5
11.3	1.33 "	70.5	18.5	6.5 φ	4.5
14.5	3.84×10^{-3}	81+	13	2 φ	4

+ Includes up to 5% of a higher nitrato complex. φ Obtained by difference.

* Includes up to 4% of Ru as RuIV. ‡ May include some (RuNO) polymer.

B. PERCENTAGE OF RUTHENIUM AS THE TRINITRATO COMPLEX AT EQUILIBRIUM IN HNO_3 SOLUTIONS CONTAINING NITRATES AT 20°C.

C_{HNO_3} (M)	Added Nitrate Salt	C_{NO_3} (M)	Ruthenium as Trinitrato Complex (%)
1	-	-	3.5
1	$UO_2(NO_3)_2$	1.7	8
2.7	-	-	6.5
1	$UO_2(NO_3)_2$	2.5	13
3.5	-	-	10
3	-	-	7
3	$NaNO_3$	2.5	20
3	$Mg(NO_3)_2$	2.5	27
3	$UO_2(NO_3)_2$	2.5	27
5.5	-	-	24.5
3	$UO_2(NO_3)_2$	1.7	22
4.7	-	-	18.5

obtained by combining chromatographic data with the distribution coefficients discussed in para. 4. To illustrate this method, the procedure used in the case of a 1M HNO_3 solution of (RuNO) nitrato complexes is quoted: three experiments were carried out:-

(i) A paper chromatogram was made of the aged 1M HNO_3 solution and from it the approximate composition was deduced.

(ii) 4 ml of the 1M HNO_3 solution were stirred with 4 ml of conditioned 20% TBP for 30 sec. at 20°C; the measured value of D_{Ru} was 0.061; a paper chromatogram was immediately made of the solvent phase (Fig. 3A).

(iii) 1 ml of the 1M HNO_3 solution was diluted to 10 ml with water and immediately extracted with 10 ml of conditioned 30% TBP at 0°C; the measured value of D_{Ru} was 0.110; a paper chromatogram was immediately made of the solvent phase (Fig. 3B).

The approximate composition of the solution (Column 2) was modified by successive approximation to give the more accurate composition (Column 3) consistent with the other experiments (Columns 5 and 7).

1	2	3	4	5	6	7
	Approx. comp. from (i)	Comp. consistent with (ii) and (iii)	Comp. of solvent phase in (ii). % Ru as complex		Comp. of solvent phase in (iii). % Ru as complex	
Complex	% Ru as complex	% Ru as complex	Calc. from Col. 3 and D_{Ru}	Observed	Calc. from Col. 3 and D_{Ru}	Observed
Trinitrato	3	3.5	53	52	35	35
Dinitrato	4	3.0	25	23	26	27
Mononitrato	25	23.5	12	13	20	21
Non-nitrato	68	70	10	12	19	20

(b) From 2 to 5M HNO_3.

Both techniques are useful in this range, but Martin's method does not distinguish between the mononitrato and non-nitrato complexes whereas paper chromatography does (Figs. 1A and 2B).

(c) Above 5M HNO_3.

Martin's method becomes of particular value in deducing accurately the proportions of the tri- and dinitrato complexes in this range. Paper chromatography permits a separate estimation of the non-nitrato complex, but it does not give accurate values for the tri- and dinitrato complexes; the values quoted in Table II A for the mononitrato complex are obtained by difference and are consistent with the histograms.

3.2.2. Effect of Temperature.

After a solution of nitrato complexes (1.3×10^{-5}M Ru) at equilibrium in cold 3M HNO_3 has been heated, paper chromatography of rapidly chilled samples indicates that the percentage of ruthenium on the solvent front (Section 17) has increased, for example:

Serial	Temperature °C	% Ruthenium on Section 17	% Ruthenium on Sections 1 and 2	D_{Ru} (30% TBP, equal volumes, 0°C)
1	20	7	35	0.125
2	65	16	30	0.163
3	100	26	27	~ 0.18

On cooling the solutions (Serial 2 and 3) to room temperature and ageing for 24 hours, 12 to 16% of the ruthenium is usually found on section 17. In spite of this being greater than the original 7%, the ruthenium distribution coefficient measured under standard conditions (see above) reverts to its original value (after heating at 65°C for half an hour, cooling and ageing for 24 hours, the observed value of D_{Ru} was 0.128). The explanation of these facts, and of the apparent contradiction between the results of paper chromatography and distribution measurements, is twofold.

(i) Some of the nitrato complexes are converted to a nitro complex on heating; this has an R_F value of about unity with methyl isopropyl ketone as the eluting solvent, but has a much lower partition coefficient than the trinitrato complex with TBP.

(ii) The equilibrium between the nitrato components of the system is shifted, at elevated temperatures, in favour of the trinitrato complex (from 7% at 20° to approximately 16% at 100°C), but reverts to the original composition after ageing at 20° for 24 hours.

The use of dibutyl cellosolve as the eluting solvent in paper chromatography enables a distinction to be drawn between the trinitrato complex and this nitro complex; this work will be reported in detail later.

3.3 Equilibria in Aqueous Nitric Acid - Nitrate Solutions.

In the processing of irradiated nuclear fuels, nitrates other than nitric acid and ruthenium complexes are present in substantial amounts. The influence of such nitrates has been examined by paper chromatography for some conditions of interest in solvent extraction processes. The results are given for the trinitrato complex in Table II B. Since these results are derived entirely from histograms they are of a lower order of accuracy than those for nitric acid alone: for solutions containing uranyl nitrate (which moves to the solvent front) there is an appreciable decrease in the R_F value of the trinitrato complex (Fig. 7).

The results in 1M and 3M HNO_3 (Table II B) indicate that the proportion of the trinitrato complex is dependent on the total nitrate concentration, and the extent to which a given concentration (2.5M) of certain nitrates, in the presence of 3M HNO_3, influences the proportion of ruthenium as the trinitrato complex at equilibrium is approximately constant.

3.4 Equilibria in TBP-Nitric Acid Solutions.

The equilibria in aqueous nitric acid solutions of (RuNO) nitrato complexes, as presented in Table II A, can be interpreted in terms of increased nitration as the nitric acid concentration increases and vice-versa. In the TBP solutions used in this work, the ratio, C_{HNO_3}/C_{H_2O}, of the nitric acid to water concentration (Table III) is considerably higher than in aqueous nitric acid, e.g. this ratio is greater (0.84) in a 30% TBP solution equilibrated with 2M nitric acid than in 16M aqueous nitric acid (0.70). Although similar nitration and denitration reactions occur in the TBP phase to those in the aqueous phase, the equilibria in the former favour the more highly nitrated complexes. An aged solution of these complexes in TBP, obtained by extraction from a solution originally at equilibrium in aqueous nitric acid, contains a higher proportion of the more highly nitrated nitrato nitrosylruthenium complexes than was present in the original aqueous solution; also, TBP complexing replaces aquo complexing. Consequently, as has been noticed by Martin(11), by Sangster(3) and by Aikin and Bruce(1), TBP solutions made in this way have ruthenium distribution coefficients (for short times of stirring) which increase on ageing to a relatively high value. Some values of D_{Ru} for nitrato complexes at equilibrium in various TBP solutions are given in Table IV.

Equilibrium is reached at room temperature in 2-3 hours, and for at least one set of conditions it is independent of the method of preparation of the solution (see D_{Ru} values of 1.64, 1.69 and 1.68 given in Table IV for three solutions aged in a 30% TBP phase in equilibrium with 3M HNO_3).

Paper chromatography and Martin's method have been used to estimate the percentages of ruthenium as certain nitrato nitrosylruthenium complexes at equilibrium in TBP solutions (Table V). The information derived from these experiments is of limited accuracy and is largely confined to Complexes A, A' and B (as defined in Table I) because,

(i) only small quantities of the mononitrato and the non-nitrato complexes are extracted into the solvent phase and analysis of the histograms for them is correspondingly difficult, and

(ii) Martin's method gives no detailed information about these less extractable species, which are probably numerous as they can contain several combinations of the groups NO_3, OH, H_2O and TBP around the central ruthenium atom.

Martin's method only yields useful information when applied to high acid solutions (Serials 4 and 5 of Table V). The results obtained with two TBP solutions (in equilibrium with 6M and 2M aqueous HNO_3 respectively) are given in Fig. 8: in the high acid case (Fig. 8A), the method divides the species into two groups; but in the low acid case, it is impossible to estimate the equilibrium composition of the solution because the curve obtained (Fig. 8B) is hyperbolic owing to the presence of several extractable complexes. Paper chromatography,

TABLE III

THE COMPOSITIONS OF CERTAIN EQUILIBRATED TBP SOLUTIONS CONTAINING WATER, NITRIC ACID AND URANYL NITRATE (25°C)

Serial	Composition of aqueous phase for equilibration		Composition of equilibrated organic phase			
	C_{HNO_3} aq	C_{UNH} aq	C_{HNO_3} org.	C_{H_2O} org.	C_{UN} org.	$\frac{C \text{ nitrate org.}}{C_{H_2O} \text{ org.}}$
			Conditions in equilibrated 30% (1.1M) TBP			
1	0.75M	-	0.12M	0.45M	-	0.27
2	1.5	-	0.30	0.51	-	0.59
3	2.0	-	0.42	0.50	-	0.84
4	3.0	-	0.60	0.34	-	1.75
5	4.3	-	0.79	0.24	-	3.3
6	6.0	-	0.92	0.19	-	4.8
7	10.0	-	1.10	0.15	-	7.3
8	1.0	0.105M (25 g/l U)	0.08	0.26	0.31M*	2.7
			Conditions in equilibrated 20% (0.73M) TBP			
9	1.0	0.21	0.04	0.044	0.25*	12.3
10	0.5	0.25	0.02	0.095	0.21*	4.6

* The U-saturation of the TBP in the three cases is 56, 68 and 57% respectively.

TABLE IV

RUTHENIUM DISTRIBUTION COEFFICIENTS FOR (RuNO) NITRATO COMPLEXES IN VARIOUS 30% TBP SOLUTIONS

Method of preparation of solution in 30% TBP	Nitric Acid concentration of aqueous phase in equilibrium with TBP solution	D_{Ru}*		Time taken for D_{Ru} to become constant at 20°C
		After 10-15 min. ageing	After ageing to equilibrium	
By extraction: after dilution of stock solutions 8M or 11.3M in HNO_3	0.75M	11.2	11.3	<10 min.
	1.5	10.5	5.9	~ 2 hours
	2.0	5.4	3.0	~ 6 "
	3.0	1.9	1.64	~ 2 "
By reduction of the nitric acid content of a TBP solution in equilibrium with 10M HNO_3 (aq) from 1.1M to 0.6M HNO_3	3.0	-	1.69	~ 2 hours
By dissolving solid trinitrato complex in the appropriate TBP phase.	3.0	1.25	1.68	~ 3 hours
	4.3	0.39	0.63	~ 3 "

* For 30 sec. stirring at 25°C of equal volumes of the TBP phase and aqueous nitric acid of the concentration used for equilibration.

TABLE V

PERCENTAGE OF RUTHENIUM AS VARIOUS (RuNO) NITRATO COMPLEXES AT EQUILIBRIUM IN 30% TBP SOLUTION AT 20°C

Serial	C_{HNO_3} in 30% TBP (M)	C_{HNO_3} in Equivalent Aqueous phase (M)	Percentage Ruthenium as Complex A'	Complex A	Complex B	Complexes C and D
1	0.01	0.1	7	30	34	29
2	0.18	1	35	38	15	12
3	0.61	3	46	24		
4	0.92	6	58			
5	1.10	10	76			

and the ruthenium distribution coefficients given in Table IV, therefore form the basis of the results for low acid solutions (Serials 1, 2 and 3 of Table V).

3.5 Equilibria in TBP-Nitric Acid-Uranyl Nitrate Solutions.

These conditions favour the formation of the complexes A' and A; this is deduced from the observed facts (Table VI),

(i) that the value of the ruthenium distribution coefficient (for 30 sec. stirring at 25°C with the corresponding HNO_3-UNH aqueous phase) increases with ageing time, and

(ii) that the equilibrium values of D_{Ru} are much higher than would be expected in the equivalent aqueous phase (e.g. for all the conditions given in Table VI, the value of D_{Ru} for the complexes at equilibrium in the equivalent aqueous phase is ~0.1).

The relative magnitudes of the equilibrium values of D_{Ru} quoted in Table VI indicate that the equilibrium proportions of these complexes are influenced by the free TBP concentration: as the % U saturation increases, the TBP available for complexing of (RuNO) is correspondingly decreased. The order in which various complexes will displace one another from TBP phases is:-

Complex			
$[UO_2(NO_3)_2(TBP)_2]$		will	displace
$[RuNO(NO_3)_3(TBP)_2]$	which	"	"
$[RuNO(NO_3)_3(H_2O)_2]$	"	"	"
$[H_2O\ TBP]$	from the TBP phase.		

3.6 The Separation of Aqueous Phases from TBP Solutions.

A phenomenon relevant to a study of equilibria in TBP phases is the formation of a relatively small volume of an aqueous phase during the ageing of certain TBP solutions of (RuNO) nitrato complexes. This has been noticed at 21 ± 0.5°C (and more particularly at 0°C) in solutions of high nitric acid concentration. Under these conditions the complex A', $[RuNO(NO_3)_3(TBP)_2]$, is formed from aquo complexes; water is liberated and supersaturates the TBP phase. This water forms a separate phase and extracts from the organic phase both nitric acid and aquo (RuNO) nitrato complexes (under high acid conditions, these have very low partition coefficients as is indicated by extrapolation of the curves in Fig. 10). On warming to 50°C there is homogenisation of the phases. The occurrence of this phenomenon can have repercussions on the techniques used for the analysis of (RuNO) - containing TBP phases from counter-current extraction systems. It can also provide automatically some decontamination of TBP phases from ruthenium.

4. PARTITION COEFFICIENTS OF NITRATO NITROSYLRUTHENIUM COMPLEXES

4.1 Aquo Complexes.

If aqueous solutions of (RuNO) nitrato complexes are equilibrated with TBP (+ diluent) for sufficiently short times of stirring (we have largely worked with

TABLE VI

RUTHENIUM DISTRIBUTION COEFFICIENTS (D_{Ru}) FOR TBP SOLUTIONS OF (RuNO) NITRATO COMPLEXES

For 30 sec. Stirring at 25°C

Conditions in TBP and equivalent aqueous phases	$C_{\text{free TBP}}$ (M)	U saturation (%)	D_{Ru}	
			After ageing for 15 min. in TBP	At equilibrium in TBP
As in Table III, Serial 8	0.40	56	1.29	1.65
" " " " " 10	0.29	57	0.58	0.80
" " " " " 9	0.19	68	0.29	0.46

30 sec. stirring at 0° or 20°C), there is no time for the conversion of aquo-complexed to TBP - complexed species in the organic phase. This makes it possible to determine the partition coefficients (K_T for the trinitrato complex, K_D for the dinitrato complex, etc.) of the various aquo - complexed species for any given set of conditions. These partition coefficients are, by definition, peculiar to a given complex and independent of

(1) The relative volumes of the organic and aqueous phases;

(2) The time of stirring (provided this is sufficiently long for complete transfer between phases):

but they are dependent on

(3) The temperature;

(4) The composition of the aqueous phase;

(5) The composition of the organic phase, i.e. the % TBP;

(6) The concentration of the species (this work has been limited to concentrations of $<10^{-2}$M Ru for which little dependence on concentration is found).

The partition coefficients, for the same conditions of equilibration, increase as nitrato complexing of (RuNO) increases (cf. R_F values given in Table I).

4.1.1 <u>Results in Nitric Acid Solution</u>.

The determination of the individual partition coefficients is made difficult by the presence of several species in any particular solution; this has been overcome, firstly by employing Martin's method (para. 3.1), secondly by paper chromatography of equilibrated phases. Various aqueous and TBP conditions have been studied.

(a) <u>Effect of Change of TBP Concentration</u>.

The partition coefficients of the tri- and dinitrato complexes between 3M HNO_3 and 10, 15, 20 and 30% TBP/OK have been determined by Martin's method (Table VII, Fig. 9); in this case the free TBP concentration varies because of changes in the total TBP concentration; for both complexes, over the range studied, a relationship of the type

$$K/C_{\text{free TBP}})^n \;=\; \text{a constant}$$

is obeyed (Fig. 9). The fact that n ~ 2 for both complexes does not necessarily mean that a 2 TBP complex is formed, because under these conditions the activity effects, although constant, may be large; however, these results, together with the work of Martin(2) and of Sangster(3), point to a 2 TBP complex.

(b) <u>Effect of Change of Aqueous Nitric Acid Concentration</u>.

Partition coefficients of the tri- and dinitrato complexes between certain aqueous nitric acid solutions and 20 or 30% TBP at 0°C have been

TABLE VII

THE DEPENDENCE OF THE PARTITION COEFFICIENTS OF THE (RuNO) TRI- AND DINITRATO COMPLEXES AT 0°C ON TBP CONCENTRATION

Aqueous HNO_3, 3M.

% TBP (= x)	C_{TBP}	$C_{free\ TBP}$	K_T	K_D	Ratio $\frac{K(30\%\ TBP)}{K(x\%\ TBP)}$ K_T	K_D
30	1.13M	0.52M	5.0	0.5	-	-
20	0.75	0.32	2.2	0.2	2.3	2.5
15	0.56	0.25	1.1	0.1	4.5	5.0
10	0.38	0.17	0.4	0.04	12.5	12.5

TABLE VIII

PARTITION COEFFICIENTS OF (RuNO) NITRATO COMPLEXES BETWEEN AQUEOUS NITRIC ACID AND TBP SOLUTIONS

Final acidity after dilution of 7.5M HNO_3 stock solution	Partition Coefficients 30% TBP at 0°C K_T	K_D	20% TBP at 0°C K_T	K_D	20% TBP at 20°C K_T	K_D	Ratio of partition coefficients $\frac{K_T}{K_D}$
0.75M HNO_3					30*	2.8*	10.7
1.88			16	1.5			10.7
3.0	5.0	0.5	2.2	0.2			10, 11
3.6					0.44*	0.041*	10.7
4.13	0.63	0.06					10.5

* Values calculated from measurements, with various solvent/aqueous ratios, by Sangster(3).

similarly determined (Table VIII). Values of the partition coefficients at other solvent concentrations and temperatures from those at which they were measured may be calculated from the relationships,

$$\frac{K(30\%\ \mathrm{TBP})}{K(20\%\ \mathrm{TBP})} = 2.4 \text{ (derived from Table VII)}$$

$$\frac{K\ (0^{\circ}C)}{K\ (20^{\circ}C)} = 1.63 \text{ (obtained from the work of Jenkins and Wain}^{(9)} \text{ on the trinitrato complex).}$$

The results, corrected to 20% TBP and 20°C, are plotted in Fig. 10. The decrease in the partition coefficients K_T and K_D with increasing aqueous nitric acid concentration ($C_{HNO_3\ aq}$) is interpreted, as previously suggested by Martin$^{(2)}$, as being due to the corresponding decrease in the free TBP concentration (Fig. 11); in this case (contrast Fig. 9) $C_{free\ TBP}$ varies because of changes in the nitric acid concentration in the TBP phase; activity effects, which are both large and variable, prevent quantitative agreement with a simple relationship such as $K/(C_{free\ TBP})^n$ = a constant.

Martin's method, in certain low acid cases, also gives values of the overall ruthenium distribution coefficient for Complexes C and D; two examples are:

Extraction Conditions	D_{Ru} for Mixture of Complexes C and D
0.75M HNO_3(aq) with 20% TBP at 20°C	0.035
1.88M HNO_3(aq) with 20% TBP at 0°C	0.017

Paper chromatography of the TBP and aqueous phases after equilibration provides a direct method for the determination of individual partition coefficients: trailing in the aqueous phase limits the accuracy of this method, particularly for the higher nitrato complexes in high acid solution. The method does, however, provide approximate values of the respective partition coefficients (K_M, K_N) for the mononitrato and the non-nitrato complex for which no other method is available:

C_{HNO_3}(aq)	Approximate Partition Coefficient with 20% TBP at 20°C	
	K_M	K_N
1M	0.03	0.008
0.1M	0.10	0.03

The values of K_M are included in Fig. 10. It may be noted that the partition coefficient of water (K_{H_2O}) between 0.75M HNO_3 and 30% TBP at 25°C is 0.01, i.e. is comparable to K_N.

4.1.2 Results in Nitric Acid-Nitrate Solutions.

The presence, at equilibrium between the two phases, of uranyl nitrate affects the partition coefficients in a number of ways. It is likely, however, that the predominant effect arises from the decrease in the free TBP concentration attendant on the uptake of uranyl nitrate by the TBP phase.

Measurements from which the individual partition coefficients in the presence of uranyl nitrate can be deduced have not been carried out, because of the difficulty of maintaining equilibrium concentrations of uranyl nitrate in the solvent and aqueous phases while carrying out Martin's method, but the gross ruthenium distribution coefficients, observed for short times of stirring, are in good agreement with calculated values (para. 6.2).

The presence of inextractable nitrates, such as sodium nitrate, will

(i) increase K_{HNO_3} and lower the free TBP for a given value of $C_{HNO_3(aq)}$;

(ii) cause Setchenow salting-out of any individual ruthenium complex(12).

These will act in opposing directions on the partition coefficient of a particular complex.

4.2 TBP Complexes originating in a TBP phase.

It is to be expected that the partition coefficient of the complex $[RuNO(NO_3)_3(TBP)_2]$ would be extremely high, and that only after ligand substitution would it enter an aqueous phase. Ruthenium distribution measurements by Martin's method support this view: a solution of the trinitrato complex aged in 30% TBP equilibrated with 6M HNO_3 was found, when stripped with various volumes of 6M HNO_3 (Fig. 8A), to contain 58% of the ruthenium as one or more species with a very high partition coefficient ($>10^3$) in favour of the solvent phase. The other 42% had a partition coefficient suggestive of the trinitrato aquo complex.

4.3 Extraction of Nitrato Complexes by Dibutyl Phosphate.

Dibutyl phosphate (DBP) is sometimes present as a hydrolysis product in TBP due to attack by radiation or by acid. This compound acts as an acid and forms salts with metallic cations: these salts, e.g. of uranyl and zirconium, favour the organic phase. The trinitrato complex cannot be a cation; the lower nitrato complexes are probably largely cationic in nitric acid solution (R.P. Bell, private communication). In spite of this, the ruthenium distribution coefficients obtained from the equilibration at 20°C of aqueous solutions of the nitrato complexes in nitric acid with 2% DBP in kerosene are extremely low:-

THE I

% TBP (= x)
30
20
15
10

Final acidit after diluti of 7.5M HNO_3 stock soluti
0.75M HNO_3
1.88
3.0
3.6
4.13

* Va
ra

C_{HNO_3}	Time of Stirring	D_{Ru}
1M	2 min.	$<10^{-4}$
	20 "	$\sim 2 \times 10^{-4}$
	60 "	
3M	2 min.	$<10^{-5}$
	20 "	
	60 "	$\sim 4 \times 10^{-5}$

The presence of DBP in TBP is therefore most unlikely to influence the decontamination factor which applies to nitrato complexes of nitrosylruthenium. In agreement with this work, no effect of DBP and MBP in TBP was found by Airey, Ashworth and Hyde(13) who used synthetic solutions containing (RuNO) nitrato complexes; and no effect with up to 1% in TBP is reported by Bruce(14) and by Naylor(5) for ruthenium in fission product mixtures.

5. RATES OF REACTIONS

5.1 Aqueous Solutions.

The main reactions occurring in aqueous nitric acid solution may be represented (for 6-coordinated ruthenium) as follows:-

$$\underset{C_1}{[\mathrm{Ru\ NO\ (NO_3)_3\ (H_2O)_2}]} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[\mathrm{Ru\ NO\ (NO_3)_2\ (H_2O)_3}]^{+}} \qquad (1)$$

$$\underset{C_2}{[\mathrm{Ru\ NO\ (NO_3)_2\ (H_2O)_3}]^{+}} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{C_3}{[\mathrm{Ru\ NO\ NO_3\ (H_2O)_4}]^{2+}} \qquad (2)$$

$$\underset{C_3}{[\mathrm{Ru\ NO.NO_3\ (H_2O)_4}]^{2+}} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \underset{C_4}{[\mathrm{Ru\ NO\ (H_2O)_5}]^{3+}} \qquad (3)$$

where k_1 etc. are rate constants and C_1 etc. are concentrations. The rates of these reactions are all first order with respect to ruthenium, and therefore independent of ruthenium concentration.

Rate constants for the disappearance of the trinitrato complex (k_1) have been measured by Jenkins and Wain(9) for solutions in 0.75 to 4M nitric acid: their results are included in Table IX. The constants for the reverse reaction (k_2), also given in Table IX, were calculated from the relative concentrations, C_1 and C_2, at equilibrium (Table II A) and from k_1 by the relationship

TABLE IX

APPROXIMATE RATES OF REACTION BETWEEN (RuNO) NITRATO COMPLEXES IN AQUEOUS SOLUTION

Reaction	Conditions			Rate Constant min^{-1}	Half-time min.
	C_{HNO_3} (M)	C_{Ru} (M)	Temp. °C		
Decomposition of Trinitrato Complex (Rate Constant k_2)	0.75	5×10^{-3}	0	0.0185	38
		5.7×10^{-5} to 3.7×10^{-2}	25	0.048	14
		5.7×10^{-4}	35	0.060	12
	2.0	"	25	0.045	15
	4.0	"	"	0.034	20
	7.5	10^{-2} to 10^{-4}	"	~0.02	~35
Formation of Trinitrato Complex (Rate Constant k_1)	0.75	5×10^{-3}	0	0.0035	198
		5.7×10^{-5} to 3.7×10^{-2}	25	0.009	77
		5.7×10^{-4}	35	0.011	63
	2.0	"	25	0.012	58
	4.0	"	"	0.026	27
	7.5	10^{-2} to 10^{-4}	"	~0.04	~17

Note: Guggenheim's method(18) was used in the deduction of rate constants from distribution coefficient data.

$$\frac{k_2}{k_1} = \frac{C_1}{C_2}$$

The rate constants given in Table IX for the 7.5M HNO_3 solution were derived from the paper chromatographic results on Solution A of Table X. As would be expected both k_1 and k_2 show some dependence on nitric acid concentration (see results for 25°C in Table IX).

There is some evidence from the histograms obtained in paper chromatography that the rate constants of Reactions 2 and 3 are of the same order as k_1 and k_2: Table X gives results obtained from two relevant histograms; the overall rate of production of the trinitrato complex for Solution A, which was largely composed of the mono- and non-nitrato complexes, is comparable with k_1 indicating that there is no very slow stage in the sequence of reactions involved. The derivation of precise kinetic data from such histograms is not possible because of trailing of the intermediate peaks, but an approximate value for k_5 in 7.5M HNO_3, calculated from the two histograms to which Table X refers, is $k_5 = 0.017$ min^{-1} ($t_{\frac{1}{2}} = 40$ min.); from the equilibria given in Table II A, a value of $k_6 = 0.004$ min^{-1} ($t_{\frac{1}{2}} = 170$ min.) is obtained for these conditions.

Certain solutions, e.g. those derived

(i) from low acid (pH >1) conditions,

(ii) from certain solid preparations of (RuNO) nitrato complexes,

may contain polynuclear complexes. The rate of nitration of these is relatively slow. An example of this is the rate observed when a particular solid preparation was dissolved in 1M HNO_3; the solution was aged to equilibrium at this acidity and then made 7.5M in HNO_3:

Time of Ageing in 7.5M HNO_3 at 20°C	% Trinitrato Complex
0	~ 2
30 min.	~ 3
135 "	~ 4
24 hours	~ 6

5.2 TBP Solutions.

Four types of reaction, all of which are first order with respect to ruthenium, which occur in TBP solutions containing nitric acid are:-

TABLE X

RATE OF CHANGE OF PROPORTIONS OF NITRATO COMPLEXES AT 20°C AS DETERMINED FROM PAPER CHROMATOGRAMS

With Solution A(i) Nitric Acid: Initial 1M Nitric Acid: During Ageing 7.5M			Solution B(ii) 3M 7.5M
Time	Ru as Non-nitrato Complex	Ru as Trinitrato Complex on the solvent front	Ru as Trinitrato Complex on the solvent front
0	68%	2 - 3%	9%
15 mins.	59	8 - 10	15
30 "	54	10 - 12	
60-70 mins.	41	26(iii)	20
135 "	33		
4 hours			26
24 "	17		26(iii)

Notes: (i) Solution A was made by dilution of Solution X: it was aged for 24 hours in 1M HNO_3 before use.

(ii) Solution B was made directly from a preparation of the complexes in a solid form.

(iii) Because of trailing of the trinitrato complex, paper chromatograms rarely show the full amount of 42% Ru on the solvent front for solutions at equilibrium in 7.5M HNO_3; $\sim$30% Ru is sometimes found (para. 3.1 c).

Reaction		Dependence of rate constant on concentration of		
Type	Example	HNO_3 (or nitrate)	H_2O	TBP
4. **Nitration**	Formation of (RuNO) trinitrato complex from lower nitrato complexes.	Dependent	Inversely dependent	Practically independent.
5. Denitration	Reversal of 4.	Inversely dependent	Dependent	"
6. TBP complex formation	Formation of (RuNO) trinitrato 2 TBP complex.	Independent except in so far as C_{HNO_3}(org) affects C_{H_2O} (org)	Inversely dependent	Practically independent as long as there is a swamping concentration of TBP.
7. Aquo complex formation	Reversal of 6.		Dependent	Inversely dependent.

The following scheme summarises these reactions; the half-times refer to the temperature range 20 to 25°C:

$$\text{Lower nitrato complexes} \underset{t_{\frac{1}{2}} \sim 25 \text{ mins.}}{\overset{t_{\frac{1}{2}} \sim 20 \text{ mins.}}{\rightleftharpoons}} [RuNO(NO_3)_3(H_2O)_2] \underset{t_{\frac{1}{2}} \sim 6 \text{ mins.}}{\overset{t_{\frac{1}{2}} \sim 3 \text{ mins.}}{\rightleftharpoons}} [RuNO(NO_3)_3(TBP)_2].$$

It will be noted that the rates of the nitrations and denitrations in TBP are about the same as in aqueous solutions (Table IX).

Ruthenium distribution coefficient measurements were used to obtain kinetic data (Table XI); the organic phase in which the reactions were occurring was stripped at various time intervals with an equal volume of an aqueous phase of suitable composition.

There are two distinct series of rate constants (and half-times):-

(a) When C_{H_2O}(org) is low (<0.2M), i.e. with high concentrations of nitric acid or uranyl nitrate in the TBP phase. Under these conditions the trinitrato complex is the predominant initial species, and a reaction with a half-time of about 3 mins. has been observed by Sangster(3), by Aikin and Bruce(1), and by ourselves (Table XI, Series A). This rather fast reaction is attributed to TBP complex formation (Reaction 6).

TABLE XI

RATES OF REACTIONS OF (RuNO) NITRATO COMPLEXES IN TBP SOLUTIONS

Series	Ageing Conditions	Reaction Accounting for slow stage	Conditions in TBP phase					Temp. (°C)	First order rate constant (min^{-1})	Half-time of reaction (min.)
			C_{TBP}		C_{HNO_3} (M)	C_{H_2O} (M)	$\frac{C_{NO_3}}{C_{H_2O}}$			
			%	Free (M)						
A	Complexes freshly extracted into TBP phase	TBP Complex formation	20	0.31	0.42	0.11	3.8	20	~0.17	~ 4 ‡
			20	0.29	0.44	0.11	4.0	20	~0.23	~ 3 ‡‡
			30	~0	1.1	0.15	7.3	25	~0.22	~ 3
B	"	Denitration	30	0.8	0.3	0.51	0.59	25	0.026	26.5
		Nitration	30	0.5	0.6	0.34	1.75	25	0.030	23.0
		"	30	0.4	0.08	0.26	2.7*	25	0.043	16.0
C	TBP phase stirred continuously with equilibrium aqueous phase (10M HNO_3)	Formation, from TBP complexes, of aquo complexes with extraction into the aqueous phase.	30	~0	1.1	-	-	25	~0.12	~ 6
								0	~0.006	~100

* This solution contained 0.31M uranyl nitrate.

‡ Sangster.

‡‡ Aikin and Bruce.

(b) When C_{H_2O}(org) is high or when the initial species in the TBP phase are lower nitrato complexes, half-times of 15-30 mins. are obtained (Table XI, Series B). The directions and rates of these changes are controlled by $C_{nitrate}/C_{H_2O}$ and are attributed to nitration and denitration reactions (Reactions 4 and 5) which are similar to those occurring in the aqueous phase (Reactions 1-3).

Information about the rate of Reaction 7, which may be represented as

(RuNO) nitrato TBP complexes ——> (RuNO) nitrato aquo complexes,

was obtained by continuously stirring a TBP solution (1.1M in HNO_3) with an equilibrium aqueous phase (10M HNO_3) originally containing no ruthenium. The values of D_{Ru} from which the rate constants given in Table XI, Series C are derived, were:-

Time of Stirring	D_{Ru}	
	0°C	25°C
30 sec.	2.34	2.8
15 min.	1.83	0.14
2 hours	0.52	0.007

Paper chromatograms on TBP solutions have confirmed, by the relative rates of growth of peaks at 0° and 20°C, that the temperature coefficient of the rate of this reaction is large.

6. RUTHENIUM DISTRIBUTION COEFFICIENTS

6.1 Factors which affect observed Ruthenium Distribution Coefficients.

Most laboratory measurements related to the plant problems which arise from fission product ruthenium have been by β and γ counting and so give distribution coefficients, D_{Ru}, which are integrated values for all the ruthenium complexes present. It follows from the previous paragraphs that any value of D_{Ru}, derived by the sampling and analysis for ruthenium of two phases which have been stirred together and separated, has no meaning unless the conditions are specified.

The distribution coefficient can depend on:-

(i) The composition of the two phases with respect to components (HNO_3, H_2O, TBP, uranyl nitrate etc.) other than ruthenium:

(ii) The proportions of the ruthenium complexes initially present (these may or may not be at equilibrium):

(iii) The temperature:

(iv) The relative volumes of the organic and aqueous phases:

(v) The time of mixing of the two phases (see 6.2 to 6.4):

(vi) The proportion of ruthenium present in other forms e.g. as RuIV or as certain (RuNO) nitro complexes (see 6.5):

(vii) The presence of DBP etc. (see 6.6).

The concentration of ruthenium is unlikely to have any appreciable effect for the acid systems under consideration, provided it is <10^{-2}M. The first three of these factors have been discussed in para. 4 for individual nitrato nitrosylruthenium complexes; an example of (iv) is given in Table XII. With regard to the mixing time, it is convenient to consider the following three cases:-

	Case	Mixing Times which apply	Remarks
A.	Proportions of (RuNO) species not appreciably changed during equilibration.	Short: less than 1 min. at 20°C.	Analogous to distribution of carbon for a mixture of stable organic compounds.
B.	Equilibrium between species reached both between and within the two phases.	Long: several hours at 20°C.	Analogous to distribution of uranium for uranyl nitrate solutions for <u>all</u> times of stirring.
C.	Some change in the proportions of species but equilibrium <u>within</u> each phase not reached.	Intermediate: minutes at 20°C.	

6.2 Case A: Short Mixing Times.

(a) In the Absence of Uranyl Nitrate.

Measurements with stirring times in the range 10-120 secs. (followed by centrifugation for about 2-3 mins. and immediate phase separation) give almost constant values of D_{Ru}

(i) for stirring times up to 2 mins. at 0°C (an example is D_{Ru} = 0.86, 0.85, 0.85, 0.85 for 15, 30, 60 and 120 secs. respectively for a solution of (RuNO) nitrato complexes aged in 1.37M HNO_3 and extracted with 30% TBP at 0°C) and

(ii) for stirring times up to 30 secs. at 20° or 25°C.

These times are reasonably short in relation to the half-times of the reaction involved.

The interpretation of measured values of D_{Ru} for all conditions to which the data of Tables II and VIII apply is possible for these short times of stirring. The agreement between observed and calculated values is presented:-

TABLE XII

COMPARISON OF OBSERVED AND CALCULATED RUTHENIUM DISTRIBUTION COEFFICIENTS OBTAINED WITH DIFFERENT RELATIVE VOLUMES OF THE SOLVENT AND AQUEOUS PHASES (MARTIN'S METHOD)

Solution X diluted to 3M HNO$_3$ and instantaneously extracted with various volumes of 30% TBP at 0°C (30 sec. stirring).

V	Ru γ cts/min/ml (x 10^{-5}) in solvent phase			Ru γ cts/min/ml (x 10^{-5}) in aqueous phase			Ruthenium distribution coefficient		
	Obs.	Calc.	$\frac{\text{Obs.}}{\text{Calc.}}$ x 100	Obs.	Calc.	$\frac{\text{Obs.}}{\text{Calc.}}$ x 100	Obs.	Calc.	$\frac{\text{Obs.}}{\text{Calc.}}$ x 100
0.2	21.77	20.38	107	6.576	6.604	99.6	3.31	3.09	107
0.35	14.69	14.86	99	5.435	5.440	99.9	2.70	2.73	99
0.5	11.45	11.80	97	4.815	4.742	101.5	2.38	2.49	95
0.75	8.626	8.817	98	4.013	4.026	99.7	2.15	2.19	98
1.0	7.032	7.063	100	3.600	3.578	100.6	1.95	1.97	99
2.5	3.287	3.264	101	2.478	2.476	100.1	1.33	1.32	100
5.0	1.728	1.742	99	1.952	1.940	100.6	0.890	0.897	99
7.0	1.275	1.268	100	1.752	1.755	99.8	0.728	0.723	101

Note: $V = \frac{\text{Volume of solvent phase}}{\text{Volume of aqueous phase}}$

(i) In Table XII, for extraction by 30% TBP from a particular stock solution (the variable is the ratio of the volumes of the solvent and aqueous phases):

(ii) In Table XIII, for extraction by an equal volume of TBP from various solutions derived from stock solutions (variables are acidity, % TBP, temperature):

(iii) In Table XIV, Serial 1, for certain experiments in which there have been successive operations ending with stripping of a TBP phase.

(b) In the Presence of Uranyl Nitrate.

Calculated values of D_{Ru} for these conditions may be obtained by using compositions derived from Fig. 6 and by the use of partition coefficients interpolated from Fig. 10. There is again good agreement (see Table XIV, Serials 2 and 3).

6.3 Case B. Equilibrium Conditions Reached (Long Mixing Times).

With sufficiently long times of stirring there will be equilibrium both in each phase and between each phase. Reaction rates have been found (para. 5) to be such that the reactions in both the aqueous and TBP phases are complete in about 2-3 hours at 20°C or in about 20 mins. at 50°C. Beyond such times further changes may occur in exceptional circumstances when polymers are involved.

Calculations of D_{Ru}, with the help of the results in paras. 3, 4 and 5, for two phases at equilibrium would be easy if transfer between the two phases was limited to one complex, say $[RuNO(NO_3)_3(H_2O)_2]$, which in turn was in equilibrium with only one other complex in each phase, e.g.

This however is a much over simplified picture, since there are other complexes in both phases and also there is exchange, between the phases, of more than one complex.

Fortunately, prolonged mixing of aqueous and TBP phases is of limited practical interest to solvent extraction systems. Values of D_{Ru} of unity or greater are often obtained for 30 secs. equilibration (Table XIII and Table XIV, Serial 1); by contrast, for prolonged stirring times, D_{Ru} is usually low (Table XV). Serials 8 and 9 of Table XV refer to conditions which might prevail if the TBP phase from a uranium solvent extraction system was stripped with 1M HNO_3 with a long time of stirring: the percentage saturation of the TBP by uranium in the two experiments was 58-61%.

TABLE XIII

COMPARISON OF OBSERVED AND CALCULATED RUTHENIUM DISTRIBUTION COEFFICIENTS OBTAINED WITH EQUAL VOLUMES OF THE SOLVENT AND AQUEOUS PHASES, 30 SEC. STIRRING AND $\sim 10^{-3}$M Ru

Aqueous nitric acid concentration				Ruthenium distribution coefficient (D_{Ru})		
Stock Solution (M)	Final Acidity (M)	TBP phase (% TBP)	Temp. °C	Observed	Calculated	$\frac{\text{Obs.}}{\text{Calc.}}$ x 100
0.75	0.75	20	20	0.041⊕	0.0405	101
0.75	0.75	30	25	0.044	0.044	100
1.0	0.1	30	0	0.110‡	0.115	96
1.37	1.37	30	0	0.085	0.084	101
1.37	1.37	30	25	0.05	0.056	90
1.5	1.5	20	20	0.05⊕	0.065	77
2.0	2.0	30	25	0.08	0.070	114
2.2	2.2	20	20	0.05⊕	0.073	70
3.0	3.0	30	0	0.124	0.124	100
3.0	3.0	30	20	0.074	0.074	100
3.6	3.6	20	20	0.041⊕	0.043	95
4.05	4.05	30	25	0.024	0.040	60
4.6	3.0	30	0	0.252‡	0.262	96
5.0	5.0	30	20	0.019	0.016	120
6.4	3.0	30	0	0.538‡	0.515	104
7.5	0.75	20	20	1.26 ⊕‡	1.27	99
7.5	0.75	30	0	1.9 ‡	1.8	105
7.5	0.75	30	25	1.46‡	1.50	97
7.5	1.5	20	20	0.99⊕‡	1.05	94
7.5	1.88	20	20	0.894‡	0.896	100
7.5	2.2	20	20	0.63⊕‡	0.74	85
7.5	3.0	10	0	0.149‡	0.145	103
7.5	3.0	15	0	0.300‡	0.311	96
7.5	3.0	20	0	0.470‡	0.473	99
7.5	3.0	30	0	0.693‡	0.697	100
7.5	3.6	20	20	0.160⊕‡	0.157	102
7.5	4.13	30	0	0.200‡	0.209	96
7.75	2.0	30	25	1.06‡	0.96	110
7.75	4.05	30	25	0.13‡	0.14	93
7.93	1.37	30	25	1.33‡	1.30	102
8.7	3.0	30	0	0.964‡	0.971	99
11.3	3.0	30	0	1.95‡	1.97	99
12.4	3.0	30	0	1.92‡	2.09	92
14.5	3.0	30	0	2.57‡	2.66	97

⊕ Results by Sangster(3).

‡ These distribution measurements were carried out immediately after dilution of the stock solutions; the ruthenium composition just prior to equilibration was therefore that of the stock solution.

TABLE XIV

COMPARISON OF OBSERVED AND CALCULATED RUTHENIUM DISTRIBUTION COEFFICIENTS OBTAINED UNDER CERTAIN SPECIAL CONDITIONS (30 SEC. STIRRING)

Serial	Conditions of Experiment	D_{Ru}		
		Observed	Calculated	$\frac{\text{Obs.}}{\text{Calc.}}$ x 100
1.	(RuNO) nitrato complexes aged in 7.5M HNO_3, diluted to 0.75M HNO_3 and:			
	(1) Extracted with an equal volume of 30% TBP at 0°C:	1.9	1.8	105
	(2) The solvent phase from (1) immediately extracted with an equal volume of 0.75M HNO_3 at 0°C:	8.3	8.45	98
	(3) The solvent phase from (1) extracted with 5 times its volume of 0.75M HNO_3 at 0°C.	17.8	16.2	110
2.	(RuNO) nitrato complexes aged to equilibrium in 1M HNO_3 containing 1.68M uranyl nitrate and extracted with an equal volume of 20% TBP containing the equilibrium amounts of HNO_3 and uranyl nitrate at 20°C.	0.016	0.015	107
3.	(RuNO) nitrato complexes aged to equilibrium in 3M HNO_3 containing 1.26M uranyl nitrate and extracted with an equal volume of 20% TBP containing the equilibrium amounts of HNO_3 and uranyl nitrate at 20°C.	0.0032	0.0038	84

TABLE XV

RUTHENIUM DISTRIBUTION COEFFICIENTS, D_{Ru}, OBTAINED WITH LONG MIXING TIMES OF THE ORGANIC AND AQUEOUS PHASES

Serial	Aqueous Phase		Organic Phase			Temp.	D_{Ru}	Results by
	C_{HNO_3}	C_{UNH}	C_{TBP}		C_{UN}			
			%	Free				
1	0.75M	-	20	0.69M	-	20°C	0.30	Sangster(3)
2	1.5	-	"	0.54	-	"	0.23	"
3	3.0	-	30	0.50	-	"	0.17	This work
4	2.2	-	20	0.40	-	"	0.14	Sangster
5	2.9	-	"	0.31	-	"	0.08	"
6	3.0	-	"	0.30	-	80	0.10	Aikin(1)
7	3.6	-	"	0.24	-	20	0.065	Sangster
8	1.0	0.135M	"	0.24	0.22M	"	0.02	This work
9	1.0	0.125	"	0.26	0.21	60	0.008	"

Notes: (1) In Serials 1 to 7, equal volumes of solvent and aqueous phases were used: in 8 and 9, the ratio of the organic volume to the aqueous volume was 3:1.

(2) In Serials 1 to 5 and 7, the ruthenium was originally in the aqueous phase: in 6, 8 and 9, it was originally in the solvent phase.

(3) Stirring times for Serials 3, 8 and 9 were 660, 400 and 30 min. respectively.

6.4 Case C. Intermediate Times of Mixing.

This case is the one of most interest to solvent extraction processes since in counter-current extraction with columns or with mixer-settlers, the mixing time is usually of the order of a few minutes. Laboratory experiments with (RuNO) nitrato complexes have, therefore, frequently been in this category. Results with TBP have been reported by Martin(2), Aikin and Bruce(1), F.R. Bruce(14) and by Holbert and Marshall(15). With acid systems (say >1M HNO_3), the important reactions (para. 5) have half-times at room temperature of about 20 mins. (nitration and denitration reactions) and about 3 minutes (complexing by TBP or by water in the organic phase). It is possible therefore to interpret the past results in terms of these reactions and their respective rates.

It is convenient to divide examples into two categories: firstly with ruthenium originally entirely in the aqueous phase; secondly with ruthenium originally entirely in the TBP phase.

(a) Ru originally in the Aqueous Phase.

With solutions initially at equilibrium, the tendency is for D_{Ru} to rise with stirring time (Table XVI). With solutions initially not at equilibrium, it is obvious that D_{Ru} can rise or fall with the stirring time depending on the relationship of the species present to the equilibration conditions used.

The variation of D_{Ru} (for synthetic solutions in which the ruthenium species were NOT initially at equilibrium) with the nitric acid concentration has been determined separately for 20% TBP at room temperature with a stirring time of 5 mins. by Martin and Gillies(2) and by Aikin and Bruce(1). Their results are included in Fig. 12 with our values for 30 secs. stirring for solutions at equilibrium: it is apparent from the curves in this figure that the relationship between D_{Ru} and C_{HNO_3aq} becomes quite different when dealing with different sets of conditions, e.g. solutions at or not at equilibrium. Our results first rise and then fall as C_{HNO_3aq} increases because of competition between the effects due to the increase in the proportion of highly extractable species and the decrease in the free TBP concentration.

The influence of uranyl nitrate on D_{Ru} (with solutions of irradiated uranium in 3M HNO_3, 30% TBP and a stirring time of 10 mins.) has been quoted by F.R. Bruce(14). The slope of the plot (Fig. 13) of log D_{Ru} against log (free TBP) concentration indicates that $D_{Ru} \alpha [\text{Free TBP}]^{2.4}$.

(b) Ru originally in the Organic Phase.

The influence of the stirring time on D_{Ru} in this case (which applies in a stripping section or a backwash extractor) can be very marked. The following is an example: a solution of (RuNO) nitrato complexes, not at equilibrium, in 20% TBP containing 52 gU/l was stirred with $\frac{1}{3}$ of its volume of 1M HNO_3 containing 33 gU/l at 20°C; the value of D_{Ru} fell with time as follows:-

TABLE XVI

THE EFFECT ON THE RUTHENIUM DISTRIBUTION COEFFICIENT, D_{Ru}, OF CONTINUOUSLY STIRRING A 3M HNO_3 SOLUTION OF (RuNO) NITRATO COMPLEXES, ORIGINALLY AT EQUILIBRIUM, WITH CONDITIONED 30% TBP AT 20°C

$Ru \sim 10^{-3}M$

Time of Stirring	D_{Ru}
30 sec.	0.074
10 min.	0.093
30 "	0.119
1 hour	0.146
3 "	0.167
11 "	0.167

Time of Stirring	D_{Ru}
2 mins.	0.97
12 "	0.54
57 "	0.20
120 "	0.087
400 "	0.02

6.5 Allowance for RuIV etc.

As RuIV nitrates are practically inextractable by TBP (e.g. $D_{RuIV} < 10^{-3}$ for 30% TBP), their presence will cause a decrease in the ruthenium distribution coefficient: also certain nitro complexes of (RuNO) are relatively inextractable(16). Thus if D_{Ru} is x for nitrato nitrosylruthenium complexes under certain conditions, D_{Ru} will be $xy/(1 + x - xy)$ for mixtures of these complexes with other inextractable forms of ruthenium, where

$$y = \frac{\text{Ruthenium Concentration as (RuNO) Nitrato Complexes}}{\text{Total Ruthenium Concentration}}$$

A further effect of the presence of RuIV nitrates is discussed below (para. 6.6).

6.6 Effect of DBP in TBP Solutions.

DBP and other hydrolysis products of TBP may occur in TBP systems due to acid hydrolysis or to radiation effects. Evidence is given in para. 4.3 that these impurities exert a negligible effect, in acid TBP systems, on the distribution coefficients obtained with (RuNO) nitrato complexes.

Due to the cationic nature of RuIV nitrates, acids such as DBP might, however, lead to the extraction in a TBP system of RuIV if any ruthenium is present in this form. Distribution measurements, similar to those described in para. 4.3, with RuIV solutions in nitric acid show that some extraction of RuIV does occur with DBP (Table XVII): as is to be expected, high acid conditions oppose the formation of a DBP complex; such extraction of RuIV as might occur in a TBP-DBP system is therefore only likely to be significant under low acid or acid deficient conditions.

An adverse effect of radiation on ruthenium decontamination has been reported by U.S.A. workers (Cathers(17)). Their results apply to acid systems. The explanation for this adverse effect must apparently be sought outside the action of DBP on (RuNO) nitrato complexes or on RuIV: there are of course other possibilities e.g. the action of other organic degradation products from TBP and its diluent or the formation of different ruthenium complexes by the action of reagents, such as nitrous acid, which are formed by radiation in the system.

7. DISCUSSION AND CONCLUSIONS

The properties of nitrato nitrosylruthenium complexes in aqueous and TBP solutions of nitric acid follow the general pattern of nitrato complexing of polyvalent cations e.g.

TABLE XVII

EXTRACTION OF RuIV FROM NITRIC ACID SOLUTIONS BY 2% (0.1M) DBP IN KEROSENE

Vol. of organic phase : Vol. of aqueous phase = 1. Temperature ~20°C.

Serial	Preparation of Initial Solution from Stock in 3.3M HNO_3	Ru Concentration	Stirring Time (mins.)	Ru Distribution Coefficient $(^O/_A)$
1.	Diluted to 1M HNO_3 and aged for 2 hours.	~ 10^{-3}M	2 20	.0004 .0014
2.	Diluted to 1M HNO_3 and extracted immediately.	"	20 60	.004 .004
3.	Diluted to 0.1M HNO_3 and extracted immediately.	~ 10^{-4}M	2 20	.069 .067

Note: The conditions in Serial 3 are relatively favourable to the formation of a RuIV-DBP complex; this is because there is little time for polymer formation, and complex formation, according to an equilibrium such as

$$RuIV^{\underline{x}+} + \underline{x}\, H(Bu_2.PO_4) \rightleftharpoons Ru(Bu_2PO_4)_{\underline{x}} + \underline{x}H^+ ,$$

is promoted by the low hydrogen ion concentration (activity).

(i) there is a series of complexes in which the higher nitrato complexes are favoured by high stoichiometric concentrations of nitric acid or of nitrate:

(ii) one of the stable forms in TBP solution is an uncharged TBP complex containing no aquo groups.

Particular points of interest which arise from this work are -

(iii) the absence of polynuclear forms (with $<10^{-2}$M Ru) in concentrations of nitric acid down to 1M and probably even to 0.1M;

(iv) the ease with which the individual complexes can be detected and estimated by paper chromatography owing to the relative slowness of the nitration and denitration reactions.

The distribution of ruthenium obtained when aqueous and TBP phases containing these complexes are mixed can now be explained, for a wide variety of conditions, from the kinetic, equilibrium and partition data given in this paper: the distribution of ruthenium can also be forecast for other conditions. Unlike the distribution of other metals, when present as nitrates, the ruthenium distribution is dependent on relatively slow reactions; this is one of the main reasons why it has behaved anomalously in many of the investigations in which fission product ruthenium, in conjunction with other fission products and with fissile and fertile elements, has been studied in nitric acid solution. The properties of these (RuNO) nitrato complexes reported in this paper can also be applied to the complicated conditions which arise in a counter-current extraction system: forecasts can be made of the effect of variables such as residence times on ruthenium decontamination factors: results will be reported in Part II for a TBP system.

We are conscious that ruthenium is anomalous compared to many of the other elements present in solutions of irradiated material in nitric acid in another important aspect, viz., its possible existence in a multiplicity of forms such as RuIV,

(RuNO) nitrato complexes and

(RuNO) nitro complexes.

The (RuNO) nitrato complexes, to which this paper is confined, are only one of these forms: dissolving and subsequent cooling conditions as well as radiation, can influence nitrous acid concentrations and therefore play an important role in determining the proportion of ruthenium as (RuNO) nitrato complexes: these matters are under investigation and it is already apparent that the (RuNO) nitrato complexes are an intermediate form between RuIV and (RuNO) nitro complexes. However, as both these other forms appear to be relatively inextractable by TBP solutions, the overall behaviour of fission product ruthenium in a TBP extraction process is probably largely controlled by the prevalence of (RuNO) nitrato complexes.

8. ACKNOWLEDGMENTS

We are grateful to many members of the Chemistry Division, A.E.R.E. for helpful discussions. We also wish especially to thank Mr. R.P. Bell for his help in the extension of the theory of Martin's method to cover the specific problems of this work (see Appendix).

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APPENDIX

TWO APPLICATIONS OF MARTIN'S METHOD TO SPECIFIC PROBLEMS RELATED TO NITRATO COMPLEXES OF NITROSYLRUTHENIUM

(by R.P. Bell* and P.G.M. Brown)

1. Definition of Terms.

Let $V = \dfrac{\text{Volume of Solvent Phase}}{\text{Volume of Aqueous Phase}}$.

K_T = partition coefficient of trinitrato (RuNO) complex.

K_D = " " " dinitrato " "

I refer to the inextractable species (in each case the assumption is made that only the tri- and dinitrato complexes extract; the term inextractable species is applied to the lower nitrato and polynuclear complexes).

C refer to concentrations in the original aqueous solution.

C_T = concentration of trinitrato (RuNO) complex.

C_D = " " dinitrato " "

C_I = concentration of Ru as inextractable Ru species.

C_{Ru} = total ruthenium concentration.

then $C_{Ru} = C_T + C_D + C_I$.

Let $\alpha = C_D/C_T$ and $\beta = K_D/K_T$.

x = concentration of ruthenium in the aqueous phase, for a given value of V, after extraction.

$x' = x - C_I$ = concentration of extractable ruthenium in the aqueous phase, for a given value of V, after extraction.

y = concentration of ruthenium in the organic phase, for a given value of V, after extraction.

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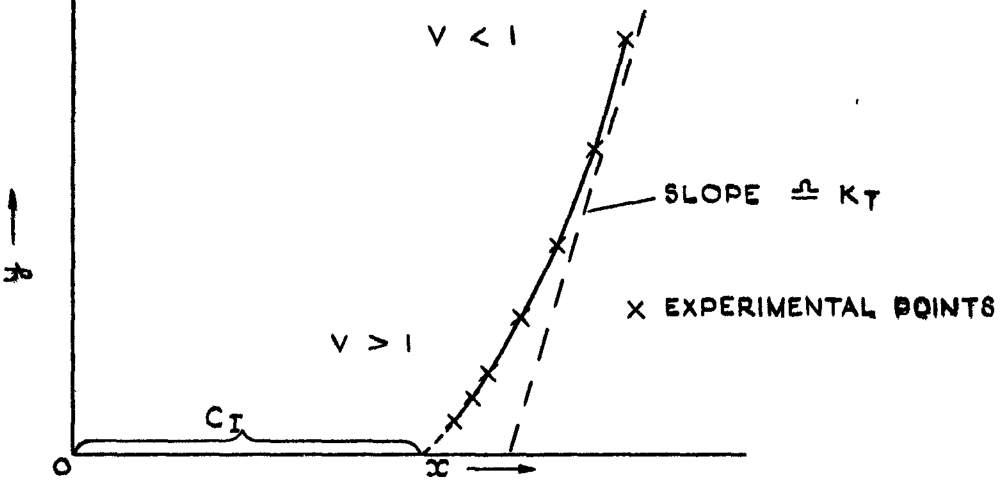
* Consultant to A.E.R.E.

2. Case I: To find C_T, C_D and K_D when C_I and K_T are known.

Note: K_T may be obtained from the approximate relationship

$$K_T \simeq \lim_{x \longrightarrow C_{Ru}} \left(\frac{dy}{dx}\right) , \tag{1}$$

or, alternately, from separate successive strip experiments. C_I is obtained directly from the intercept of the plot of x against y on the x-axis. These points are illustrated below (see Fig. 5):



Now for two extractable species, T and D, and one inextractable species I,

$$x = \frac{C_T}{1+VK_T} + \frac{C_D}{1+VK_D} + C_I \tag{2}$$

and

$$y = \frac{K_T C_T}{1+VK_T} + \frac{K_D C_D}{1+VK_D} ; \tag{3}$$

by rearrangement of (2) and (3) with substitution of

$$\alpha = C_D/C_T \quad \text{and} \quad \beta = K_D/K_T ,$$

we derive the equation

$$\frac{(1 + VK_T)\, K_T\, x'}{y - K_T\, x'} = \frac{1 + \alpha}{\alpha(\beta-1)} + \frac{(\alpha + \beta)\, K_T}{\alpha(1-\beta)}\, V \tag{4}$$

which gives a straight line plot when

$$\frac{(1 + VK_T)\, K_T\, x'}{y - K_T\, x'} \qquad (= \varphi)$$

is plotted against V; the slope (s) of the plot is given by

$$s = \frac{(\alpha + \beta)\, K_T}{\alpha(1-\beta)} , \tag{5}$$

and the intercept on the φ axis (i) is given by

$$i = \frac{1 + \alpha}{\alpha(1-\beta)} . \tag{6}$$

When (5) and (6) are solved for α and β, we obtain

$$\frac{1}{\alpha} = i - \frac{s}{K_T} \tag{7}$$

and

$$\beta = 1 - \frac{1 + 1/\alpha}{i} . \tag{8}$$

s and i are known (also K_T), hence α and β, and therefore C_D, C_T and K_D, may be calculated.

It is worth noting that if equation (4) is divided throughout by V, and the left hand side of the equation is plotted against $1/V$, the roles of the slope and the intercept are reversed. This causes the points to bunch differently, and acts as a very good check on the method; in certain cases this method of plotting is more suitable to the analysis of the results.

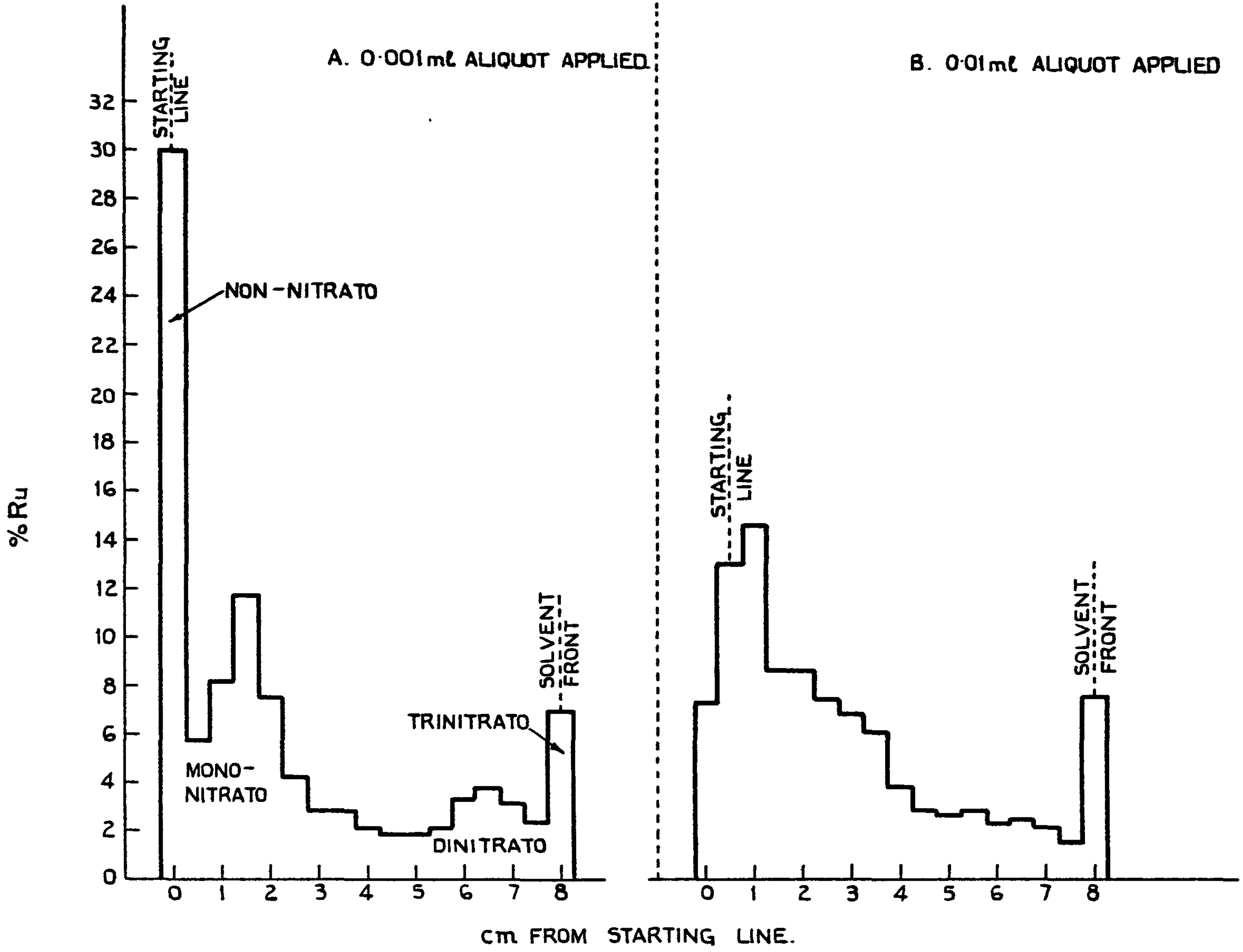
3. Case II: To find K_T and K_D when C_T, C_D and C_I are known.

Again from equations (2) and (3), by rearrangement, we may deduce the expression

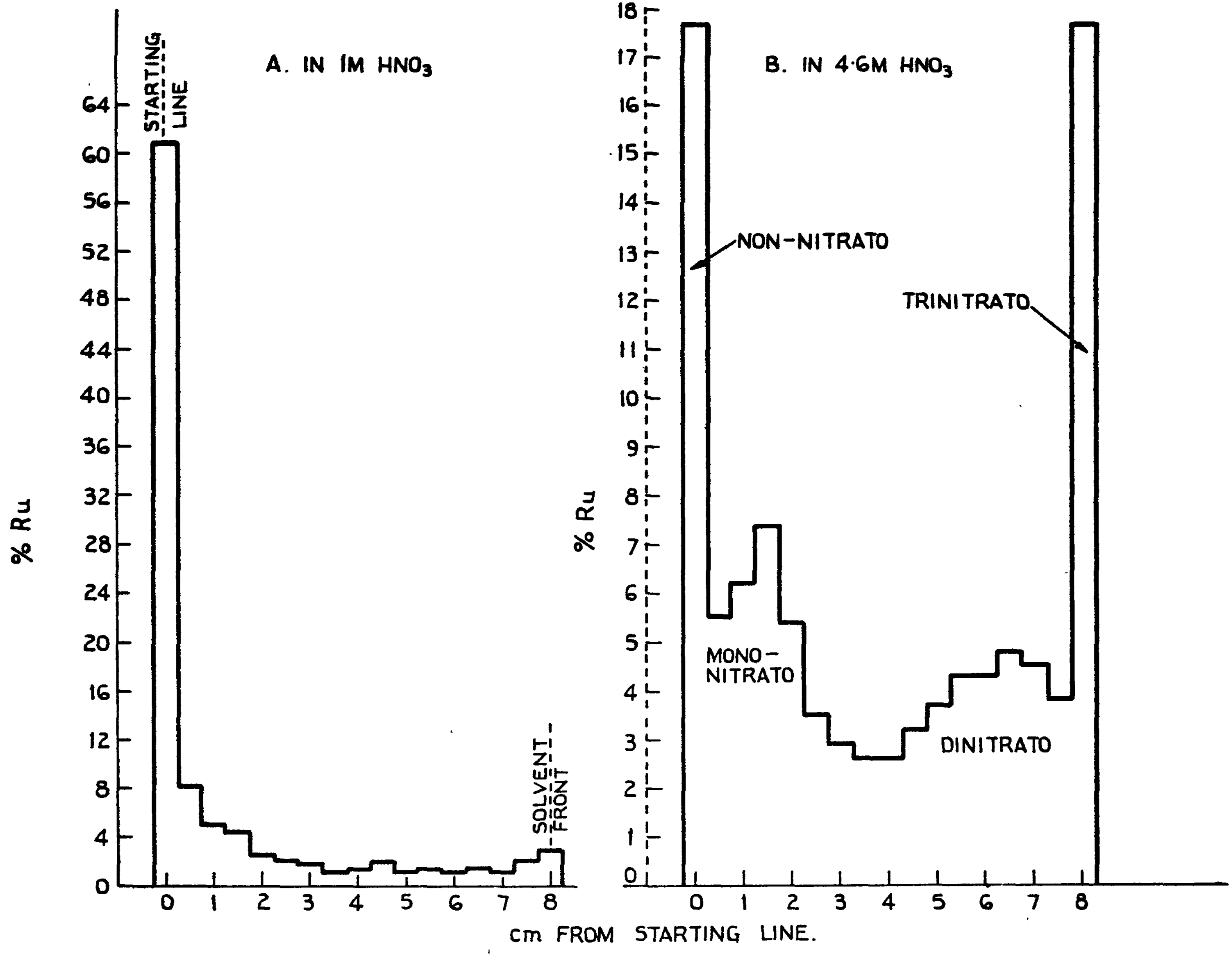
$$y\,(1 + VK_D) = K_T\, x'\,(1 + VK_D) - C_D\,(K_T - K_D) . \tag{9}$$

In this case we apply a method whereby a value of K_D is chosen, and then corrected by successive approximation, such that when $y\,(1 + VK_D)$ is plotted against $x'\,(1 + VK_D)$, a straight line is obtained whose intercept on the $y\,(1 + VK_D)$ axis when the x' term is zero is given by

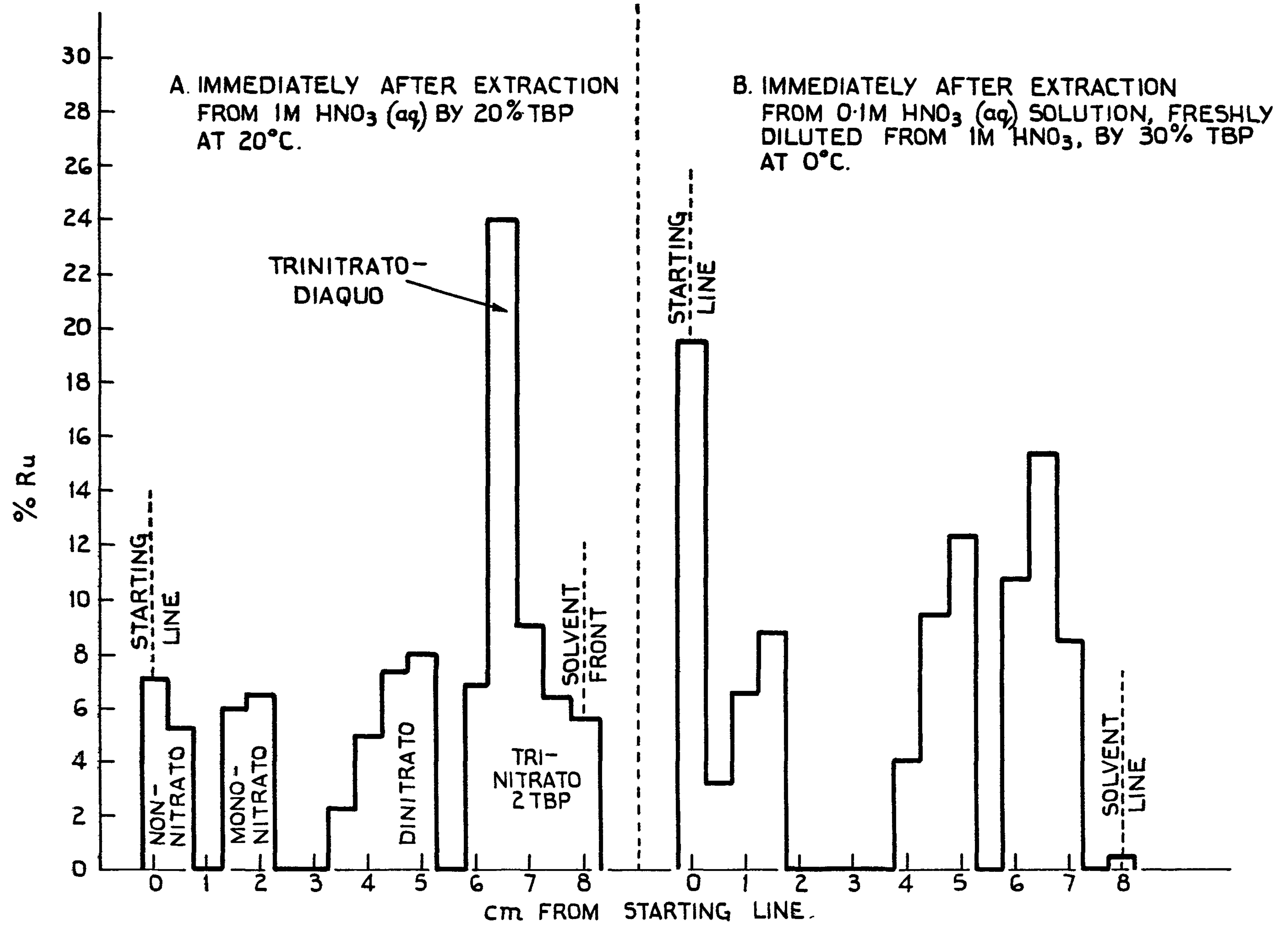
$$i = -\,C_D\,(K_T - K_D) . \tag{10}$$



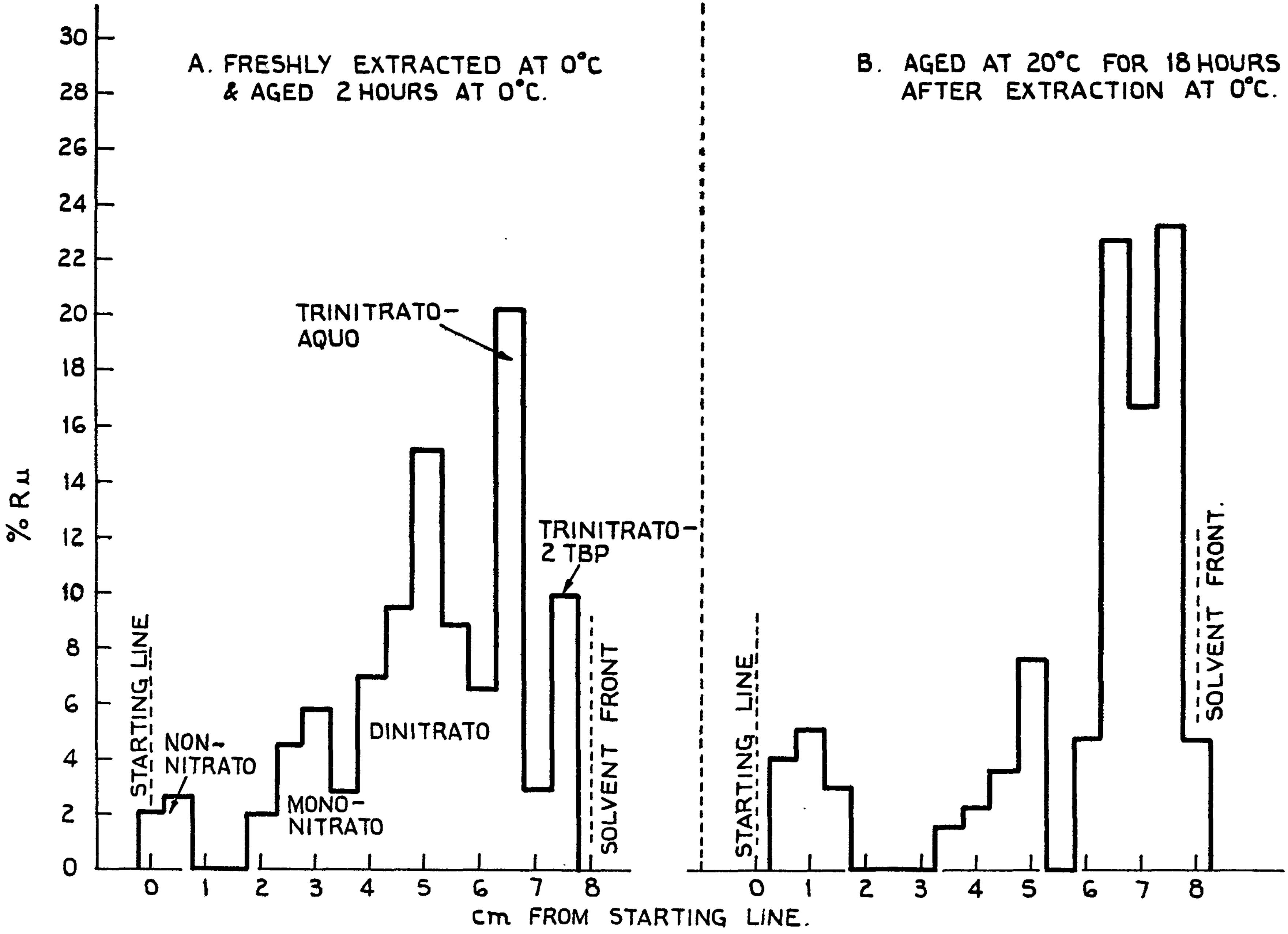
AERE. C/R 2260. FIG. 1. PAPER CHROMATOGRAMS OF (RuNO) NITRATO COMPLEXES AGED IN 3 M HNO_3
(SOLVENT: METHYL ISO-PROPYL KETONE)



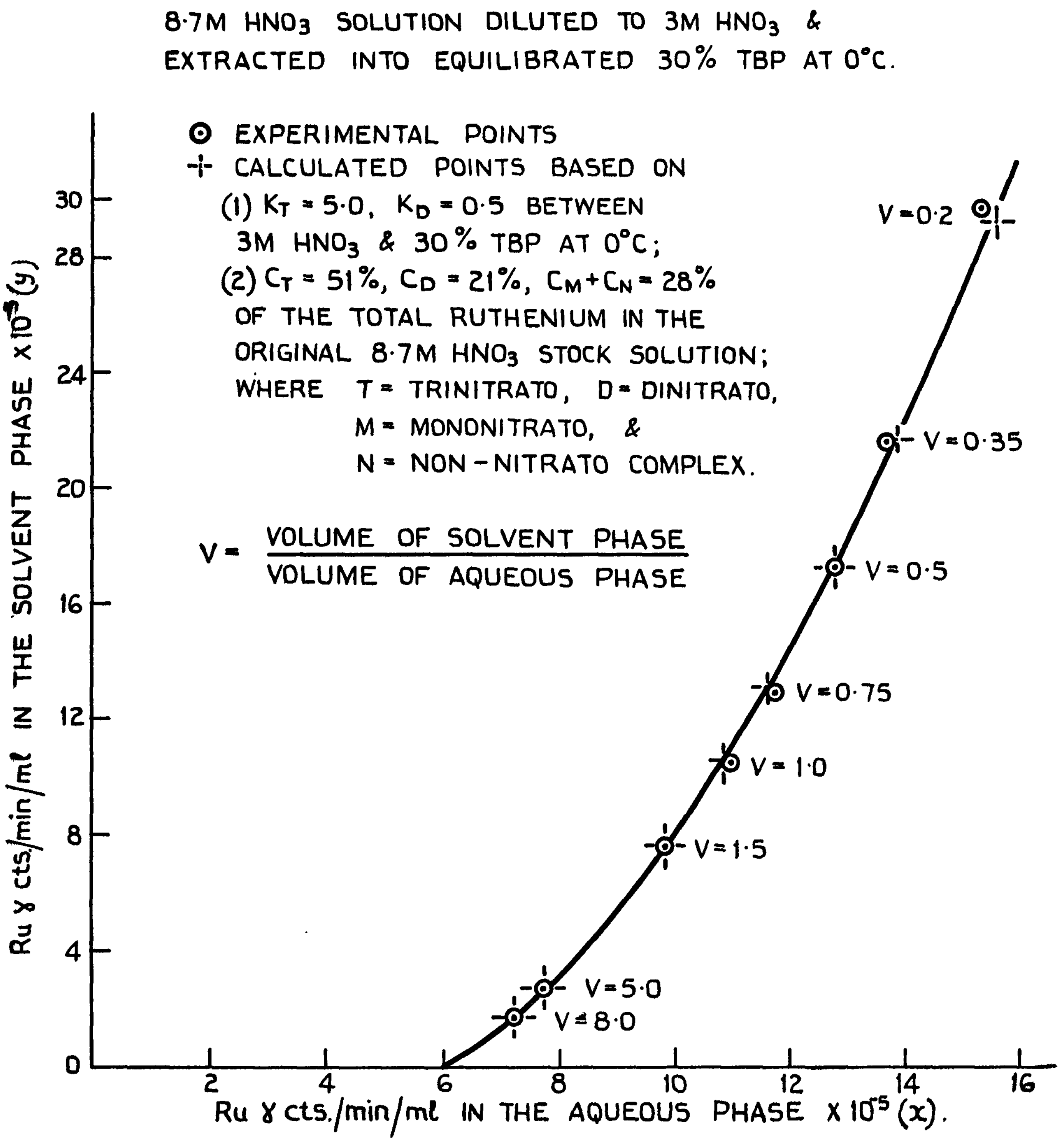
AERE. C/R 2260. FIG. 2. PAPER CHROMATOGRAMS OF (RuNO) NITRATO COMPLEXES AT EQUILIBRIUM IN AQUEOUS HNO_3 SOLUTIONS.



AERE. C/R 2260. FIG. 3. PAPER CHROMATOGRAMS OF (RuNO) NITRATO COMPLEXES IN TBP PHASES.



AERE. C/R 2260. FIG. 4. PAPER CHROMATOGRAMS SHOWING THE AGEING OF (RuNO) NITRATO COMPLEXES IN 30% TBP CONDITIONED WITH 1MHNO_3



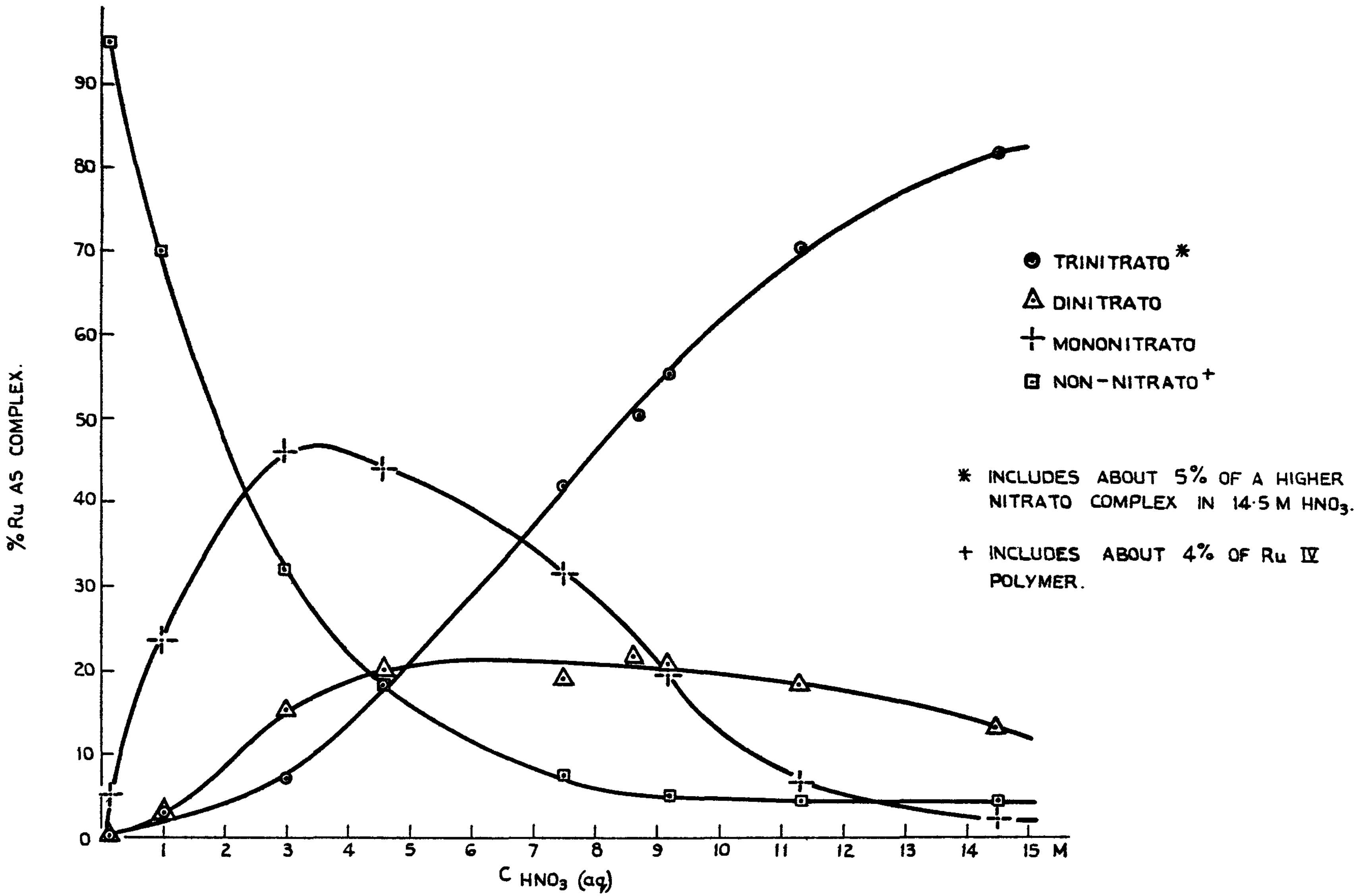
8·7M HNO_3 SOLUTION DILUTED TO 3M HNO_3 & EXTRACTED INTO EQUILIBRATED 30% TBP AT 0°C.

⊙ EXPERIMENTAL POINTS

-¦- CALCULATED POINTS BASED ON
(1) $K_T = 5{\cdot}0$, $K_D = 0{\cdot}5$ BETWEEN 3M HNO_3 & 30% TBP AT 0°C;
(2) $C_T = 51\%$, $C_D = 21\%$, $C_M + C_N = 28\%$ OF THE TOTAL RUTHENIUM IN THE ORIGINAL 8·7M HNO_3 STOCK SOLUTION;
WHERE T = TRINITRATO, D = DINITRATO,
M = MONONITRATO, &
N = NON-NITRATO COMPLEX.

$$V = \frac{\text{VOLUME OF SOLVENT PHASE}}{\text{VOLUME OF AQUEOUS PHASE}}$$

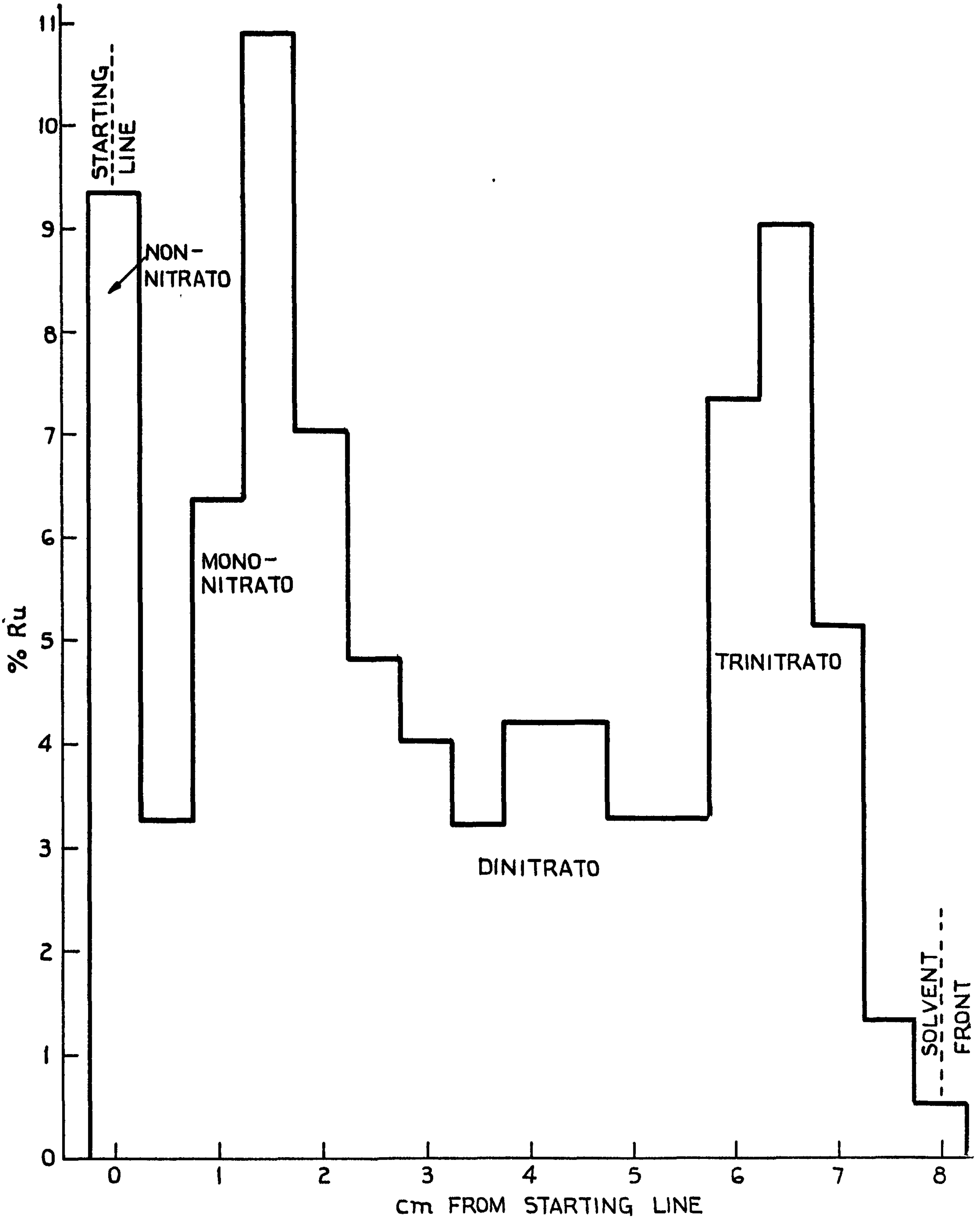
AERE. C/R 2260. FIG. 5. MARTIN'S METHOD APPLIED TO A SOLUTION OF (RuNO) NITRATO COMPLEXES AT EQUILIBRIUM IN 8·7M HNO_3



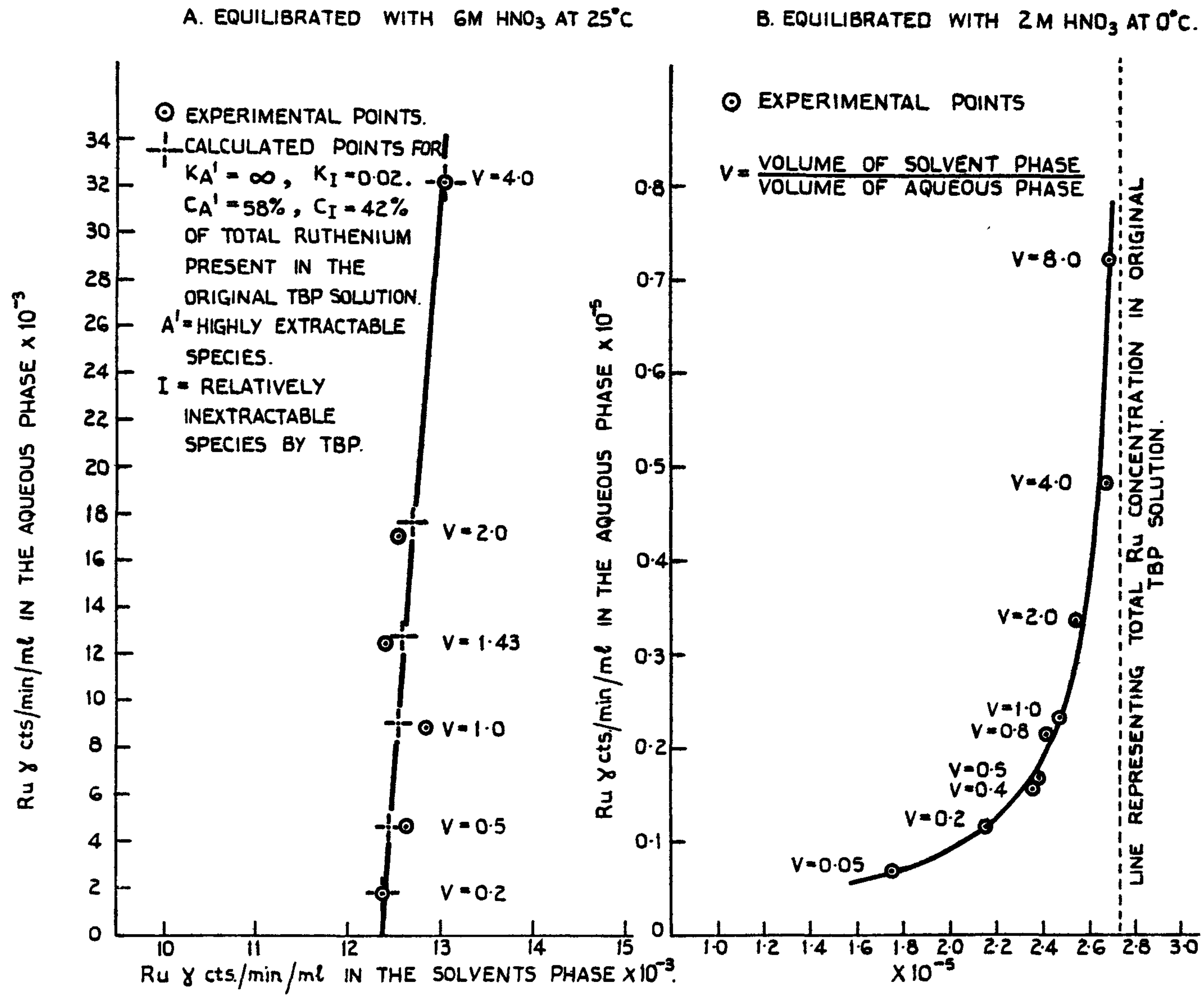
* INCLUDES ABOUT 5% OF A HIGHER NITRATO COMPLEX IN 14·5 M HNO_3.

\+ INCLUDES ABOUT 4% OF Ru IV POLYMER.

AERE. C/R 2260. FIG. 6. COMPOSITION OF SOLUTIONS OF (RuNO) NITRATO COMPLEXES AT EQUILIBRIUM IN NITRIC ACID.

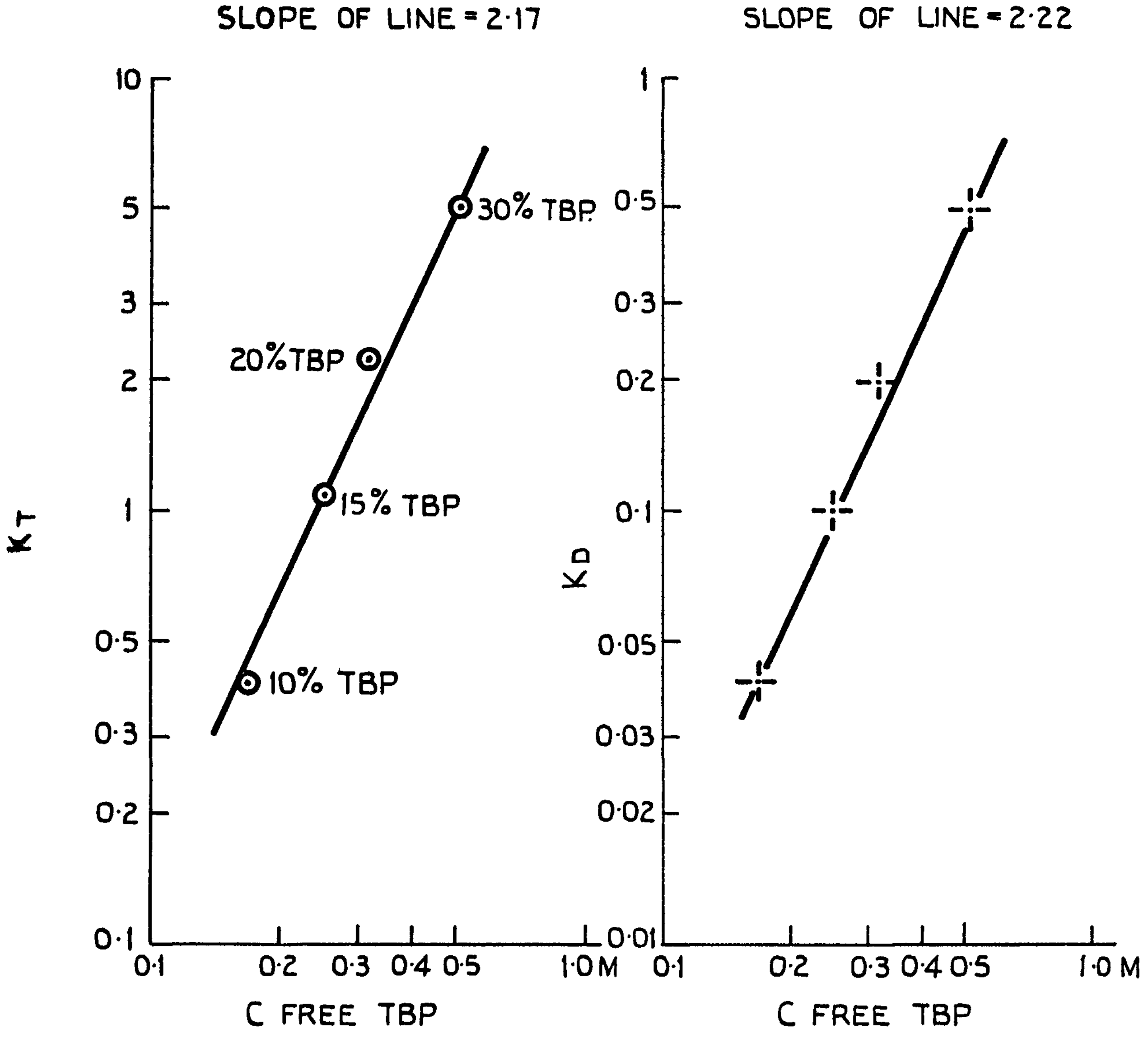


AERE. C/R 2260. FIG. 7. PAPER CHROMATOGRAM OF (RuNO) NITRATO COMPLEXES AT EQUILIBRIUM IN 3MHNO_3 SOLUTION CONTAINING 300 g U/l



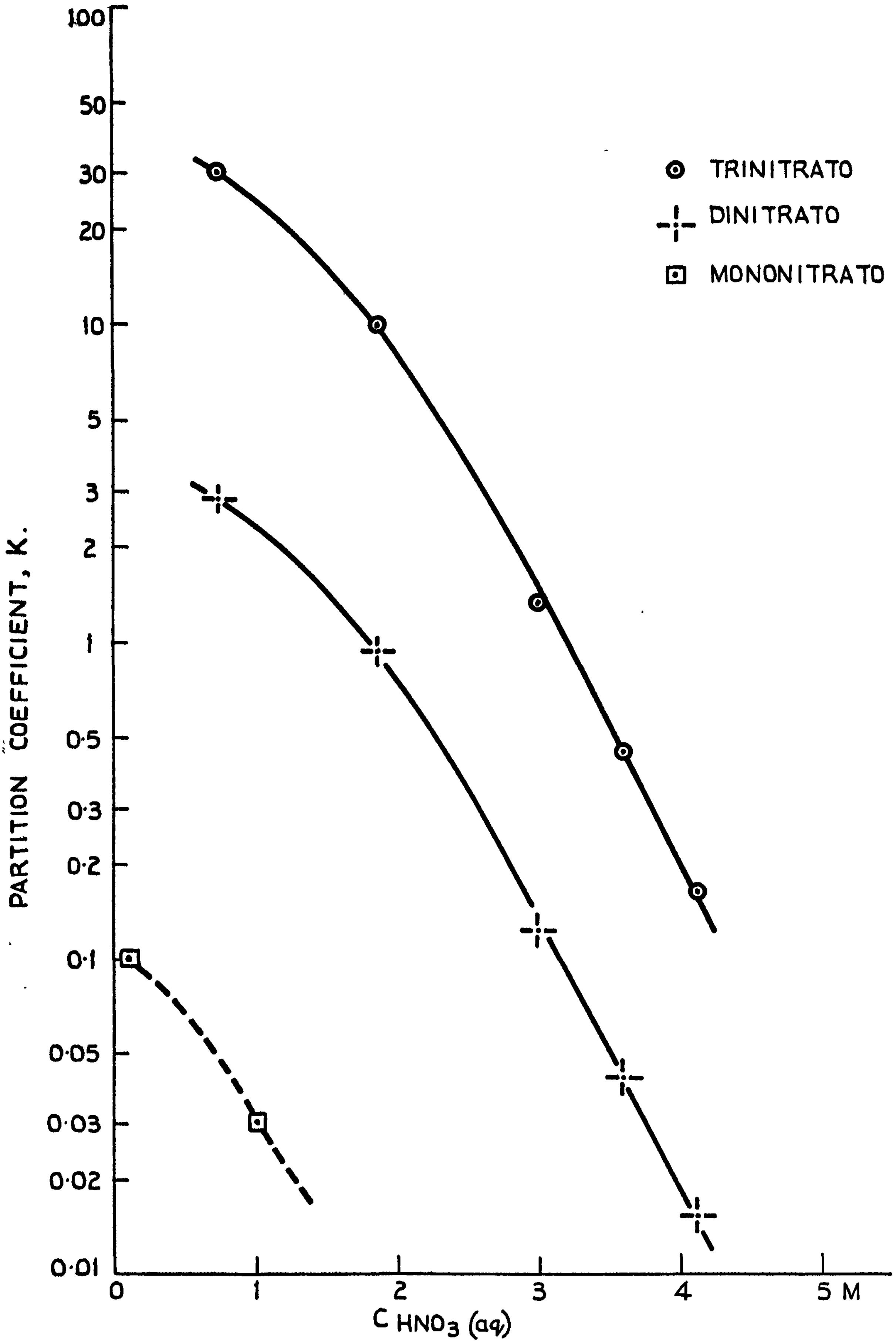
AERE. C/R 2260. FIG. 8. MARTIN'S METHOD APPLIED TO SOLUTIONS OF (RuNO) NITRATO COMPLEXES IN 30% TBP.

FREE TBP VARIED BY VARIATION OF STOICHEIOMETRIC TBP CONCENTRATION.

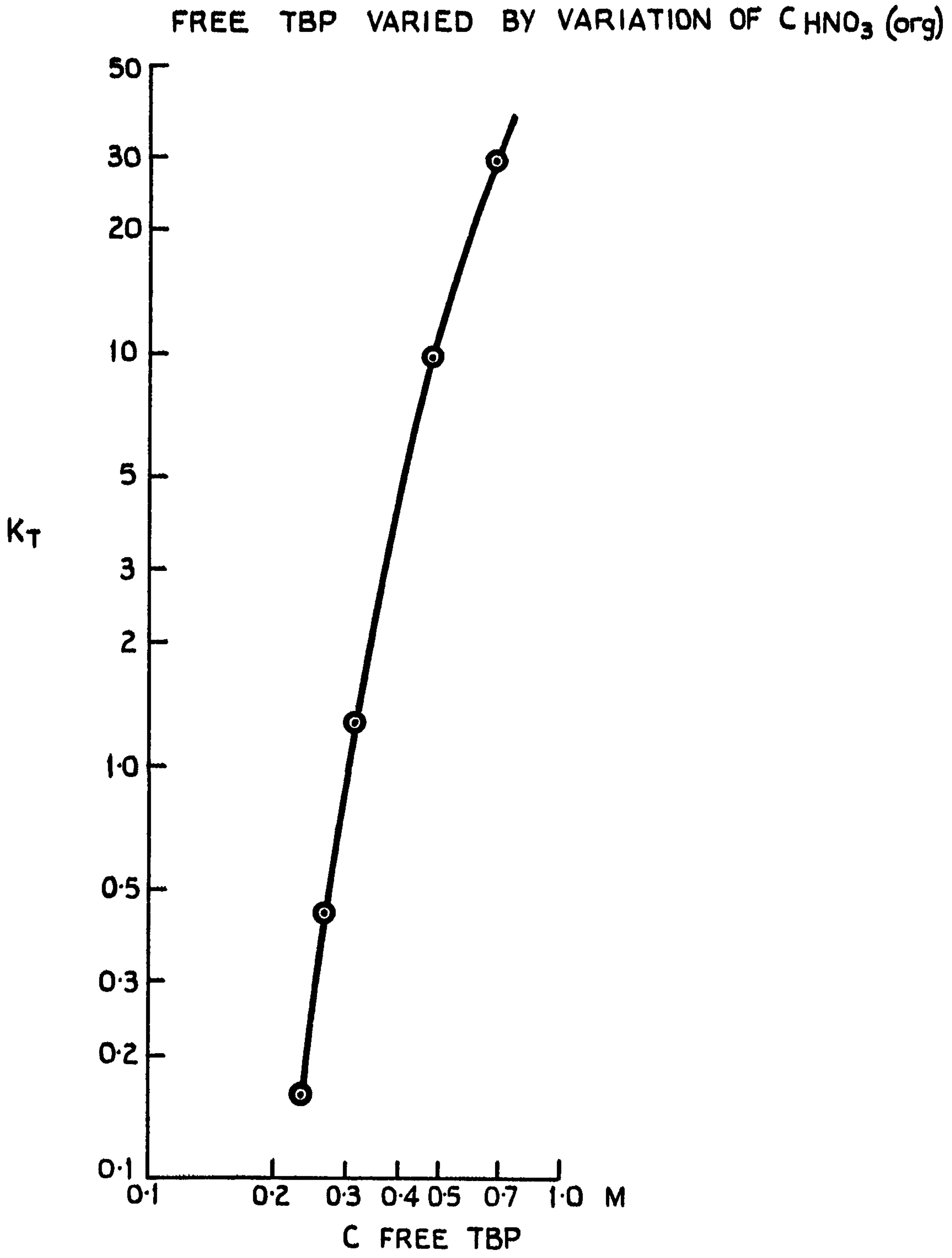


AERE. C/R 2260. FIG. 9. DEPENDENCE OF THE PARTITION COEFFICIENTS OF THE DI-AND TRINITRATO COMPLEXES OF NITROSYLNUTHENIUM ON FREE TBP CONCENTRATION.

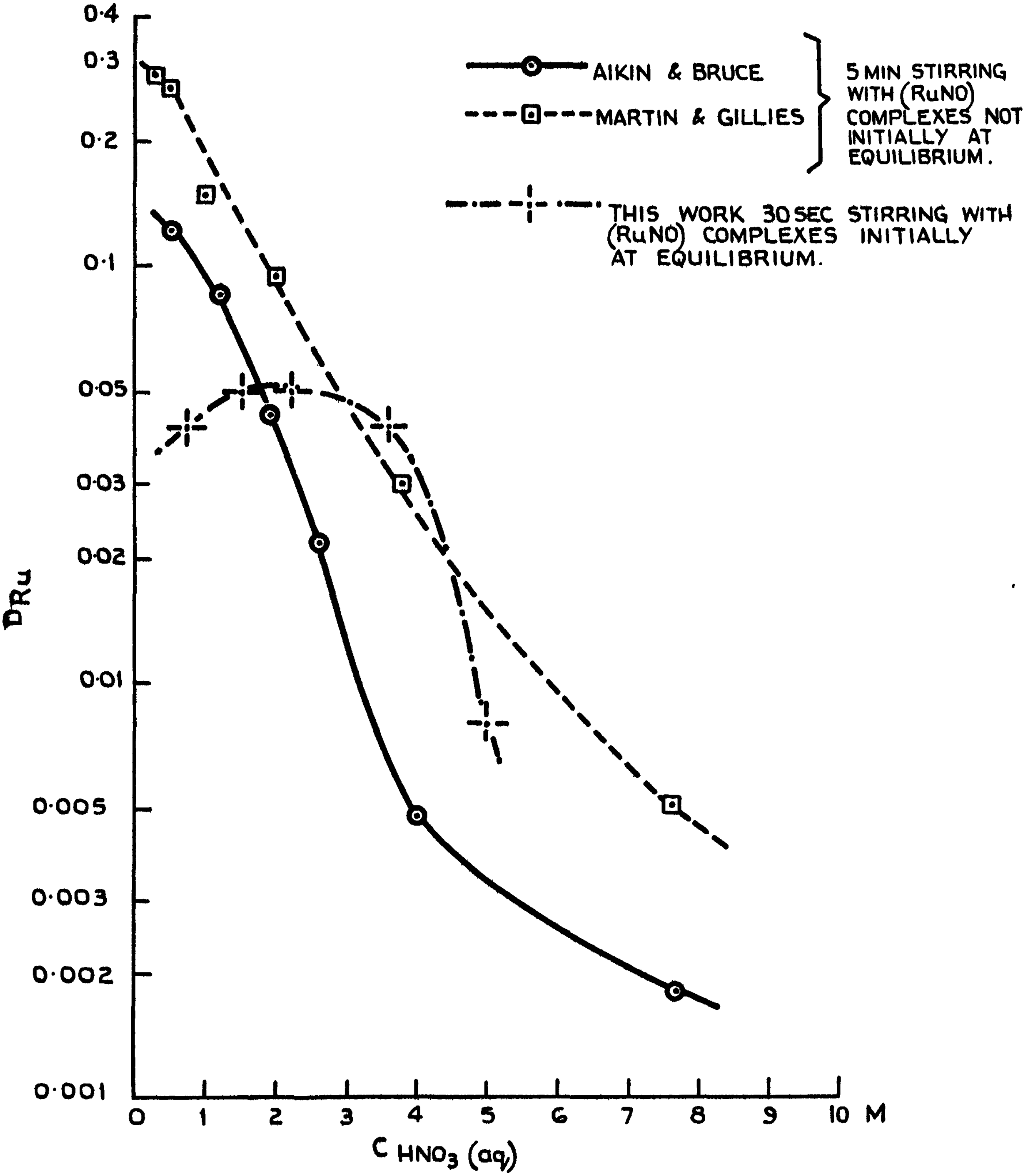
$C_{HNO_3(aq)}$ = 3 M. TEMPERATURE = 0° C. C_{Ru} = $3{\cdot}53 \times 10^{-3}$ M.



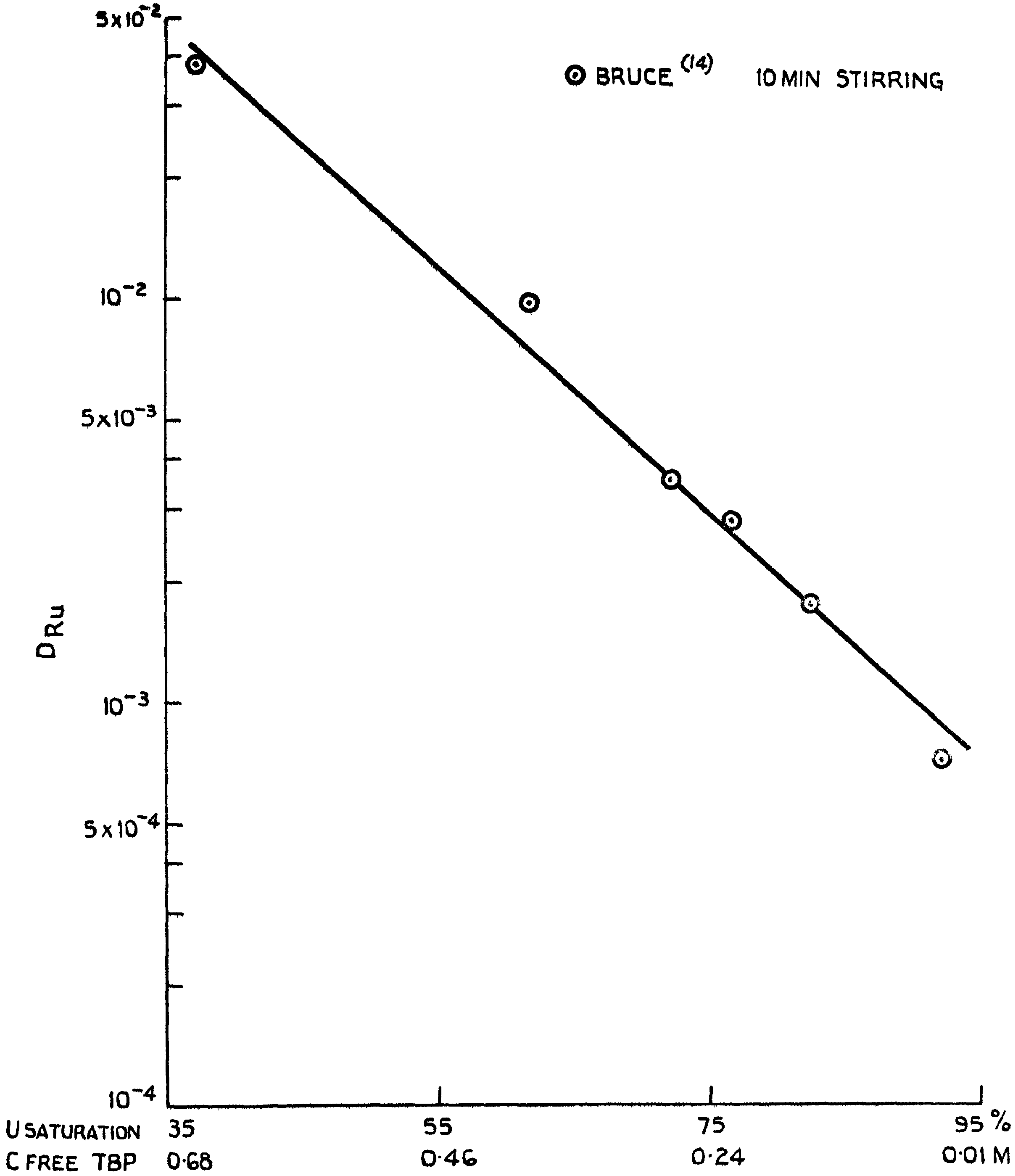
AERE. C/R 2260. FIG. 10. VARIATION, WITH NITRIC ACID CONCENTRATION, OF THE PARTITION COEFFICIENTS OF THE (RuNO) NITRATO COMPLEXES BETWEEN AQUEOUS NITRIC ACID AND 20% TBP AT 20° C.



AERE. C/R 2260. FIG. 11. DEPENDENCE OF THE PARTITION COEFFICIENT OF THE TRINITRATO COMPLEX ON FREE TBP CONCENTRATION.



AERE. C/R2260. FIG. 12. RUTHENIUM DISTRIBUTION COEFFICIENTS AS A FUNCTION OF NITRIC ACID CONCENTRATION FOR 20% TBP AT 20° C.



AERE. C/R 2260. FIG. 13. THE INFLUENCE OF URANYL NITRATE ON THE RUTHENIUM DISTRIBUTION COEFFICIENT BETWEEN 3M HNO_3 & 30 % TBP.