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EQUILIBRIUM EXTRACTION CHARACTERISTICS OF ALKYL AMINES AND NUCLEAR FUELS METALS IN NITRATE SYSTEMS

PROGRESS REPORT XIII

October 1, 1963 - May 30, 1964

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August 3, 1964

Work Performed Under Subcontract No. 1327

Under Contract No. W - 7405 - Eng - 26

with

Union Carbide Nuclear Corporation

Oak Ridge, Tennessee

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1.0 Summary

1.1 Multicomponent Metal Extraction

The extraction of Cu and Ag was studied using radiotracers by extracting both metals simultaneously from a single aqueous phase. The extraction coefficient for silver was >0.1 at acid concentrations >8M, for 0.2M trilaurylamine in toluene. The copper extraction coefficient was at a maximum of 0.0005 from 3M nitric acid, for the same amine concentration.

Gold extraction was studied using a radiotracer from pure nitrate solution, a gold foil after irradiation being dissolved electrolytically. The distribution coefficient was at a maximum of 40 at 3M nitric for 0.2M amine nitrate in toluene. Partial reduction of the gold on standing at room temperature, and in contact with an organic phase, made a study of the simultaneous extraction of Cu, Ag and Au impossible. However, it was felt that the technique of following the decay of the radioactive species involved to determine the various distribution coefficients simultaneously, was too laborious to warrant further study, even though it was capable of yielding accurate information. An alternative technique for studying the simultaneous extraction of two metals, based upon the variation of distribution ratio with phase ratio, is discussed.

1.2 Extraction of Nitrosylruthenium

The extraction of the nitrato complexes of nitrosylruthenium was studied further in an attempt to determine the nature of the extractable species. The mole fractions of the two extractable species were studied as a function of delay time in rapid dilution experiments. There was less ruthenium present in the more extractable state than in the less extractable. Within the narrow range of delay times so far examined, the species appear to be hydrolyzed according to first order kinetics with rate constants $k_1 \approx 0.03$ per min. for the less extractable species, and $k_2 = 0.20$ per min. for the more extractable species. The net increase in the number of nitrate ions transferred to the organic phase for each ruthenium transferred was studied. More than 3 nitrate ions were transferred in each case, and the calculations indicated that there was an increase of 5 nitrate ions for each of the less extractable species, and 3 nitrate ions for each of the more extractable species. If this is correct, the less extractable species appear to be polynuclear.

The computer program for analysis of mole fractions and partition coefficients is described.

2.0 Multicomponent Metal Extraction

2.1 Introduction

In studying new solvent extraction processes, particularly those suitable for the reprocessing of fissile material, it is necessary to have some idea of the distribution of elements throughout the periodic table. Normally this involves repeated experimentation studying the distribution of each element individually. This process might be made less laborious if techniques could be developed for studying the distribution of two or more elements simultaneously.

Initially it was intended to study the distribution of copper, silver and gold simultaneously by using radiotracers, and observing the decay curve of the aqueous and organic phases. Preliminary tests using hypothetical data generated on the assumptions that $D_{Cu} \approx 10^{-4}$, $D_{Ag} \approx 10^{-3}$ and $D_{Au} \approx 10^{1} - 10^{4}$, showed that it would be extremely difficult to determine D_{Cu} accurately if $D_{Au} > 10^{1}$, since even under ideal conditions the accuracy with which the gold could be counted in the organic phase was of the same order of magnitude as the total number of counts due to the copper. It was therefore decided first to study the distribution of copper and silver simultaneously, then to study the distribution of gold and finally, only if the gold distribution was in a suitable range, to study the distribution of all three metals simultaneously.

2.2 Distribution of Copper and Silver

A 7.5 day Ag^{111} tracer in nitric acid solution was purchased from the isotopes division, ORNL. A 12.9 hr. Cu^{64} was prepared by the irradiation of electrolytic copper wire in the MITR. Typically, 0.5 gm. of Cu was irradiated in a thermal flux of 8×10^{12} n cm^{-2} sec^{-1} for 40 sec. After a cooling period of 1 hr. to allow for the decay of 5.1 min. Cu^{66} to less 50 μc, the Cu wire, containing approximately 2 mc Cu^{64}, was dissolved in 10 ml. of 6N HNO_3. The relatively low specific activity copper was used to prevent significant activity from any contaminants that might be present, and a check of the γ spectrum of the copper failed to reveal any activities other than those of Cu^{64} and Cu^{66}.

Aliquots of either the Cu or Ag solutions, or of both, were added to large volumes of 1, 3, 6, 9 and 12M nitric acid to give solutions of activities between 100,000 and 300,000 counts per minute per ml. of solution of each activity.

The organic phase was prepared by dissolving weighed amounts of tri-n-dodecylamine (Eastman No. 7727) in A.R. grade toluene. The molecular weight of the tri dodecylamine (TLA) was determined by titration against standard perchloric acid in dioxane (molecular weight found = 528.2, theoretical 522.0). Before use, the TLA was equilibrated twice at 2:1

aqueous to organic phase ratio with nitric acid at the relevant concentrations.

The extraction of the metals was carried out by shaking 5 ml. of each phase for 1 minute in a 50 ml centrifuge tube, at room temperature. The phases were separated by centrifuging, and 1.0 ml. samples of each phase were taken for counting in thin-walled screw-top glass vials. A well-type scintillation counter was used, with all counts above 0.10 Mev being recorded.

The counting efficiency of the aqueous and organic phases was compared by counting samples of each, evaporating as close to dryness as was practical, and counting each sample again. The relative increase in the number of counts was the same in each case, within the limits of experimental error, so the relative counting efficiency of each phase was taken to be identical.

The decay of the samples was followed by counting each sample for 1 minute, initially every hour, and after about 24 hours, once every twelve hours. The initial activities in each phase were calculated via a least squares analysis of the decay curve using a desk calculator, in the case of the extraction of only one metal at a time, and via the FRANTIC program (1) in the case of simultaneous extraction of the two metals.

Typical decay curves are shown in Figure 1. The scatter in the results is largely due to the fact that the background varied during the course of the experiments, which was only traced to a faulty cooling fan within the counting equipment after the conclusion of the experiments.

A comparison of the distribution coefficients determined both individually and simultaneously is made in Figures 2 and 3. The agreement between these is satisfactory except for the copper distribution data at the lower amine concentration. Here both sets of data have a considerable uncertainty, which is due to the low activity of copper in the organic phase, as indicated by the low distribution coefficients.

It could be concluded that this method is capable of yielding satisfactory information on the distribution coefficients of at least two species simultaneously. It was felt, however, that the time spent in counting and analyzing the experiments definitely exceeded the time saved by performing the extractions simultaneously. Were automated counting and data processing equipment available, however, the method might be more practical.

Some limitations were observed during the testing of the FRANTIC program. Statistical uncertainties in counting limit the range of the method to approximately the region $10^{-4} < D < 10^{4}$, while the ratio between the distribution

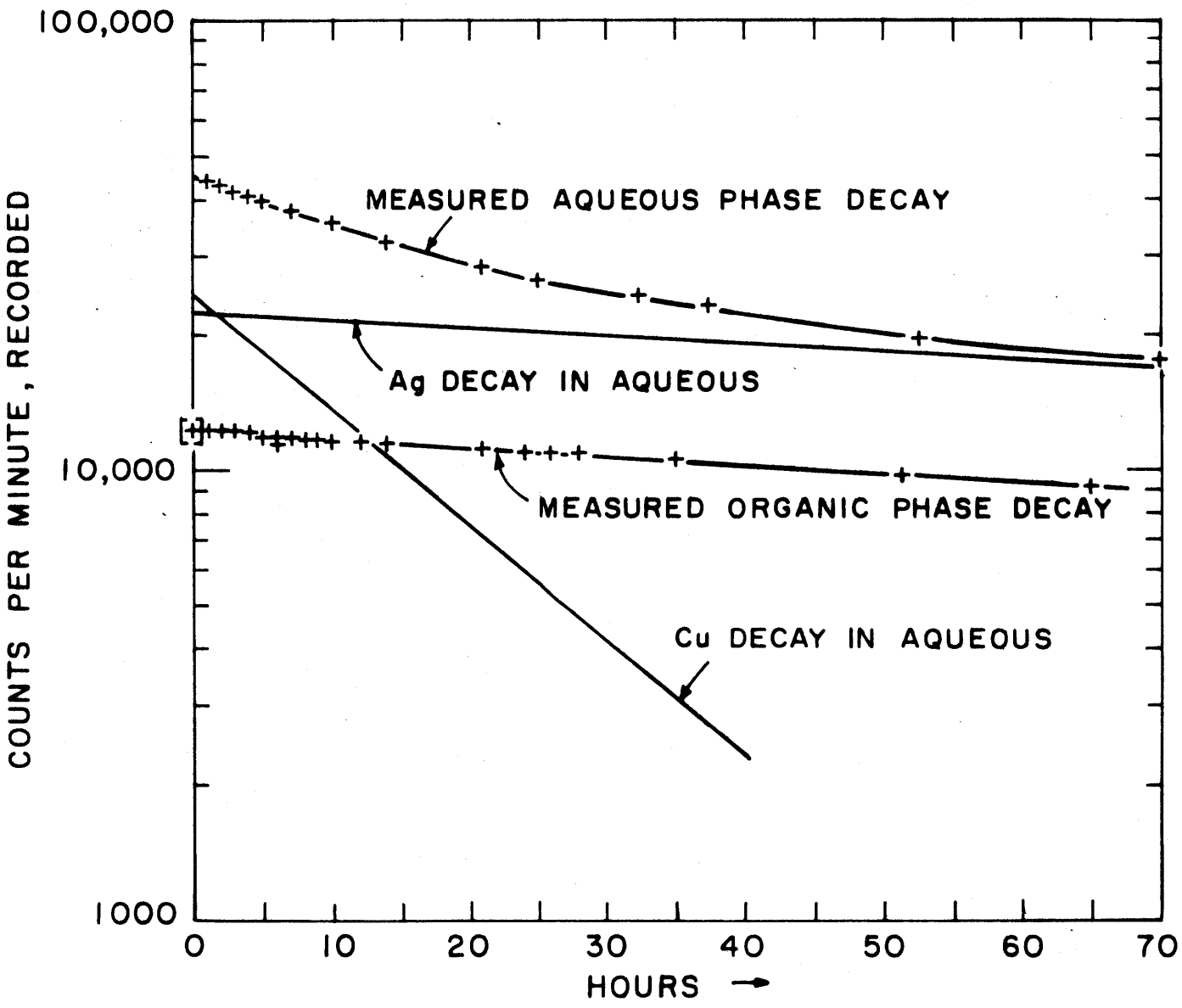

FIGURE 1. DECAY CURVES OF AQUEOUS AND ORGANIC PHASES.

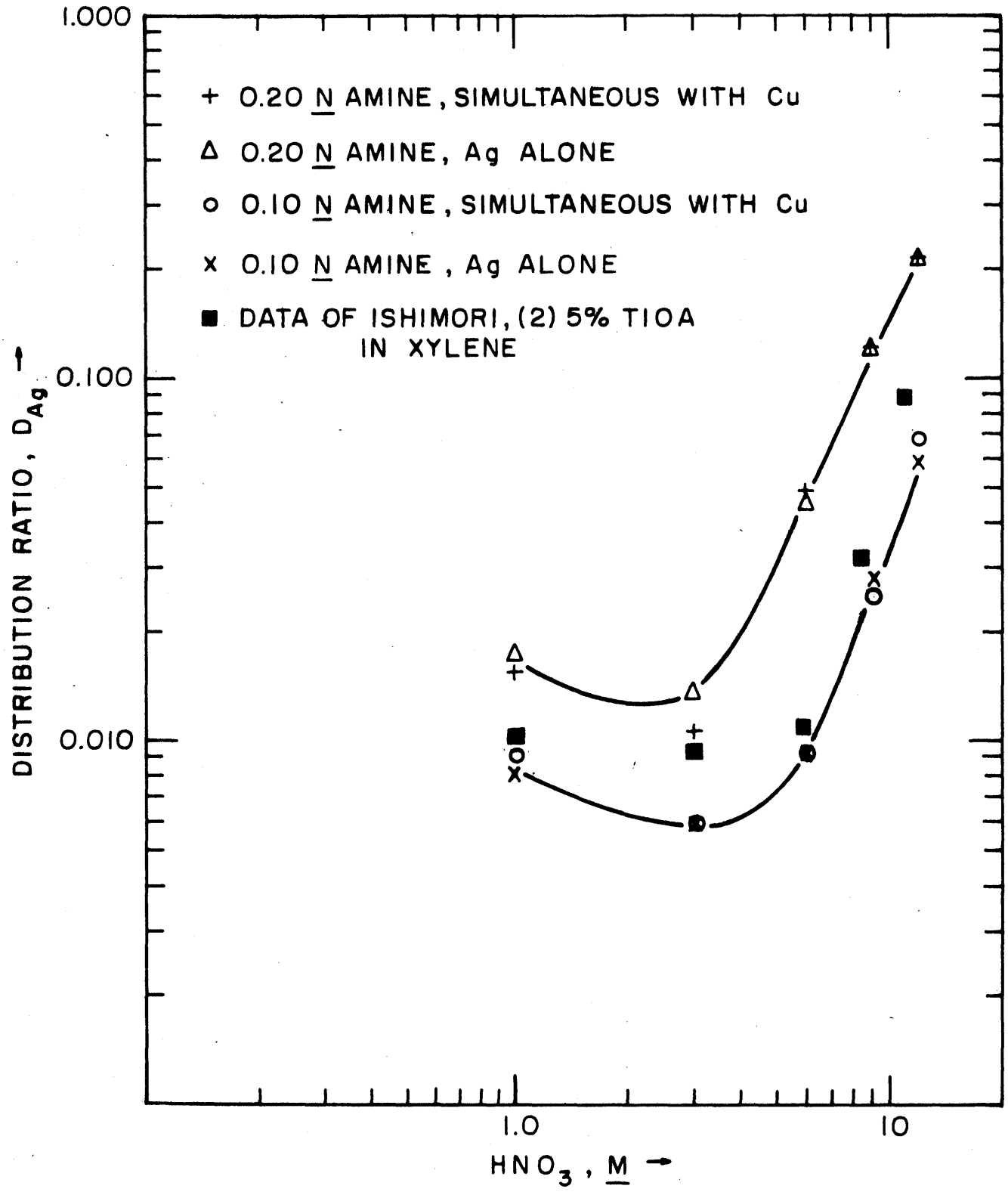

FIGURE 2. EXTRACTION OF Ag FROM HNO SOLUTION BY TLA IN TOLUENE.

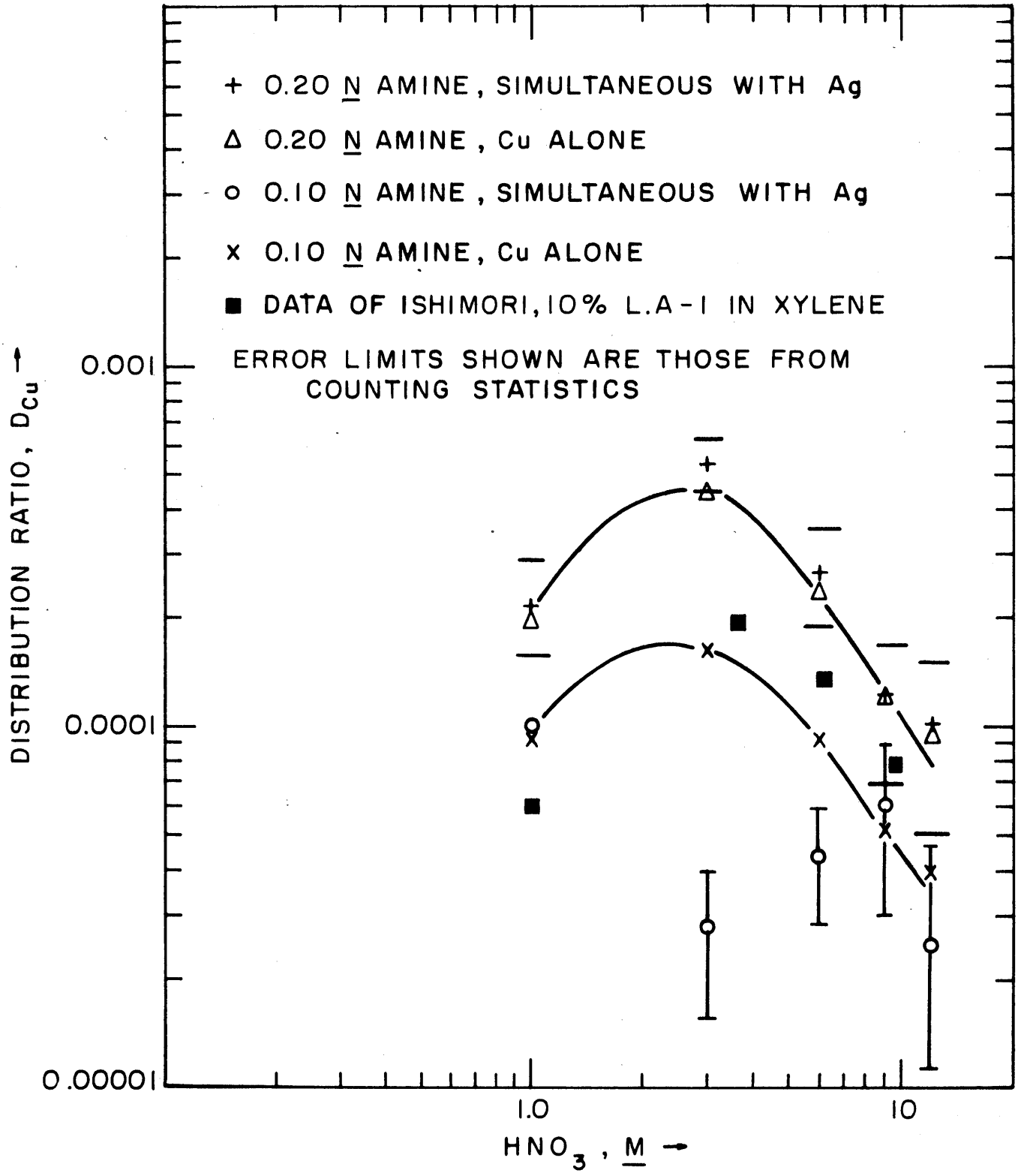

FIGURE 3. EXTRACTION OF Cu FROM HNO_3 SOLUTION BY TLA IN TOLUENE.

coefficients of the most and least extractable species should be less than 10^4.

2.3 Distribution of Gold

Previous studies (2) on the extraction of gold from nitrate solutions have been carried out with the gold present as the chloro complex in which state it has one of the highest distribution coefficients recorded. The chloride concentration in most reprocessing solutions is, however, very low, and it was therefore of interest to study the extraction of gold from pure nitrate solution.

Studies were carried out on the preparation of stable solutions of gold nitrate. Attempts to precipitate the chloride from $AuCl_3$ solutions with $AgNO_3$ failed, the gold being precipitated with the silver at room temperatures, and no precipitate forming at elevated temperatures, even after boiling under reflux in concentrated nitric acid solutions.

Precipitation of the gold as the hydroxide, according to the method of Johnston and Leland (3), failed to yield a product that was entirely soluble in sulfuric or nitric acid. It was thought that this might be due to reduction by light or heat to metallic gold on the surface of the precipitate, but neither precipitation in the dark nor at reduced temperatures rectified this.

Solutions of $AuCl_3$ in dilute or concentrated nitric acid were passed over cation and anion exchange resins of varying degress of cross linking. There was no significant absorption on cationic resins, while the complex absorbed so strongly onto the nitrate form of the anion exchange resins that neither concentrated nitrate solutions nor nitric acid were able to elute it.

An electrolytic method for the preparation of gold nitrate (4) was tested and found suitable. A gold foil connected directly to a graphite rod formed the anode and a graphite rod the cathode. The anode and cathode compartments were separated by a fine sintered glass disk. Both compartments were filled with 10N HNO_3 and stirred vigorously by teflon-coated magnetic stirrer bars. The apparatus was placed in an ice bath and the electrolyte maintained at less than 10°C.

In a typical run, 0.75 gm. of gold was dissolved from a foil weighing 2.35 gm. by electrolysis for 11 hours at 12 volts, 1.4 amp. The anode area was approximately 5 cm^2 initially. The anolyte was a yellow brown solution of 30 ml. volume, and was stored at 0°C in the dark. Qualitative tests were made on the stability of this solution. Gold was precipitated continuously as a fine red brown or black mass over a period of three weeks. Aliquots of the fresh anolyte were diluted 100, 200 and 500 times in 1, 3, 6 and 12N HNO_3, and stored in the dark at 0°C. All showed some instability

over a period of three weeks, though in each case the dilutions in 12M acid were the most stable.

For the extraction experiments, an Au foil was irradiated in the MITR to an activity of 1 mc Au^{198} per gm. 0.75 gm. of the foil was dissolved electrolytically, and the anolyte was filtered and diluted to 1 liter in 6M HNO_3. Two ml. of this solution were diluted to 100 ml. with 1, 3, 6, 9 and 12M nitric acid. The organic phase was prepared as described above (section 2.2), and 10 ml. of each phase was contacted by hand shaking for 1 min. in a 50 ml. centrifuge tube. The phases were separated by centrifuging for 30 minutes, which also removed gold reduced by contact with the organic phase. One ml. of each phase was taken for counting. Each phase was counted over a period of 36 hours with all counts above 0.15 Mev being recorded. The activity in each phase at the time of contact was calculated by a least-squares analysis of the decay curve on a desk calculator.

The results are shown as a function of nitric acid and amine concentration in Figure 4. It should be noted that in each case the sum of the activities in both phases was approximately 70% of the activity per ml. in the initial aqueous phase. It is believed that most of the loss was due to the reduction of some of the gold by contact with the organic phase—a black precipitate of Au was formed at the interface immediately after contact, and clean separation between the phases required prolonged centrifuging.

2.4 Discussion of the Decay Analysis Method

Comparison between the variation of distribution coefficient with nitric acid concentration for the three metals studied reveals a similarity between the behavior of Cu and Au and a distinct difference in the behavior of Ag. The curves for Cu and Au both possess maxima in the region 4-6M nitric acid, whereas the curve for Ag passes through a minimum in the region 2-3M. In view of the similarities between these metals, this seems difficult to understand. However, probably only Ag is present in the univalent state; Cu is almost entirely present as the Cu^{2+} ion, and Au probably in the Au^{3+} state. Divalent Cu and Au^{3+} have a strong tendency to form 4 coordinate complexes (5). It may be that the polyvalent Cu and Au are able to form extractable anionic complexes in dilute nitric acid, and their extraction falls off at higher nitric acid concentrations due to the formation of complexes of the type $H_2Cu(NO_3)_4$ and $HAu(NO_3)_4$, whereas in the same region extractable anionic complexes of Ag^+ are only starting to be formed.

The simultaneous determination of the distribution of Cu and Ag has been shown to be feasible, if laborious; in view of the instability of gold nitrate solutions and the high ratio D_{Au}/D_{Cu} it was felt that it would be impractical to study the simultaneous distribution of Cu, Ag and Au, as had originally been intended.

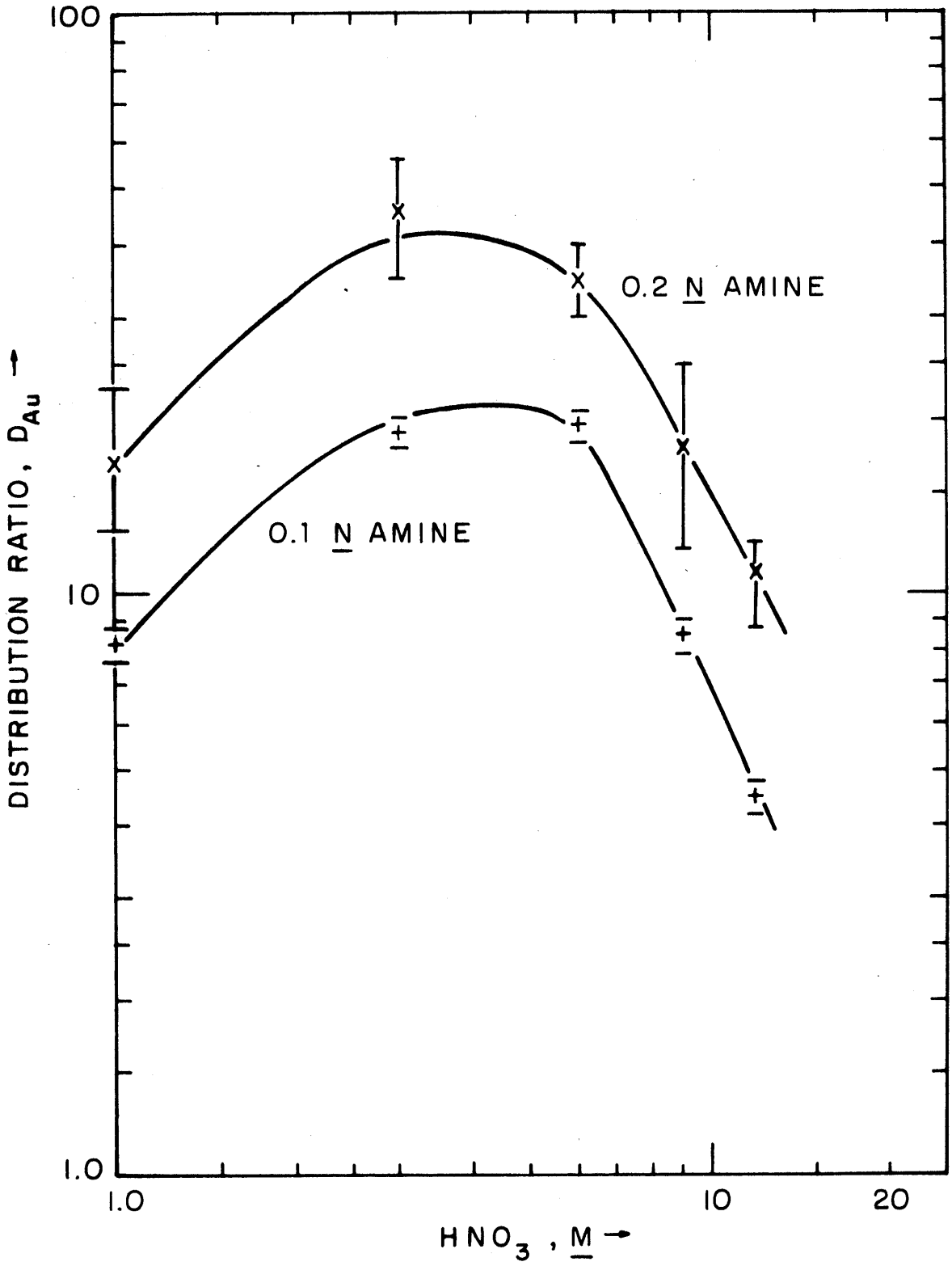

FIGURE 4. EXTRACTION OF GOLD NITRATE FROM HNO_3 SOLUTION BY TLA IN TOLUENE. ERROR LIMITS SHOWN ARE THOSE FROM COUNTING STATISTICS.

2.5 Proposed Technique Based Upon Phase Ratio Variation

A possible modified technique for studying simultaneous distribution is proposed, based upon the method adopted in the study of the distribution of ruthenium species (6). It is proposed that the simultaneous distribution of tracers be followed as a function of phase ratio. Then the distribution is governed by the equation

$$\frac{D}{D+T} = \sum_{i=1}^{n} \frac{P_i}{D+P_i} \cdot X_i \qquad (1)$$

where D is the measured distribution coefficient at phase ratio, aqueous to organic, T; n is the number of species present, and P_i and X_i are the partition coefficient and mole fraction initially present of species i. In order to determine P and X it is necessary to perform 2n experiments at different phase ratios, all other conditions being kept constant. However, for radiotracer work, it is relatively simple to arrange that the initial activity of each species in the aqueous phase is constant, so that $X_1 = X_2 = X_i$. Then equation (1) becomes

$$\frac{D}{(D+T)X} = \sum_{i=1}^{n} \frac{P_i}{T+P_i} \qquad (2)$$

and only experiments at n different phase ratios are required to determine the P_i.

Preliminary experiments along these lines were carried out with Cu and Ag. However, erratic operation of the counting equipment made the experiments impossible to interpret. It is hoped to repeat the experiments later.

A potential advantage of this method may be noted. While it would probably be difficult to use short-lived tracers, it would be possible to use tracers of similar half lives, which is impossible in the technique of decay curve analysis.

3.0 Extraction of Nitrosylruthenium

3.1 Introduction

Previous studies at M.I.T. (6) have indicated that there are probably two species of nitrosylruthenium extractable by amines from nitric acid solution, though there is some doubt as to the nature of these species. That there are two extractable species was concluded from rapid dilution experiments, in which aged nitrosylruthenium complexes in nitric acid were rapidly diluted and extracted at varying phase ratios. By application of equation (1) (section 2.4 above) values of M_1, M_2, P_1 and P_2 were determined as a function of nitric acid concentration. This treatment will be valid if it is assumed that redistribution between the extractable species is relatively slow, and that the extraction is very rapid.

Timmins (6) analyzed some 50 extractions in this manner. Since all but one of the experiments could be fitted on the assumption of only two extractable species, it was concluded that only two species were in fact extractable. Skavdahl (6) attempted to identify the species by potentiometric titration, but his results have not been able to be reproduced (7).

This further study was therefore undertaken in an attempt a) to identify extractable complexes and b) to test the assumption of only two extractable species.

3.2 Experimental

Nitrosylruthenium nitrato complexes were prepared by the method described previously (6). A solution in 11.4M nitric acid was aged for at least 40 days in the dark in order for equilibrium to be reached before extraction took place.

The organic phase was 0.26M TLA in toluene, prepared as described above (section 2.2). Shortly before use it was pre-equilibrated with nitric acid of the relevant concentration.

Extraction was performed by dilution of the aged ruthenium solution in water to give a final solution of known volume that was 3.0M in nitric acid. A measured volume of pre-equilibrated organic phase was carefully introduced above the aqueous phase, and at a known time after the dilution, the phases were mixed by hand shaking for 30 seconds, immediately separated by centrifuging for 1 minute, and the organic phase drawn off with a syringe.

In some cases, when relatively large quantities of ruthenium were extracted, the conductivity of the organic phase was immediately measured in order to determine the unbound nitric acid concentration (7). Some of the organic phase was then stripped by repeated contact with 1M NaOH in

order to determine the ruthenium and total nitrate concentrations. Otherwise the samples were immediately taken for the direct determination of the ruthenium concentration.

Total nitrate in the strip solution from the organic phase was determined gravimetrically by precipitation with nitron from acetic acid solution. The hydrogen ion concentration of the aqueous phase was determined by potentiometric titration with 1M NaOH, a correction being applied for the hydrolysis of ruthenium complexes by assuming that all the ruthenium was initially present as $RuNO(NO_3)_3$ and present as $RuNO(OH)_3$ above pH 6.

Difficulty was experienced in the determination of ruthenium. The method of Belew, Wilson and Corbin (8) was initially adopted, but it was found impossible to obtain reproducible results. The method is based on the oxidation of Ru to RuO_4 with AgO, extraction of the RuO_4 by CCl_4, and development of a blue color due to a thiocyanate complex. Various precautions were taken; CCl_4 was purified by distillation at reduced pressure, or freed of reducing impurities by contact with HNO_3 - H_2O_2; AgO both prepared in the laboratory and purchased from a commercial supplier was used; and the equipment, with teflon stopcocks and plastic stoppers, was rinsed with HNO_3 - H_2O_2 before use. In spite of these precautions it was evident that some of the RuO_4 was being reduced, since the color recorded for a standard sample was usually less than a fairly definite maximum, as indicated in Table 1.

Table 1

Color of NaCNS Solution Ostensibly Due to 0.12 mg. Ru in Standard Sample, Measured at 590 mμ in 1 cm. Cells

Sample	Optical Density	
1	.628	
2	.607	
3	.597	
4	.593	Mean = 0.596,
5	.592	Relative Standard
6	.590	Deviation = 1.0%
7	.568	
8	.558	
9	.537	
10	.522	
11	.509	
12	.498	

The method of Marshall and Rickard (9), based upon the color of potassium ruthenate in potassium hydroxide was tested. It was found that the solutions had a marked tendency to lose color and give a black precipitate on standing, even when rigorous precautions were taken to exclude dust. This tendency was particularly marked if the solution was warmed slowly in order to dissolve the fusion cake. The technique therefore adopted was as follows. The sample, containing less than 3 mg. Ru was evaporated in a nickel crucible very slowly on a hot plate to dryness, in the presence of 0.5 gm. solid KOH. One gm. of KNO_3 was added, and the sample slowly fused over a period of about 1 minute. It was carefully warmed until any gaseous reaction had ceased, then heated strongly until bubbling took place from the otherwise clear fusion. The crucible was immediately cooled in an ice bath, and 5-10 ml. of 2N KOH added. After standing for two minutes, the crucible was heated strongly to boil the KOH and so dissolve the fusion cake. The crucible was immediately replaced in the ice bath. After cooling for 5 minutes, the solution was made up to 50 ml. with 2M NaOH. The absorbancy was immediately determined at 465 mμ against a 2M KOH blank. Standardization was performed with weighed amounts of pure ruthenium, the solution being made up to 250 ml. The standard curve is shown in Figure 5. It is linear and passes through the origin, presumably due to the use of 2M KOH as a blank rather than water, as used by Marshall and Rickard. The molar absorbancy is 1760, in good agreement with the value of 1742 ± 12 determined previously (9).

The experimental results are given in Table 2.

3.3 Discussion

Initially attempts were made to follow the net increase in the number of nitrate ions in the organic phase as a function of ruthenium concentration, as outlined in a previous report (7). It was very shortly realized that the previously published figures on the partition coefficients and mole fractions of the various ruthenium species (6) were not sufficiently accurate to enable a good estimate to be made of the concentration of each species of ruthenium in the organic phase.

In order to improve upon estimates of the mole fractions and partition coefficients, a smoothing technique was attempted. Skavdahl (6) previously suggested that the two species extracted were hydrolyzed via a first order reaction, following "rapid dilution." Experiments were therefore carried out in which the distribution of ruthenium at varying phase ratios was determined as a function of delay time. From each set of experiments at a given delay time, it was thought that values of the mole fractions, X_i, and partition coefficients, P_i, could be calculated according to equation (1). The values of X_i could then be corrected so that the values of P_i were constant with delay time, and a plot of X_i as a function of time could be drawn up. Values of the reaction rate constants could

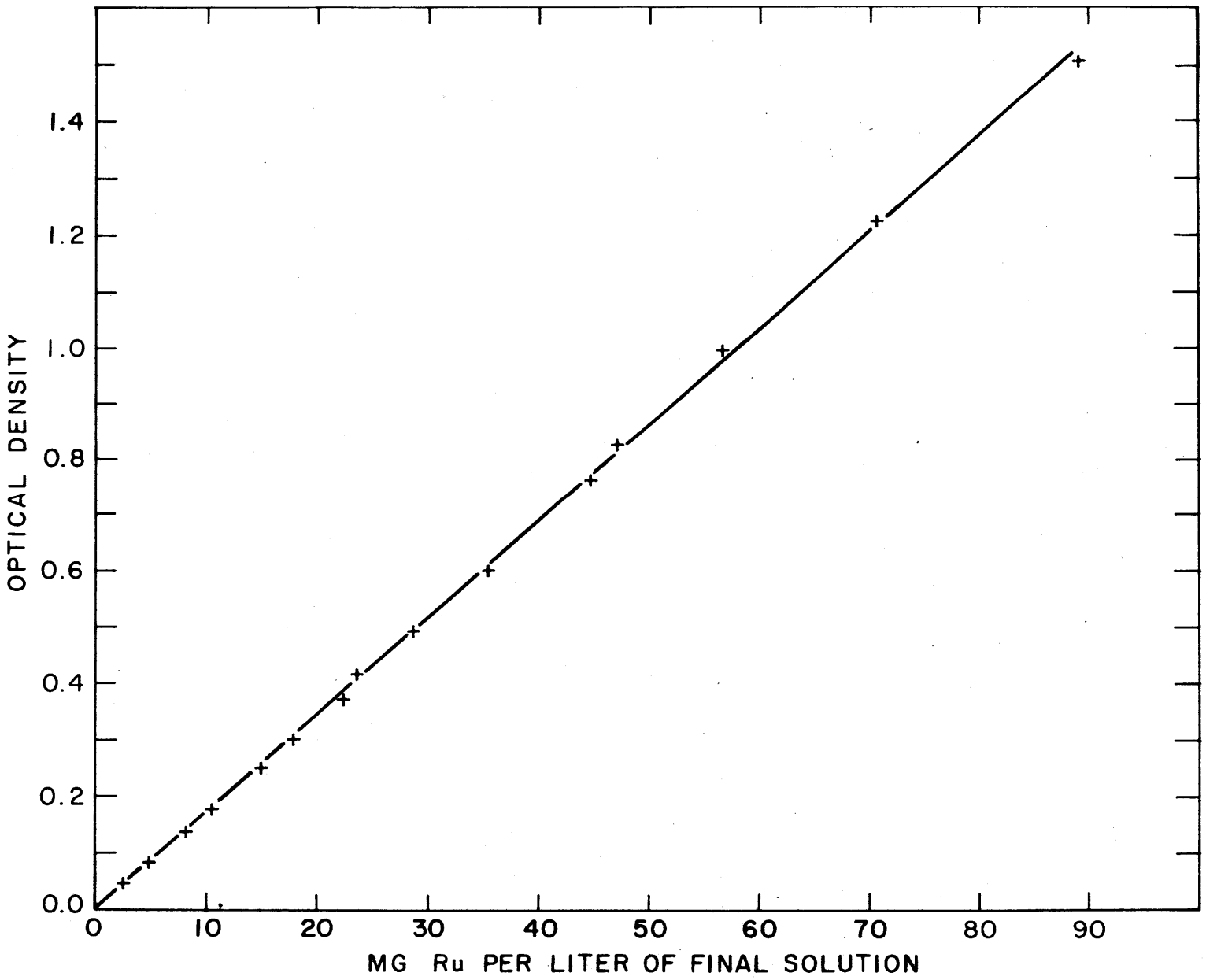

FIGURE 5. COLOR OF POTASSIUM RUTHENATE SOLUTION IN 2M KOH, AT 465 mμ IN 10 cm CELLS.

Table 2

Extraction of Aged Nitrosylruthenium Complexes from 11.34M HNO_3, 0.101M Ru, by 0.264M Tri-n-dodecylamine in Toluene

Sample No.	Phase Ratio A/O	Delay Time Secs.	Ru Org. Concn. M	Ru Aq. Concn. M	D_{Ru} O/A	Unbound HNO_3 Concn. M	Total Org. NO_3 Concn. M
1	2	30	0.0309	0.0850	0.363	0.057	0.430
2	4	30	0.0450	0.0890	0.505	0.041	0.469
3	1	30	0.0200	0.0804	0.249	0.073	0.422
4	3	30	0.0388	0.0878	0.444	0.042	0.451
5	0.5	30	0.0129	0.0745	0.173	0.097	0.410
6	6	Sample Spilt					
7	1	90	0.0162	0.0841	0.193	0.090	0.412
8	2	90	0.0233	0.0886	0.263	0.064	0.426
9	3	90	0.0292	0.0906	0.322	0.057	0.436
10-13		Samples Diluted Incorrectly					
14	0.25	300	0.00448	0.0824	0.0544	—	—
15	0.50	300	0.00735	0.0855	0.0860	—	—
16	1	300	0.01075	0.0896	0.120	0.107	0.408
17	2	300	0.0161	0.0924	0.173	0.103	0.426
18	4	300	0.0214	0.0950	0.225	—	—
19	0.379	90	0.00894	0.0768	0.116	—	—
20	0.50	90	0.01055	0.0793	0.133	0.105	0.419
21	0.758	30	0.0174	0.0774	0.225	—	—
22	0.25	∞	0.000725	0.0866	0.00837	—	—
23	0.33	∞	0.000800	0.0871	0.00919	—	—
24	0.5	∞	0.000950	0.0876	0.0108	—	—
25	1	∞	0.00124	0.0883	0.0140	—	—
26	2	∞	0.00154	0.0887	0.0174	—	—
27	3	∞	0.00181	0.0889	0.0204	—	—
28	4	∞	0.00202	0.0890	0.0227	—	—

then be derived and Skavdahl's hypothesis of first order kinetics could be tested. Skavdahl made an attempt to test this hypothesis, but as he determined only four points in each experiment as a function of time, to which six parameters M_1, M_2, P_1, P_2, k_1 and k_2, were applied, the results are probably not significant, and in fact he noted a discrepancy between his own results and hydrolysis rates determined from paper chromatography measurements (10).

For each value of the delay time, values of M_1, M_2, P_1 and P_2 were determined by the PARTIFRAC program described in the appendix. Two least squares criteria were tested—a least square difference between the calculated and experimental values of D/D+T, referred to as the C criterion, and the relative least square difference between the calculated and experimental values of D, referred to as the D criterion, i.e., the C criterion was $\delta^2/\delta P_1 \delta P_2 (D^*/D^*+T - D/D+T)^2 = 0$ and the D criterion was $\delta^2/\delta P_1 \delta P_2 (D^*-D/D^*)^2 = 0$ where D^* is the calculated value of D. The results of the computer study are shown in Table 3. The best fit to the data using the C criterion seemed to show variable values for the two partition coefficients, and the D criterion was therefore introduced so that runs at different delay times could be compared. Since in some runs only 5 experimental points were obtained, from which four parameters were calculated, the results from these runs could not be considered very significant. By combining runs and assuming constant values of the partition coefficients, the number of degrees of freedom available is increased.

It is apparent that the data for the value of P_1 at infinite delay time is not consistent with the data at shorter delay times. The aqueous phase in this case was prepared by mixing the aqueous phases from various rapid dilution experiments, and allowing the mixture to stand for three weeks. It is possible that the solution was not at equilibrium, though the trend in values of P_2, X_1 and X_2 is relatively consistent. It is also possible that P_1 may in fact be decreasing with increasing delay time, but before this view can be acceptable, further experiments at longer delay times are necessary.

Weighted average values of X_1, X_2, P_1 and P_2 from both criteria were calculated using weighting functions proportional to the number of degrees of freedom associated with each point. Values derived from combinations with the suspect data at infinite delay were ignored. The results are shown in Table 4.

Skavdahl (6) showed that if it is assumed that the species are hydrolyzed via first order kinetics, the decay of species 2 is governed by

$$(X_2 - X_2^*) = (X_2^o - X_2^*)\, e^{-k_2 t} \qquad (3)$$

Table 3

Computer Analysis of Distribution Data
The Determination of Mole Fractions and Partition Coefficients of Ru Species in 11.3M HNO_3 Diluted Rapidly to 3.0N HNO_3, Aged for the Given Delay Time, and Extracted for 30 Secs. by 0.26M TLA in Toluene

Delay Time Secs.	Combined With Runs at	P_1	P_2	X_1	X_2	σ^2 C Criterion(a)	σ^2 D Criterion(b)
30		0.68	16.4	0.302	0.086	33.642	—
90		0.20	4.0	0.330	0.132	8.429	—
300		0.54	8.5	0.199	0.044	10.997	—
∞		0.15	9.5	0.068	0.004	0.831	—
30		0.57	10.3	0.297	0.105	—	1210
90		0.56	40.0	0.303	0.053	—	420
300		0.41	4.6	0.187	0.067	—	1179
∞		0.15	8.0	0.074	0.004	—	869
30	90	0.43	8.1	0.307	0.124	—	1764
90	30	0.43	8.1	0.293	0.082	—	1764
90	300	0.46	6.5	0.278	0.086	—	2135
300	90	0.46	6.5	0.196	0.054	—	2135
30	90-300	0.515	8.4	0.293	0.116	—	3397
90	30-300	0.515	8.4	0.282	0.073	—	3397
300	30-90	0.515	8.4	0.200	0.046	—	3397
30	90-300-∞	0.125	4.0	0.420	0.196	—	11658
90	30-300-∞	0.125	4.0	0.437	0.138	—	11658
300	30-90-∞	0.125	4.0	0.273	0.097	—	11658
∞	30-90-300	0.125	4.0	0.079	0.006	—	11658

(a) $$\sigma^2 = \sum_{T=1}^{n} \left(\frac{D^*}{D^*+T} - \frac{D}{D+T} \right)^2$$

(b) $$\sigma^2 = \sum_{\text{No. of Combinations}} \left(\sum_{T=1}^{n} \left(\frac{D^*-D}{D^*} \right)^2 \right)$$

Table 4

Weighted Average Values of X_1, X_2, P_1 and P_2 as a Function of Delay Time

Delay Time Secs.	Mole Fraction of Ruthenium in Aqueous Phase		Partition Coefficients	
	X_1	X_2	P_1	P_2
30	0.299	0.113	0.50	8.6
90	0.282	0.080	0.47	7.9
300	0.198	0.050	0.49	7.7
∞	0.071	0.004	(0.15)	(8)

and that of species 1 by

$$(X_1 - X_1^*) = (X_1^o - X_1^*)\, e^{-k_1 t} + \frac{k_2}{(k_2 - k_1)} (X_2^o - X_2^*)(e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

where X_1^o, X_i and X_i^* are the mole fractions of species i present initially, at time t, and in equilibrium, respectively, and k_1 and k_2 are reaction rate constants for species 1 conversion to inextractable species and species 2 conversion to species 1, respectively.

A value of k_2 may be estimated from the slope of a semilog plot of $(X_2 - X_2^*)$ against delay time. In the absence of reliable data for X_1^* it is difficult to estimate k_1, but an order of magnitude estimate may be made from the initial slope of a semilog plot of $(X_1 - X_1^*)$ versus delay time, since in this case the second term on the right hand side of equation (3), referring to the formation and decay of species 1 from species 2, must be negligible. Such plots are shown in Figure 6, where the delay time is increased by 15 seconds to allow for the additional decay during the course of mixing the two phases. The error limits shown are the maximum and minimum values found in the computer analysis of the results.

From the slope of the plot of X_2 versus t, a value of k_2 = 0.00[illegible]0 per sec., or 0.[illegible] per min. may be derived. The slope of the plot of X_1 versus t is equivalent to a value of $k_1 \approx$ 0.0[illegible] per minute. Skavdahl estimated a value of 0.50 per minute for k_2 and 0.055 for k_1, while Fletcher (10) found a value of k = 0.024 per minute for the overall hydrolysis of the "Group D" complexes, i.e., all nitrosylruthenium nitrato complexes which are not cationic. Our results are not in agreement with Fletcher's.

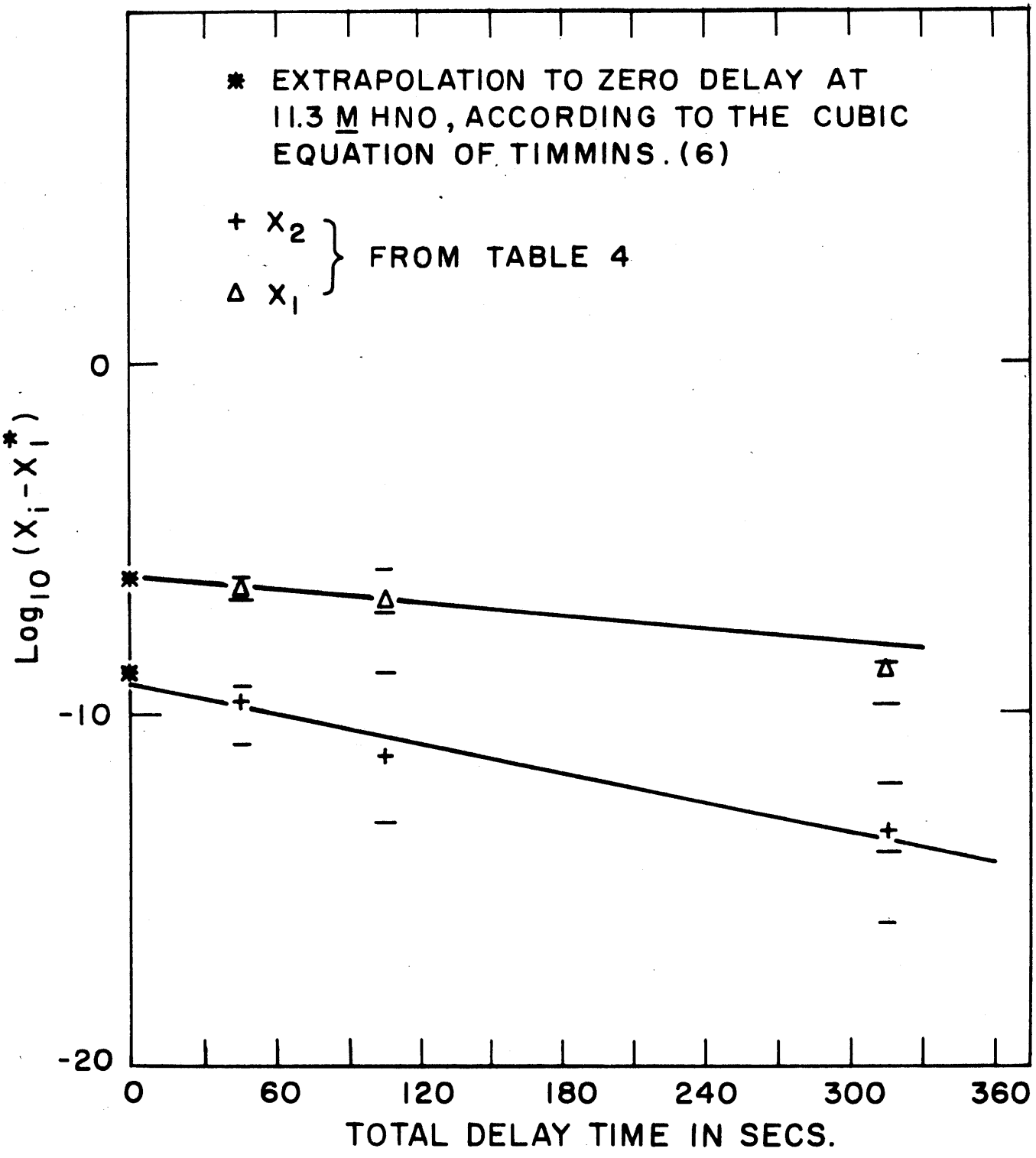

FIGURE 6. VARIATION OF MOLE FRACTION EXCESS WITH TIME

Analysis of the results on nitrate distribution were made using the smoothed data of Figure 6 and the partition coefficients in Table 5. The concentration of ruthenium in each state in the organic phase is given by

$$Ru_{o_i} = TRu_a \frac{X_i P_i}{T+P_i}$$

where Ru_a is the initial concentration of Ru in the aqueous phase. Then the net increase in nitrate ions for each species of ruthenium transferred is given by

$$aRu_a + bRu_{o_2} = C$$

where C = Total NO_3 — Amine — Unbound HNO_3. Then A and B may be calculated by a least squares simultaneous solution of a set of these equations. The calculation is outlined in Table 5.

The values of a and b calculated are non-integral, but integral values are required. The best values of these are probably 5 and 3; i.e., there is a net increase of 5 nitrate ions in the organic phase for each ruthenium of the first species (less extractable) transferred to the organic phase, and an increase of 3 nitrate ions for each ruthenium of the second species. Values of a = 5 and b = 3 yield the experimental values of the net increase in nitrate concentration to $\pm 5.2\%$ at the 90% confidence level; values of a = 4 and b = 4, and a = 4, b = 3 yield the experimental values to $\pm 6.5\%$ and $\pm 8.2\%$ respectively, at the same level. Other integral values of a and b led to even larger relative standard deviations.

What this means in terms of the actual species involved is difficult to understand, since the extraction of any mononuclear nitrosylruthenium species by any usual amine extraction route requires a net increase of only 3 nitrate ions per ruthenium in the organic phase. It is possible that there is a consistent analytical bias. The total amine concentration and the total nitrate in the organic phase are probably relatively accurate, while the agreement between ruthenium stripped from the organic phase and determined in the organic phase directly was good, so there is no cause to suspect bias here. The conductrimetric method for determining unbound nitric acid seems the most likely source of error (7). It may consistently give values that are too low due to a decrease in the conductivity in the presence of ruthenium. There seems to be no method of checking whether such a decrease occurs, but it may be possible to check the concentration of nitric acid by some other method.

If the values of a = 5 and b = 3 are real, then species 1 may be polynuclear, or else it may be the protonated pentanitrato complex. The latter alternative seems unlikely since the mole fraction of species 1 is higher than that of species 2.

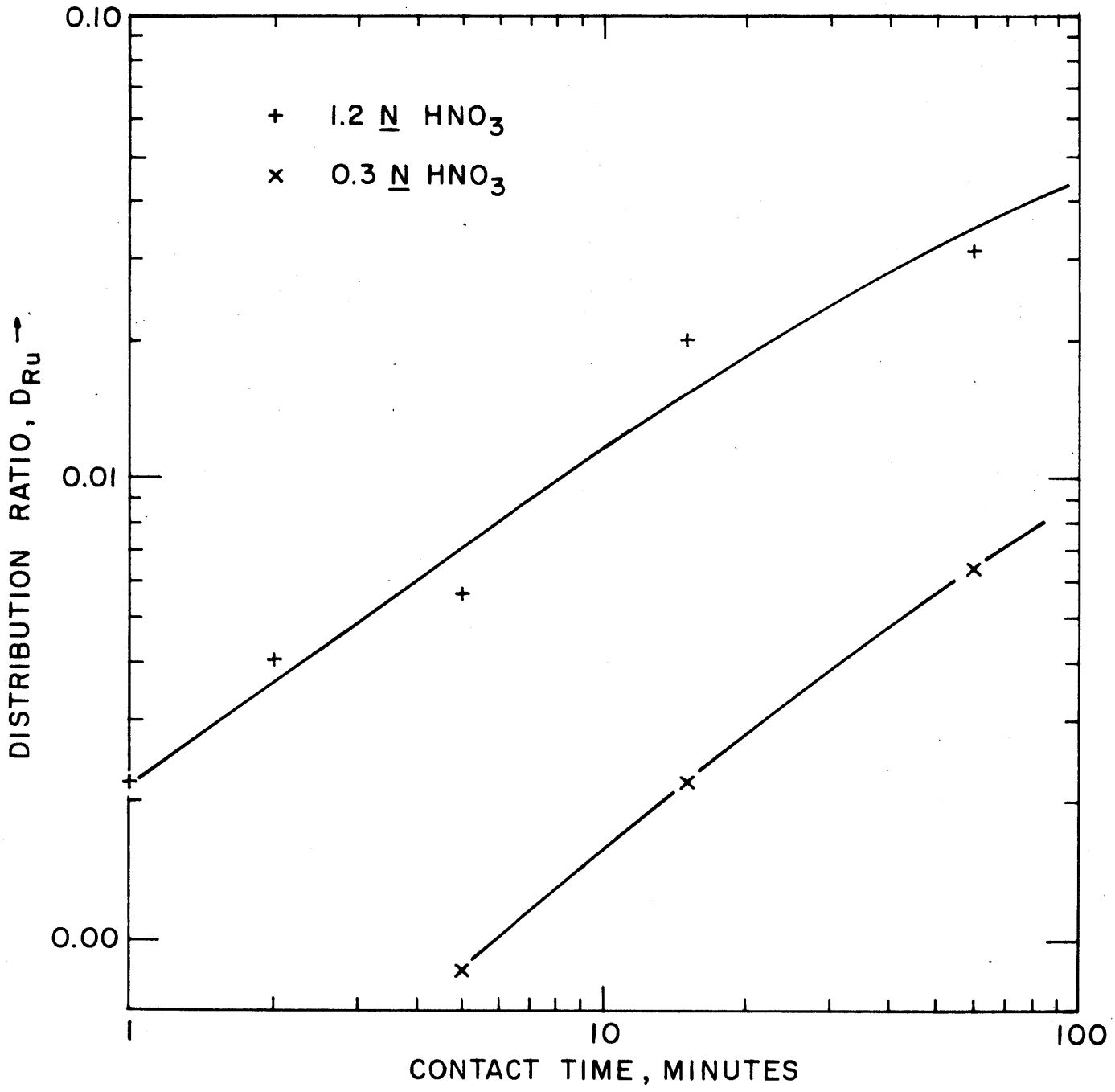

FIGURE 7. EXTRACTION OF AGED RuNO-NITRATO COMPLEXES WITH 0.26 M TLA IN TOLUENE AS A FUNCTION OF CONTACT TIME (6).

Table 5

Calculations of the Net Increase in the Number of Nitrate Ions for Each Ruthenium Species Transferred

Sample No.	Ruthenium 1 M A	Ruthenium 2 M B	Total Org. Ru Calculated M A+B	Experimental M	Increase in NO_3^-, C M	Ratio C/A+B
1	.01213	.01859	.0307	.0309	.109	3.53
2	.01348	.03128	.0448	.0450	.164	3.64
3	.01011	.01026	.0204	.0200	.085	4.25
4	.01299	.02548	.0385	.0388	.145	3.74
5	.00758	.00541	.0130	.0129	.049	3.77
7	.00914	.00720	.0163	.0162	.058	3.58
8	.01088	.01295	.0238	.0233	.098	4.20
9	.01161	.01764	.0293	.0292	.115	3.94
16	.00660	.00449	.0111	.0108	.037	3.43
17	.00790	.00805	.0160	.0161	.059	3.66
20	.00693	.00381	.0107	.0106	.050	4.72

$$a = \Sigma AC \times \Sigma B^2 - \Sigma AB \times \Sigma BC/D$$

$$b = \Sigma BC \times \Sigma A^2 - \Sigma AB \times \Sigma AC/D$$

$$D = \Sigma A^2 \times \Sigma B^2 - (\Sigma AB)^2$$

$\Sigma AC = .0106355$ $\quad \Sigma A^2 = .0011480$

$\Sigma BC = .0165349$ $\quad \Sigma B^2 = .0027380$

$\Sigma AB = .0016540$ $\quad D = .000000407508$

$a = .00000177127/D = 4.35$

$b = .0000013909/D = 3.41$

The low values of the rates of hydrolysis of species 1 and 2 lead to the question of the rates of nitration of these species. It has been supposed, on a basis of the time required for the solutions of nitrosylruthenium to reach equilibrium, that the rates of nitration are slower than the rates of hydrolysis. Skavdahl (6) studied the variation of distribution ratio with contact time, with the results shown in Figure 7. The variation was explained in terms of rapid extraction of the two extractable species, and slow nitration of inextractable species to form more extractable species. However, the rate of increase in extraction is greater than can be accounted for on this basis, if the rate of hydration is in fact faster than that of nitration. In future work it is therefore intended to study also the variation of the mole fractions of the extractable species with contact time as well as delay time.

4.0 Appendix

4.1 PARTIFRAC II Program

PARTIFRAC II is a program written in FORTRAN for the 32K IBM-7090. It is designed to calculate the best values for the mole fractions and partition coefficients of two extractable species, from experimental data on the variation of the overall distribution coefficient as a function of phase ratio. A range of values of the partition coefficients is assumed, and for each pair of values within the range, the best values of the mole fractions are calculated. Using these values of the mole fractions and the assumed values of partition coefficients, the distribution coefficients are calculated as a function of phase ratio, and compared to the experimental values a least-squares criterion is calculated. Output takes the form of a listing of the assumed partition coefficients, the best values of the mole fractions calculated from them, and the calculated least-squares criterion. By inspection of trends in the least-squares criterion, the best values of the partition coefficients may be found, provided the range of partition coefficients was selected correctly.

It may happen that from one set of experiments to another, the mole fractions vary though the partition coefficients remain constant. In this case it is possible to analyze up to 9 sets of experiments (or "runs"), each consisting of up to 10 experimental points. The least-squares criterion is first calculated for each run, and then summed over the number of runs involved.

4.2 Mathematical Background

The distribution of two species is governed by the equation

$$\frac{D}{D+T} = \frac{P_1}{T+P_1} X_1 + \frac{P_2}{T+P_2} X_2$$

For given experimental data on the variation of D with T the equation becomes linear for given P_1 and P_2,

$$C = AX_1 + BX_2$$

For any one run, there results a series of equations of this type, there being one such equation for each value of D and T. In matrix form, these may be written

$$[AB] \{X\} = \{C\}$$

where [ ] represents a matrix and $\{\ \}$ a column vector.

Premultiplying by $[AB]^T$, the transform of $[AB]$, gives

$$[AB]^T[AB] \{X\} = [AB]^T \{C\}$$

and $[AB]^T[AB]$ is then the least-squares matrix, which is non-zero and square. Therefore we may write

$$\{X\} = \left([AB]^T[AB]\right)^{-1} [AB]^T \{C\}$$

In the special case where $[AB]$ is a $2 \times n$ matrix, the solution of this reduces to

$$X_1 = \left[\left(\frac{\Sigma AC}{n}\right) \times \left(\frac{\Sigma B^2}{n}\right) - \left(\frac{\Sigma AB}{n}\right) \times \left(\frac{\Sigma BC}{n}\right)\right] / D'$$

$$X_2 = \left[\left(\frac{\Sigma BC}{n}\right) \times \left(\frac{\Sigma A^2}{n}\right) - \left(\frac{\Sigma AB}{n}\right) \times \left(\frac{\Sigma AC}{n}\right)\right] / D'$$

where $D' = \left(\frac{\Sigma A^2}{n}\right) \times \left(\frac{\Sigma B^2}{n}\right) - \left(\frac{\Sigma AB^2}{n}\right)^2$.

In this form the calculation is perfectly tractable on a desk calculator which has the ability to carry running totals, or on a computer. The computed values of X_1 and X_2 are the "best" values for the input P_1, P_2, D and T values.

An estimate of the fit may be obtained by comparing the square of the difference between the calculated and experimental values of C. However, this has the effect of weighting the values of D at the lower values of T, since in this region C is largest. For the relatively low values of D recorded in this study, the absolute error in the determination of D should not vary much with T, and all values of D should be weighted equally. It was therefore decided to estimate the fit by comparing the square of the difference between the calculated and experimental values of D. It should be noted, however, that the equations are not linear in D, and therefore linear statistics may not be rigorously applied.

4.3 Outline of the Program

A single set of data may include from one to nine runs, all examined over the same ranges of P_1 and P_2. The input data for each set consists of a) one card identifying the data in that set and b) one card giving the number of runs in that set (NORUN) the lowest values of P_1 and P_2 to be used (P(1) and Q(1)), and the scale factors by which P_1 and P_2 are to be increased (¥1 and ¥2). The data for each run consists of a) one card giving the number of phase ratios studied in that run (NOT) and b) up to ten cards of data giving the phase ratio and associated distribution coefficient.

In operation $P(P_1)$ is increased by Y1 x P; $Q(P_2)$ is increased twenty times by Y2 x Q. Each time Q is increased, the best values of X_1 and X_2, and the least-squares criterion are computed and stored. P is then increased by Y1 x P nineteen more times, each time the above cycle of computation taking place. The ranges of P_1 and P_2 covered are therefore from P(1) + Y1 x P(1) to P(1) + 20Y1 x P(1) and from Q(1) + Y2 x Q(1) to Q(1) + 20Y2 x Q(1).

If only one run is being analyzed, the results are then printed out. If more than one run is being analyzed, the least-squares criteria for each run at each pair of values of P and Q are added before printout takes place.

Finally it is a simple matter to scan the printout to select the minimum value of the least-squares criterion for a given value of P_1; and to follow the trends in this minimum value to find the best value of P_1. It may happen that minimum values do not occur in the range selected—generally, the best technique was to perform two analyses, the first with large scale factors to cover a wide range of P_1 and P_2 to show the region in which minima were likely to occur, and the second with small scale factors to cover the minimal region.

The program as written is especially suited to the MIT Computation Center. Before use at other centers it is necessary to check that the logical tape unit numbers used in the input-output statements correspond to the actual tape unit numbers concerned. Modification to the input-output statements may also be necessary if absolute values of T or $D > 10^2$ are used, or at installations where the acceptable printed line is of 120, rather than 132, characters.

A listing of the data format with an example of data input, an example of each of the outputs, and a listing of the program is given in the following tables.

This work was performed in part at the MIT Computation Center, whose assistance is most gratefully acknowledged.

TABLE A1.

DATA INPUT FORMAT.

CARD NO.	CARD TYPE	COLUMNS	DATA NAME	FORMAT
1	IDENTIFICATION CARD	1-80	ANY DESIRED INFORMATION.	
2	DATA CONTROL CARD	1-2	NORUN	(I2)
		4-12	P(1)	(E9.5)
		14-22	Y1	(E9.5)
		24-32	Q(1)	(E9.5)
		34-42	Y2	(E9.5)
3	DATA SIZING CARD	1-2	NOT	(I2)
4-	DATA CARDS	1-9	T	(E9.5)
		11-19	D	(E9.5)

EXAMPLE OF DATA INPUT FOR THE ANALYSIS OF 1 AND 3 RUNS.

```
     RUTHENIUM AT 30 SECOND DELAY TIME.
+1 550000-01 100000-02 100000+01 100000-02
+6
500000-01 172600-01
758000-01 225300-01
100000+00 249000-01
200000+00 362900-01
300000+00 444000-01
400000+00 505000-01


     RUTHENIUM AT 30,90 AND 300 SECOND DELAY TIMES.
+3 500000-01 100000-02 750000+00 333333-02
+6
500000-01 172600-01
758000-01 225300-01
100000+00 249000-01
200000+00 362900-01
300000+00 444400-01
400000+00 505000-01
+5
379000-01 116400-01
500000-01 133100-01
100000+00 193200-01
200000+00 262600-01
300000+00 322400-01
+5
250000-01 544000-02
500000-01 860000-02
100000+00 119900-01
200000+00 173300-01
400000+00 227400-01
```

TABLE A2,OUTPUT FOR 1 RUN, RUTHENIUM AT 30 SECOND DELAY TIME.

T	D
.50000	.17260
.75800	.22530
1.00000	.24910
2.00000	.36290
3.00000	.44440
4.00000	.50500

P1	P2	X1	X2	SIGMA X 10(6)
.5610				
	10.1000	.296835	.105902	1210.4952
	10.2000	.297429	.105548	1210.3368
	10.3000	.298011	.105202	1210.4991
	10.4000	.298581	.104863	1210.9675
	10.5000	.299140	.104531	1211.7268
	10.6000	.299689	.104206	1212.7625
	10.7000	.300227	.103887	1214.0611
	10.8000	.300755	.103575	1215.6100
	10.9000	.301274	.103268	1217.3982
	11.0000	.301782	.102968	1219.4121
	11.1000	.302281	.102673	1221.6417
	11.2000	.302772	.102384	1224.0764
	11.3000	.303253	.102100	1226.7057
	11.4000	.303726	.101822	1229.5208
	11.5000	.304190	.101549	1232.5110
	11.6000	.304647	.101281	1235.6692
	11.7000	.305095	.101017	1238.9865
	11.8000	.305536	.100759	1242.4549
	11.9000	.305969	.100505	1246.0665
	12.0000	.306395	.100255	1249.8147
.5665				
	10.1000	.296007	.105552	1211.2216
	10.2000	.296597	.105199	1210.5880
	10.3000	.297175	.104853	1210.2799
	10.4000	.297742	.104515	1210.2821
	10.5000	.298298	.104183	1210.5794
	10.6000	.298844	.103858	1211.1573
	10.7000	.299379	.103540	1212.0030
	10.8000	.299903	.103228	1213.1033
	10.9000	.300418	.102922	1214.4457
	11.0000	.300924	.102622	1216.0185
	11.1000	.301420	.102328	1217.8127
	11.2000	.301907	.102039	1219.8132
	11.3000	.302385	.101756	1222.0141
	11.4000	.302855	.101478	1224.4048
	11.5000	.303317	.101205	1226.9748
	11.6000	.303770	.100937	1229.7161
	11.7000	.304216	.100674	1232.6210
	11.8000	.304654	.100416	1235.6803
	11.9000	.305084	.100162	1238.8879
	12.0000	.305507	.099913	1242.2352
.5720				
	10.1000	.295201	.105202	1212.7415
	10.2000	.295787	.104849	1211.6425
	10.3000	.296362	.104504	1210.8722
	10.4000	.296926	.104166	1210.4163
	10.5000	.297478	.103835	1210.2594
	10.6000	.298020	.103511	1210.3892
	10.7000	.298552	.103193	1210.7887
	10.8000	.299073	.102881	1211.4480
	10.9000	.299585	.102576	1212.3528
	11.0000	.300087	.102276	1213.4942
	11.1000	.300581	.101982	1214.8580
	11.2000	.301065	.101694	1216.4356
	11.3000	.301540	.101411	1218.2145
	11.4000	.302007	.101134	1220.1875
	11.5000	.302466	.100861	1222.3463
	11.6000	.302916	.100594	1224.6789
	11.7000	.303359	.100332	1227.1778
	11.8000	.303794	.100074	1229.8354
	11.9000	.304222	.099820	1232.6463
	12.0000	.304642	.099572	1235.5987
.5775				
	10.1000	.294416	.104852	1215.0406
	10.2000	.294999	.104500	1213.4840
	10.3000	.295570	.104155	1212.2595
	10.4000	.296130	.103818	1211.3549
	10.5000	.296679	.103487	1210.7537
	10.6000	.297218	.103163	1210.4411
	10.7000	.297746	.102846	1210.4050
	10.8000	.298265	.102535	1210.6310
	10.9000	.298773	.102230	1211.1078
	11.0000	.299273	.101931	1211.8220
	11.1000	.299763	.101637	1212.7666
	11.2000	.300244	.101350	1213.9265
	11.3000	.300716	.101067	1215.2936
	11.4000	.301180	.100790	1216.8566
	11.5000	.301636	.100518	1218.6083
	11.6000	.302084	.100251	1220.5404
	11.7000	.302524	.099989	1222.6413
	11.8000	.302957	.099732	1224.9057
	11.9000	.303382	.099479	1227.3241
	12.0000	.303800	.099230	1229.8899

TABLE A3, OUTPUT FOR 3 RUNS,RUTHENIUM AT 30,90, AND 300 SEC. DELAY.

T	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D
.500	.173	.379	.116	.250	.054	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
.758	.225	.500	.133	.500	.086	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
1.000	.249	1.000	.193	1.000	.120	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
2.000	.363	2.000	.263	2.000	.173	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
3.000	.444	3.000	.322	4.000	.225	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
4.000	.505	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.

P1	P2	X1	X2	X1	X2	X1	X2	X1	X2	X1	X2	X1	X2	X1	X2	X1	X2	X1	X2	SIGMA X 10(6)
.5050																				
	7.7500	.287	.121	.280	.076	.199	.0480.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3416.1
	8.0000	.290	.119	.281	.076	.200	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3401.4
	8.2500	.292	.118	.283	.075	.200	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3399.4
	8.5000	.294	.116	.284	.074	.201	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3408.3
	8.7500	.297	.115	.285	.074	.202	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3426.4
	9.0000	.299	.114	.286	.073	.202	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3452.6
	9.2500	.301	.113	.287	.072	.203	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3485.5
	9.5000	.303	.112	.287	.072	.203	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3524.3
	9.7500	.304	.111	.288	.071	.204	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3568.0
	10.0000	.306	.110	.289	.071	.204	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3616.0
	10.2500	.308	.109	.290	.070	.205	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3667.6
	10.5000	.309	.108	.291	.070	.205	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3722.1
	10.7500	.311	.107	.291	.069	.206	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3779.3
	11.0000	.312	.106	.292	.069	.206	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3838.5
	11.2500	.313	.106	.292	.068	.206	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3899.5
	11.5000	.315	.105	.293	.068	.207	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3961.9
	11.7500	.316	.104	.294	.068	.207	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4025.4
	12.0000	.317	.104	.294	.067	.207	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4089.8
	12.2500	.318	.103	.295	.067	.208	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4154.9
	12.5000	.319	.103	.295	.067	.208	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4220.4
.5100																				
	7.7500	.286	.120	.280	.076	.199	.0480.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3428.5
	8.0000	.289	.119	.281	.075	.199	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3406.6
	8.2500	.291	.117	.282	.074	.200	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3397.6
	8.5000	.294	.116	.283	.074	.201	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3399.6
	8.7500	.296	.115	.284	.073	.201	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3411.1
	9.0000	.298	.114	.285	.072	.202	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3430.9
	9.2500	.300	.113	.286	.072	.202	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3457.6
	9.5000	.302	.111	.287	.071	.203	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3490.4
	9.7500	.303	.110	.288	.071	.204	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3528.3
	10.0000	.305	.110	.288	.070	.204	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3570.6
	10.2500	.307	.109	.289	.070	.204	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3616.7
	10.5000	.308	.108	.290	.069	.205	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3665.9
	10.7500	.310	.107	.291	.069	.205	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3717.9
	11.0000	.311	.106	.291	.068	.206	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3772.1
	11.2500	.312	.105	.292	.068	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3828.2
	11.5000	.313	.105	.292	.068	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3885.9
	11.7500	.315	.104	.293	.067	.207	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3944.8
	12.0000	.316	.103	.293	.067	.207	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4004.8
	12.2500	.317	.103	.294	.067	.207	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4065.5
	12.5000	.318	.102	.295	.066	.208	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4126.9
.5150																				
	7.7500	.285	.120	.279	.076	.198	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3446.1
	8.0000	.288	.119	.280	.075	.199	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3417.1
	8.2500	.290	.117	.281	.074	.200	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3401.2
	8.5000	.293	.116	.282	.073	.200	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3396.6
	8.7500	.295	.115	.284	.073	.201	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3401.7
	9.0000	.297	.113	.284	.072	.202	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3415.1
	9.2500	.299	.112	.285	.071	.202	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3435.8
	9.5000	.301	.111	.286	.071	.203	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3462.6
	9.7500	.302	.110	.287	.070	.203	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3494.8
	10.0000	.304	.109	.288	.070	.204	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3531.6
	10.2500	.306	.108	.289	.069	.204	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3572.3
	10.5000	.307	.107	.289	.069	.205	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3616.4
	10.7500	.309	.107	.290	.068	.205	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3663.3
	11.0000	.310	.106	.291	.068	.205	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3712.6
	11.2500	.311	.105	.291	.068	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3763.9
	11.5000	.312	.104	.292	.067	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3816.9
	11.7500	.314	.104	.292	.067	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3871.4
	12.0000	.315	.103	.293	.067	.207	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3926.9
	12.2500	.316	.103	.293	.066	.207	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3983.4
	12.5000	.317	.102	.294	.066	.207	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4040.6
.5200																				
	7.7500	.284	.120	.278	.075	.198	.0470.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3468.9
	8.0000	.287	.118	.280	.074	.199	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3432.9
	8.2500	.289	.117	.281	.074	.200	.0460.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3410.3
	8.5000	.292	.115	.282	.073	.200	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3399.1
	8.7500	.294	.114	.283	.072	.201	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3397.8
	9.0000	.296	.113	.284	.072	.201	.0450.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3405.2
	9.2500	.298	.112	.285	.071	.202	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3419.8
	9.5000	.300	.111	.286	.070	.203	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3440.9
	9.7500	.301	.110	.286	.070	.203	.0440.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3467.5
	10.0000	.303	.109	.287	.069	.203	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3498.9
	10.2500	.305	.108	.288	.069	.204	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3534.3
	10.5000	.306	.107	.289	.069	.204	.0430.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3573.2
	10.7500	.308	.106	.289	.068	.205	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3615.2
	11.0000	.309	.106	.290	.068	.205	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3659.7
	11.2500	.310	.105	.291	.067	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3706.3
	11.5000	.311	.104	.291	.067	.206	.0420.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3754.8
	11.7500	.313	.103	.292	.067	.206	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3804.8
	12.0000	.314	.103	.292	.066	.207	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3856.1
	12.2500	.315	.102	.293	.066	.207	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3908.4
	12.5000	.316	.102	.293	.066	.207	.0410.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3961.6

TABLE A4 FORTRAN LISTING OF PARTIFRAC II

```
*       XEQ
*       LIST
*       LABEL
C   MAIN
C   PARTIFRAC II, PROGRAM FOR THE ANALYSIS OF TWO SPECIES DISTRIBUTION.
        DIMENSION P(22),Q(22),X1(22,22,9),X2(22,22,9),SIG(22,22,9),T(10
       1,10),D(10,10),FMT(14),SSIGMA(22,22),NOT(10)
        COMMON P,Q,X1,X2,SIG,T,D,SSIGMA,NOT
C       INPUT
  101 FORMAT (13A6,A2)
  102 FORMAT (I2,4(1X,E9.5))
  103 FORMAT (E9.5,1X,E9.5)
  104 FORMAT (I2)
  250 READ INPUT TAPE 4,101,(FMT(I),I=1,14)
        READ INPUT TAPE 4,102,NORUN,P(1),Y1,Q(1),Y2
        DO 107 J=1,NORUN
        READ INPUT TAPE 4,104,NOT(J)
        NT=NOT(J)
  107 READ INPUT TAPE 4,103,(T(I,J),D(I,J),I=1,NT)
C       CALCULATION SECTION.
        DO 150 K=1,NORUN
        DO 110 I=2,21
        P(I)=Y1*P(1)+P(I-1)
        DO 108 J=2,21
        Q(J)=Y2*Q(1)+Q(J-1)
        SASQ=0.0
        SBSQ=0.0
        SAB=0.0
        SAC=0.0
        SBC=0.0
        NT=NOT(K)
        DO 105 L=1,NT
        A=P(I)/(T(L,K)+P(I))
        B=Q(J)/(T(L,K)+Q(J))
        C=D(L,K)/(T(L,K)+D(L,K))
        SASQ=SASQ+A*A
        SBSQ=SBSQ+B*B
        SAB=SAB+A*B
        SAC=SAC+A*C
        SBC=SBC+B*C
  105 CONTINUE
        X1(I,J,K)=(SAC*SBSQ-SAB*SBC)/(SASQ*SBSQ-SAB*SAB)
        X2(I,J,K)=(SBC*SASQ-SAB*SAC)/(SASQ*SBSQ-SAB*SAB)
        SIG(I,J,K)=0.0
        DO 106 L=1,NT
        A=P(I)/(T(L,K)+P(I))
        B=Q(J)/(T(L,K)+Q(J))
        CCALC=X1(I,J,K)*A+X2(I,J,K)*B
        DCALC=CCALC*T(L,K)/(1.0-CCALC)
  106 SIG(I,J,K)=SIG(I,J,K)+(D(L,K)-DCALC)*(D(L,K)-DCALC)/(DCALC*DCALC)
  108 CONTINUE
  110 CONTINUE
  150 CONTINUE
        IF (NORUN-1) 151,300,151
  151 DO 120 I=2,21
        DO 119 J=2,21
        SSIGMA(I,J)=0.0
```

```
      DO 118 K=1,NORUN
  118 SSIGMA(I,J)=SSIGMA(I,J)+SIG(I,J,K)
  119 CONTINUE
  120 CONTINUE
C     OUTPUT
C     OUTPUT FOR MORE THAN ONE RUN
      NOTM=NOT(1)
      DO 160 I=1,NORUN
      IF (NOTM-NOT(I))170,160,160
  170 NOTM=NOT(I)
  160 CONTINUE
  221 FORMAT (//25X,13A6,A2)
  222 FORMAT (/2X,9(6X,1HT,5X,1HD))
  223 FORMAT (4X,9(2X,F5.3,1X,F5.3))
  224 FORMAT (/4X,2HP1,7X,2HP2,3X,9(3X,2HX1,3X,2HX2),4X,13HSIGMA X 10(6)
     1)
  225 FORMAT (/F9.4)
  226 FORMAT (8X,F10.4,2X,18(F5.3),6PF15.1)
      WRITE OUTPUT TAPE 2,221,(FMT(I),I=1,14)
      WRITE OUTPUT TAPE 2,222
      DO 230 L=1,NOTM
  230 WRITE OUTPUT TAPE 2,223,(T(L,K),D(L,K),K=1,9)
      WRITE OUTPUT TAPE 2,224
      DO 240 I=2,21
      WRITE OUTPUT TAPE 2,225,P(I)
      DO 235 J=2,21
      WRITE OUTPUT TAPE 2,226,Q(J),(X1(I,J,K),X2(I,J,K),K=1,9),
     1SSIGMA(I,J)
  235 CONTINUE
  240 CONTINUE
      GO TO 250
C     OUTPUT FOR ONE RUN ONLY.
  301 FORMAT (/20X,13A6,A2)
  302 FORMAT (/32X,1HT,12X,1HD)
  303 FORMAT (25X,F10.5,2X,F10.5)
  304 FORMAT (/5X,2HP1,10X,2HP2,10X,2HX1,10X,2HX2,8X,13HSIGMA X 10(6))
  305 FORMAT (F10.4)
  306 FORMAT (12X,F10.4,2F12.6,6PF18.4)
  300 WRITE OUTPUT TAPE 2,301,(FMT(I),I=1,14)
      WRITE OUTPUT TAPE 2,302
      NT=NOT(1)
      DO 307 L=1,NT
  307 WRITE OUTPUT TAPE 2,303,T(L,1),D(L,1)
      WRITE OUTPUT TAPE 2,304
      DO 309 I=2,21
      WRITE OUTPUT TAPE 2,305,P(I)
      DO 308 J=2,21
  308 WRITE OUTPUT TAPE 2,306,Q(J),X1(I,J,1),X2(I,J,1),SIG(I,J,1)
  309 CONTINUE
      GO TO 250
      END
*     DATA
```

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