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Authors

Hicks, T.E.

Rubin, B.

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Chemistry-Separations Processes for Plutonium

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THE CHELATE PROCESS III
PRELIMINARY CONTINUOUS-OPERATION STUDIES

B. Rubin and T. E. Hicks

Special Review of Declassified Reports
Authorized by USDOE JK Bratton
Unclassified TWX P182206Z May 79

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Page 2

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Page 3

The Chelate Process III
Preliminary Continuous-Operation Studies

B. Rubin and T. E. Hicks

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ABSTRACT

The rate of extraction of Pu^{IV} in either direction between benzene-TTA and aqueous HNO₃ solutions is shown in the present study to be fast enough so that application of the chelate process to continuous operation should be feasible.

This conclusion is based on two primary considerations:

1. The mechanism limiting the rate of extraction appears to be diffusion- and not chemical-reaction-limiting.
2. The extraction may be controlled by adjustment of the system conditions to give almost any desired specifications of rate and/or equilibrium.

A continuous process involving multiple extraction stages with a controlled pH gradient is proposed for obtaining maximum decontamination and plutonium recovery.

The work described in this paper was done under the auspices of the Atomic Energy Commission.

The Chelate Process III
Preliminary Continuous-Operation Studies

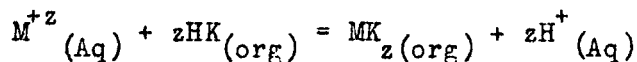
B. Rubin and T. E. Hicks

INTRODUCTION

Previous work^(1,2) with the organic diketone thenoyltrifluoroacetone (TTA) has demonstrated its use in batch operation for the separation of plutonium from uranium and fission products.

This compound has been tested⁽²⁾ for its extraction power on most of the heavy-metal and fission product ions, and it exhibits a marked variation in specificity which permits extractive separation of many different ones.

As the metal chelates are predominantly organic in character, they are soluble essentially only in the benzene or organic phase. Accordingly an equilibrium is set up:



where the chelating organic ion is represented by K^- . The equilibrium expression for this reaction is

$$K_{eq} = \frac{(MK_z)_o (H^+)_o^z}{(M^{+z})_a (HK)_o^z} \quad (0)$$

The following table shows the order of extraction of various ions from 0.5 M HNO_3 into 0.01 M TTA, and includes where known, approximate values of K_{eq} (6), (7)*.

* Note: The K for Zr^{IV} (6) was calculated for the equilibrium expression

$$K = \frac{(ZrK_4)(H^+)^3}{(Zr(OH)^{+3})(HK)^3} ;$$

all other K's are based on equation (0) above.

Table 1

Order of Extraction of Metallic Ions with TTA

 $\text{HNO}_3 = 0.5 \text{ M}$ $\text{TTA} = 0.01 \text{ M}$

Zr ^{IV}	K	3×10^8
Pu ^{IV}	K	2×10^6
Np ^{IV}		
Ce ^{IV}		
U ^{IV}	K	1.5×10^4
Cb ^V		
Th ^{IV}	K	5
Y ^{III}	K	10
UO ₂ ⁺⁺	K	1.2×10^{-2}
Pu ^{III}		
Pu ^{VI}		
La ^{III}	K	3×10^{-10}

The large spread in the values of those equilibrium constants that are known shows that TTA is specific in its extraction power and that widely different hydrogen-ion and TTA concentrations would be necessary to provide equal extraction for all ions. Ions of the alkali, alkaline-earth, and rare-earth groups (with the exception of Ce^{IV}) show very little tendency to extract.

Extraction of Plutonium

Crandall and Thomas⁽²⁾ have exhaustively investigated the kinetics of the reaction between Pu^{IV} and TTA in water-benzene systems at hydrogen-ion concentrations of about 0.5 M. They have shown that the actual rate-determining step may be considered as a homogeneous reaction in the aqueous phase involving the addition

or removal of the third organic radical, and that the overall rate expression has the form

$$+ \frac{d(\text{Pu})_{\text{org}}}{dt} = \frac{k_1 (\text{Pu})_{\text{Aq}} (\text{HK})_{\text{org}}^2}{R (\text{H}^+)_{\text{Aq}}^2} - \frac{k_2 (\text{Pu})_{\text{org}} (\text{H}^+)_{\text{Aq}}^2}{R (\text{HK})_{\text{org}}^2} \quad (1)$$

where R is a volume-ratio term and is defined as:

$$R = \frac{V_{\text{org}}}{V_{\text{Aq}}} \quad (2)$$

From the results of their studies of semi-micro and tracer extraction experiments, Crandall and Thomas were able to devise a batch extraction process which fulfilled the requirements for plutonium separation and decontamination from fission products. This process operated by utilizing both selectivity of chelation with TTA and changes in oxidation state, and may be diagrammed as shown in Fig. 1⁽⁸⁾.

Kinetic Effects

It would appear feasible that by proper control of hydrogen-ion and TTA concentrations, one could extract plutonium and ions which extract better than plutonium into an organic phase and away from those ions below plutonium in Table I; then in a succeeding process reverse the conditions and extract the plutonium back into an aqueous phase, away from the ions above plutonium in the table.

Changes in oxidation state would not appear necessary for operation of the process provided the sharpness of separation of the various ions is good enough and that the rate of extraction is high enough. The first provision is met easily in any continuous countercurrent process of sufficient extraction stages; the second question as to rate of extraction must be further resolved.

As mentioned previously, Crandall and Thomas showed that the extraction rate equation for Pu^{IV} is of the form

$$+ \frac{d(\text{Pu})_{\text{o}}}{dt} = \frac{k_1 (\text{Pu})_{\text{a}} (\text{HK})_{\text{o}}^2}{R (\text{H}^+)_{\text{a}}^2} - \frac{k_2 (\text{Pu})_{\text{o}} (\text{H}^+)_{\text{a}}^2}{R (\text{HK})_{\text{o}}^2} \quad (1)$$

It is of interest to note that for equilibrium, $d(\text{Pu})_o/dt = 0$, and

$$\frac{k_1 (\text{Pu})_a}{R} \frac{(\text{HK})_o^2}{(\text{H}^+)_a^2} = \frac{k_2 (\text{Pu})_o}{R} \frac{(\text{H}^+)_a^2}{(\text{HK})_o^2} \quad (3)$$

$$K = \frac{(\text{Pu})_o}{(\text{Pu})_a} \frac{(\text{H}^+)_a^4}{(\text{HK})_o^4} = \frac{k_1}{k_2} \quad (4)$$

Let us make the following definitions:

$$1. C_A = (\text{Pu})_a + R(\text{Pu})_o \quad (5)$$

This relation is of use when extraction of plutonium is from the aqueous phase; if the initial plutonium concentration in the organic phase is zero, C_A becomes the initial concentration in the aqueous phase.

$$2. C_O = (\text{Pu})_o + (\text{Pu})_a/R \quad (6)$$

This expression is of use when extraction occurs from the organic phase.

C_O and C_A bear no relation to each other; they represent essentially the total amount of plutonium which has been used and which remains constant in any particular batch extraction.

$$3. E = \frac{(\text{Pu})_o}{(\text{Pu})_a} = K \frac{(\text{HK})_o^4}{(\text{H}^+)_a^4}, \text{ the extraction coefficient.} \quad (7)$$

$$4. A = k_1 \frac{(\text{HK})_o^2}{(\text{H}^+)_a^2} + \frac{k_2 (\text{H}^+)_a^2}{R (\text{HK})_o^2} = \frac{\sqrt{k_1 k_2}}{R} \frac{(1 + ER)}{\sqrt{E}} \quad (8)$$

A is a modified rate constant which takes into account both the forward and backward extraction rates.

Equation (1) now may be rearranged in the form

$$+ \frac{d(\text{Pu})_o}{dt} = \frac{C_A \sqrt{k_1 k_2} \sqrt{E}}{R} - A(\text{Pu})_o \quad (9)$$

and integration of this equation between appropriate limits gives the result for the plutonium concentration at any time:

$$(Pu)_O = \frac{C_A E}{1 + ER} (1 - e^{-At}) \quad (10)$$

for extraction from water, and

$$(Pu)_A = \frac{C_O R}{1 + ER} (1 - e^{-At}) \quad (11)$$

for extraction from benzene.

It may be observed from the form of these expressions that $\frac{C_A E}{1 + ER}$ and $\frac{C_O R}{1 + ER}$ represent the final equilibrium concentrations, and the exponential term represents the time-dependent approach to that equilibrium.

Crandall and Thomas showed that extractions from water with extraction coefficients of 100 and higher occurred very rapidly, in agreement with calculations from the above equations. For the second step of their process, in which re-extraction from benzene occurs, they continued to operate at very high extraction coefficients where the equilibrium was unfavorable for Pu^{IV} to be in the water; however at this point advantage was taken of chemical reduction to Pu^{III} in the aqueous phase to effect the transfer between phases.

They found that very slow extraction occurred; times in the order of seven hours (2) in glass apparatus were required for equilibrium to be attained. Operations in stainless steel containers (8) did decrease the required extraction times to about three hours, and an unknown catalyst was postulated to explain this occurrence.

The reasons for maintaining such an unfavorable equilibrium for the Pu^{IV} were to present an even more unfavorable equilibrium to any fission-product ions present in the benzene; it was felt that shifting to a more favorable Pu^{IV} equilibrium would materially lessen the decontamination from such ions.

Demonstration of batch decontamination of plutonium on a two-liter scale by Crandall and Thomas using dissolved uranium slurs from the Clinton pile points the way clearly to full-scale industrial operation of a batch process. It has been the purpose of the present study to investigate the possibilities of converting their batch process into a continuous process, utilizing all available equilibrium and rate information, and to make any simplifications commensurate with the overall process requirements of maximum recovery, decontamination, and economy.

EXTRACTION KINETICS IN CONTINUOUS OPERATION

In order for a continuous countercurrent process to operate successfully, it is desirable for the transfer of plutonium between phases to occur as rapidly as possible.

Diffusion-limited extractions are entirely familiar in chemical engineering procedure, and the TTA process should present no exceptional difficulties as to design if it can be demonstrated that the rate of plutonium transfer is either diffusion-limited or at least kinetically of the same order of magnitude as diffusion. However, if chemical kinetics should limit the rate of extraction so that much more than ten minutes were required for attaining a close approach to equilibrium, the throughput of any reasonable-sized column would become very small and the process would be impractical. Therefore the three hour re-extraction time of Crandall and Thomas presents a very serious obstacle to successful continuous operation.

Mathematical analysis of Crandall and Thomas' operating conditions shows clearly the reasons for the slow re-extraction achieved, and gives also the conditions under which rapid and favorable extraction should occur.

According to equation (11), and because of the numerical values of the constants involved, equilibrium conditions should be attained very rapidly at an extraction coefficient of 100. However, Crandall and Thomas destroyed the equilibrium⁽²⁾

by reducing the Pu^{IV} to Pu^{III} as soon as it appeared in the aqueous phase; by so doing they reduced the term involving k₁ in equation (1) essentially to zero. Therefore equation (11), which resulted from an integration of equation (1) no longer applies and in order to find the Pu_a^{IV} concentration as a function of time, integration of the following equation should be carried out:

$$+ \frac{d(\text{Pu})_o}{dt} = - \frac{k_2 (\text{Pu})_o (\text{H}^+)_a^2}{R (\text{HK})_o^2} \quad (12)$$

Integration between limits gives the result

$$(\text{Pu})_a = RC_0 (1 - e^{-Bt}) \quad (13)$$

where

$$B = \frac{\sqrt{k_1 k_2}}{R \sqrt{E}} \quad (14)$$

It should be noticed that in equation (13), as contrasted with equation (11), RC₀ does not represent a final equilibrium concentration; at infinite time instead, all of the Pu^{IV} will have been transferred because of the blocking of the back-extraction by chemical reduction.

The desired mathematical comparison between ordinary extraction and extraction combined with reduction can now be made.

Both equations (11) and (13) are of the same form in that they show the Pu_a^{IV} concentration to approach final conditions exponentially. It is obvious that the rate of percentage approach to final conditions in each case will depend upon how fast the exponential terms approach zero, which quantities in turn depend upon the magnitudes of the exponential coefficients A and B.

Figure 2 is a graph of A and B versus E and shows clearly the effect of E on the rate of extraction for both systems; for large ordinates the rate will be high. In the case of equation (11) which involves A, large ordinates can be attained for both large and small E's, but in the case of equation (13) which

involves B, the ordinates will be large only for small E's. For extraction from benzene, the large ordinate at high E is of no advantage because although the rate is high, the equilibrium is so unfavorable that operation under these conditions is undesirable without some additional extraction mechanism such as reduction.

The reason for the rates of extraction which Crandall and Thomas obtained are now apparent. When extracting from water, they were at point (a) in Figure 2, where the exponential coefficient A was large and rate was fast, but when extracting from benzene, and even though using the device of reduction, the change in conditions placed them at point (b) where the coefficient B was small and rate was slow.

Because the equilibrium constants for fission-product contaminants are different than for plutonium, it appears likely that sufficient decontamination can be achieved by provision of enough extraction stages, and hence that extraction at low E is possible without accompanying reduction. The solution of the problem as applied to continuous operation at once becomes apparent: one should extract from benzene at a very low E so that both rapid rate and favorable equilibrium are attained.

Proposed Process

A flowsheet for plutonium separation which utilizes the above proposal is shown in Figure 3. It is proposed to center-feed the columns so that advantage may be taken of acid neutralization (or dilution if necessary) at this point to provide a pH gradient and thus to effect a change in the equilibrium state for the system. The columns would then operate in a manner analogous to distillation columns in which both stripping and rectifying sections are present with the following flow:

Uranium-slug dissolver solution, after chemical pretreatment to obtain all plutonium in the plus-four oxidation state, would be fed to the center of column I

where E equals 100 and pass downward counter-current to a TTA-benzene solution. Rapid and complete extraction into the benzene of plutonium and all fission products which extract better than plutonium (mainly zirconium) should occur. The benzene phase would flow into the upper section of the column where a higher acid concentration makes the E about unity. Some of the plutonium will therefore transfer back into the acid phase and be kept in continuous circulation between the upper and lower sections of the column. More important however, any fission products which extract more poorly than plutonium and which may have extracted into the benzene will be transferred back to an extent that will increase with the number of transfer steps in the section.

The benzene solution containing plutonium and fission products of higher E is then center-fed to column II which operates similarly to column I, except that the E 's are so adjusted that it is now the plutonium which is favored by the aqueous phase, while the more easily extracted fission products remain in the benzene.

Aqueous Pu^{IV} is produced at the bottom of column II in a form suitable for subsequent metal-purification; the benzene solution produced at the top may be used both for isolation of radioactive zirconium and TTA recovery.

It should be emphasized that an E of 100 (or 0.01 as the case may be) implies an extraction of 99 per-cent per extraction stage, and even if only 90 percent of equilibrium is attained per actual stage, very few actual stages should be necessary to obtain the required extraction, whether it is conducted in packed towers or countercurrent mixed-tank reactors.

Selection of Conditions for Rate Studies

Reference to the "A" curve of Figure 2 will show that in the neighborhood of E equal to unity, there will be a minimum A , and accordingly, a minimum rate of percentage approach to equilibrium. The exact expression for this condition may be found by differentiating equation (8) and equating to zero; the result is

$$E_{\min} = \frac{1}{R} \quad (15)$$

Equation (15) gives the conditions for which the rate of approach to equilibrium will be lowest, once these conditions have been set by the initial hydrogen-ion and TTA concentrations.

In order to obtain sensitivity in experimentally following the rate of extraction, relatively low rates must be used. Thus for a volume-ratio of unity, equation (15) gives the condition that E should be unity for lowest rate; for best results therefore, experiments should be conducted at this condition. The purpose of such experiments should be, first, to see whether the rate is high enough at low E's for favorable continuous extraction operations, and second, to confirm that (with comparable stirring) the rates of extraction would be higher at E's different from the minimum E as predicted by equation (15).

DISCUSSION OF EXPERIMENTAL RESULTS

A series of extractions from water at low extraction coefficients was carried out with R equal to unity. Numerical results are summarized in Tables II and III. The majority of the experiments were not carried to final equilibrium because the rate information desired could be obtained from the initial portions of the extraction curves. However, for those experiments which were carried to final equilibrium by allowing the solutions to stand for eighteen or twenty hours, good agreement with calculation from the previous equilibrium data of Reas⁽¹¹⁾ was found. For the other experiments, therefore, reliance could be placed in similarly calculated values of the extraction coefficients which were used for the preparation of Table III.

Table III lists percentage-equilibrium values which were calculated from the experimental concentration-time extraction curves by dividing the concentration at the chosen time by the final equilibrium concentration. The information listed

in Table III is interpreted conveniently from Figures 4 and 5. Figure 4 is a plot of percentage-equilibrium values versus time for extractions of comparable slow stirring at different extraction coefficients.

Excellent demonstration of the change in rate of extraction with E is given; slowest extraction occurs with E in the neighborhood of unity and for both higher and lower E 's, (except for Run #6), the rate is higher, in accord with theory. The slow extraction of Run #6 may be explained by the fact that exceptionally slow stirring was used during that experiment.

Table II

Equilibrium Data

Run No.	E(calculated)	E(measured)	(H ⁺)	(TTA)	Stirring
3	19.6	--	1.0	0.05	slow
4	0.181	--	1.0	0.0155	slow
5	0.181	--	1.0	0.0155	slow
6	2.52	--	1.0	0.0310	very slow
7	2.52	0.725(?)	0.50	0.0155	slow
8	2.52	--	1.0	0.0310	slow
9	2.88	2.0	0.50	0.0155	slow
10	2.52	--	1.0	0.0310	fast
11	2.52	--	1.0	0.0310	fast
12	2.52	--	1.0	0.0310	very fast
13	2.52	--	1.0	0.0310	very fast
14	2.88	2.0	0.50	0.0155	very fast
15	2.88	2.3	0.50	0.0155	very fast

Note: The agreement between calculated and measured E's above was considered to be good in view of the fourth-power magnification of possible error in hydrogen-ion and TTA concentrations during calculation of E.

Table III
Rate Data

Values are Percentages of Final
Equilibrium

Run No.	Time in Minutes								
	0	1	3	5	7	10	15	25	
3	0	0.40	0.78	0.92	0.98	-----	-----	-----	
4	0	0.25	0.57	0.75	0.85	0.94	0.98	-----	
5	0	0.26	0.58	0.76	0.86	0.95	0.99	-----	
6	0	0.09	0.21	0.33	0.43	0.55	0.69	0.87	
7	0								
8	0	0.15	0.33	0.51	0.64	0.78	0.90	0.95	
9	0	0.19	0.41	0.59	0.71	0.84	0.94	0.98	
10	0	0.29	0.75	0.88	0.94	0.96	0.98	0.99	
11	0	0.18	0.46	0.67	0.80	0.90	0.95	0.98	
12	0	0.44	0.87	0.94	0.96	0.97	0.98	0.99	
13	0	0.47	0.83	0.92	0.95	0.97	0.98	0.99	
14	0	0.39	0.76	0.88	-----	-----	-----	-----	
15	0	0.20	0.47	0.69	-----	-----	-----	-----	

Figure 5 is a plot of percentage-equilibrium values versus time for experiments which were all of the same E, but which were conducted at different stirring speeds. The effect of stirring on the rate of extraction is at once apparent.

These results resolve the question as to whether the rate is diffusion or kinetically-limited. For an E which in Figure 4 produced a very slow extraction, continually increased stirring produced eventually a rate which was too high to follow analytically with the techniques employed. This means that with the degree of stirring used in these experiments, the chemical reaction must be occurring as fast as the transfer between phases, and there is no reason to suppose that still greater rates of stirring would not further increase the rate until diffusion becomes no longer limiting and the homogeneous chemical reaction-rate becomes controlling.

For this reason no concrete conclusions about the rate constants may be drawn. The rate mechanism, as proposed by Crandall and Thomas for the conditions under which they worked, postulates that it is the formation of the species (PuK_2^{+2}) which is the rate-limiting step. The present study shows diffusion to be limiting; however the rate-effects obtained agree qualitatively with those that would be predicted from Crandall and Thomas' equations. It would appear, therefore, in order for the same equations to govern both situations that it is the same (PuK_2^{+2}) species which does the actual diffusing and thus limits both extraction mechanisms.

If this conclusion is valid, and if it is assumed that the true rate is displayed in the fastest extraction found (run 14), the rate constants may be calculated in the following manner:

Transform equation (11) to the form

$$\ln \frac{C_0}{C_0 - \frac{1 + ER}{R} (Pu)_a} = At \quad (16)$$

Then if the quantity on the left side of equation (16) is plotted versus time, the slope of the straight line so obtained will be the quantity A. Figure 6 is such a plot for run 14; A is found to be 0.495. Then by equation (8),

$$\sqrt{k_1 k_2} \approx 0.232$$

Using the value of the equilibrium constant as determined by Reas⁽¹¹⁾:

$$K = \frac{k_1}{k_2} = 2.3 \times 10^5$$

$$k_1 \approx 111 \quad \text{moles liter}^{-1} \text{min}^{-1}$$

$$k_2 \approx 4.84 \times 10^{-4} \quad \text{moles liter}^{-1} \text{min}^{-1}$$

It should be stated at this point that the value of K just mentioned was obtained from calculations which included activity coefficients. The rate constants given by Crandall and Thomas⁽²⁾ were obtained on the basis of constant ionic-strength experiments, and although consistent in themselves they were not calculated with activity coefficients. The inclusion of such coefficients can change the calculated value of K by as much as 100 and therefore in order to compare the above calculated rate constants with those of Crandall and Thomas, a short discussion of activity coefficients must be included at this point.

Equation (4) should be modified to become:

$$K = \frac{(\text{PuK}_4)_o \gamma_{\text{PuK}_4} (\text{H}^+)_a^4 (\text{NO}_3^-)_a^4 \gamma_{\text{HNO}_3}^8}{(\text{Pu}^{\text{IV}})_a (\text{NO}_3^-)_a^4 \gamma_{\text{Pu}^{\text{IV}}}^5 \text{Pu}(\text{NO}_3)_4 (\text{HK})_o^4 \gamma_{\text{HK}}^4} \quad (17)$$

Reas^(10,11) has shown that γ_{PuK_4} and γ_{HK} are about equal over the range of concentrations investigated; therefore equation (17) simplifies to

$$K = \frac{(\text{PuK}_4)_o (\text{H}^+)_A^4 \gamma_{\text{HNO}_3}^8}{(\text{Pu}^{\text{IV}})_A (\text{HK})_o^4 \gamma_{\text{Pu}^{\text{IV}}}^5 \text{Pu}(\text{NO}_3)_4 \gamma_{\text{HK}}^3} \quad (18)$$

and this is the equation which was used for all calculations in the present study. Activity coefficients for the various ions concerned in this system are tabulated in Table IV.

Table IV
Activity Coefficients

Aqueous Phase		
(H ⁺)	γ_{H^+}	$\gamma_{Pu^{IV}}$
.1	.788	1.295
.5	.718	.993
1.0	.720	1.00
1.7	.76	.984
Benzene Phase		
(HK)	γ_{HK}	γ_{PuK_4}
.01	.995	.995
.02	.985	.985
.03	.97	.97
.05	.96	.96

Application of these activity coefficients to recalculation of Crandall and Thomas' equilibrium and rate constants gives the results:

$$K = 1.6 \times 10^5$$

$$k_1 = 130 \quad \text{moles liter}^{-1} \text{min}^{-1}$$

$$k_2 = 1.24 \times 10^{-4} \quad \text{moles liter}^{-1} \text{min}^{-1}$$

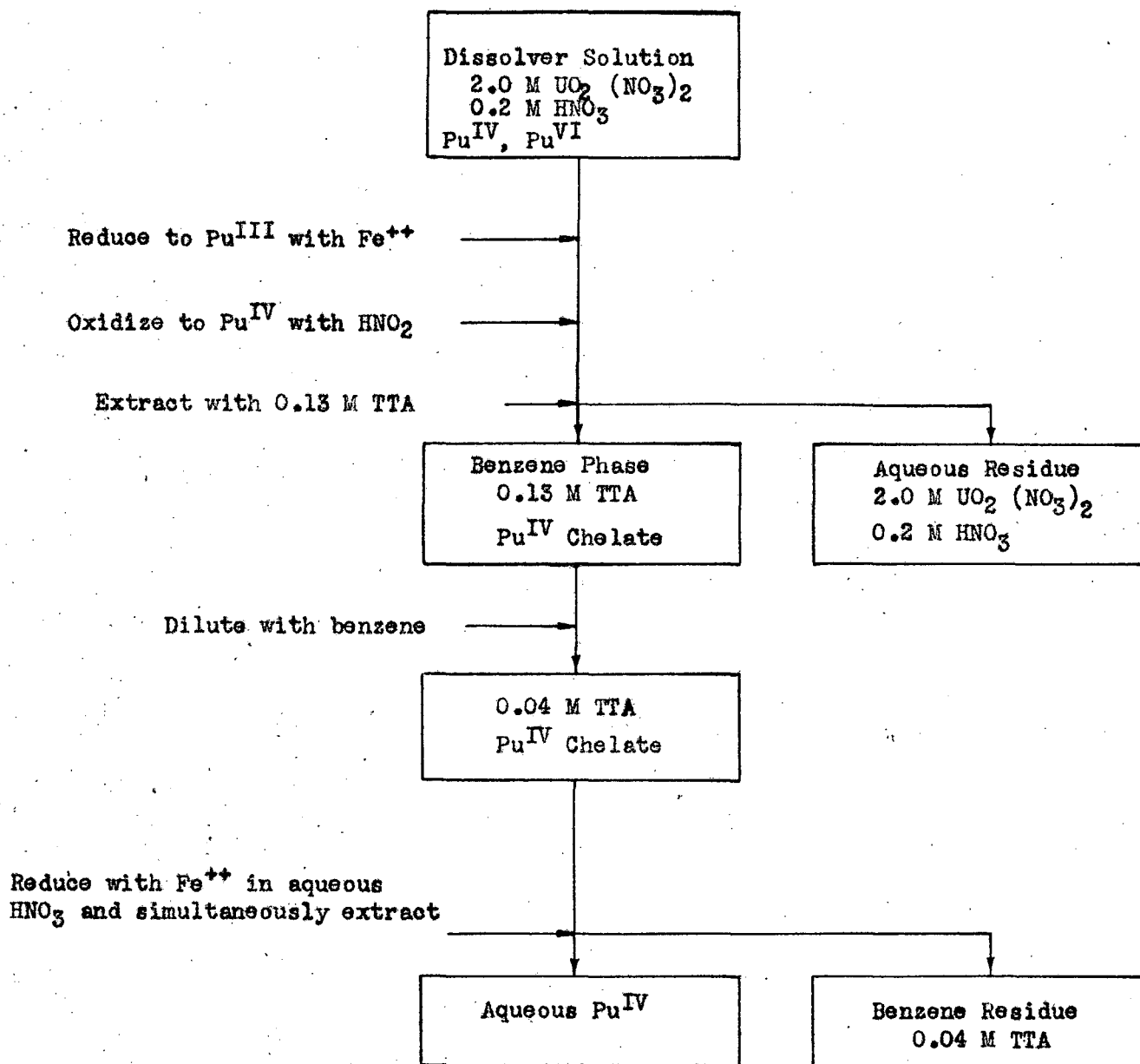
in qualitative agreement with the more recently found values listed above.

This work was performed under the auspices of the Atomic Energy Commission.

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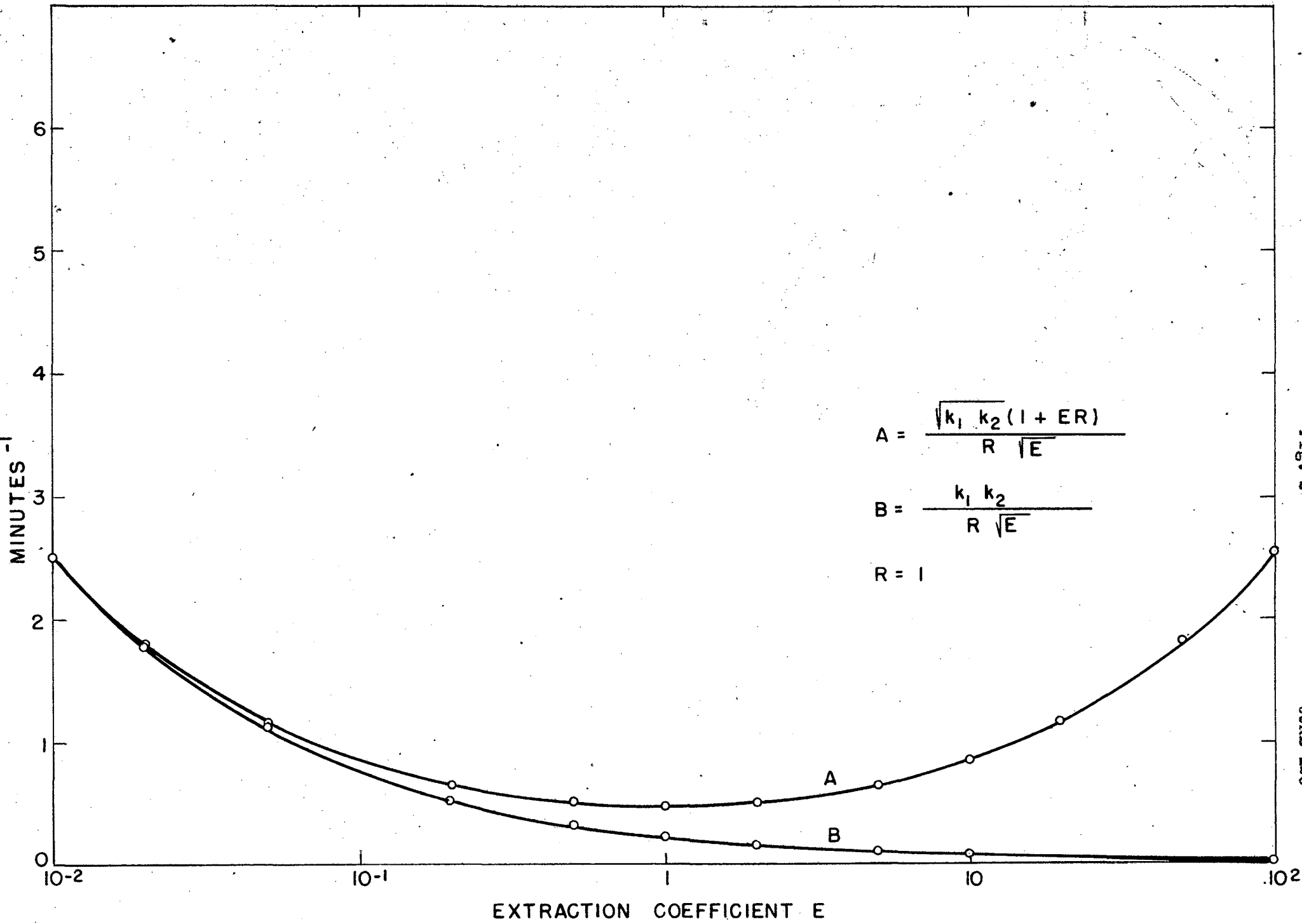
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Batch-Extraction Flow Sheet



This cycle to be carried through three times.

Fig. 1



GRAPH OF EXPONENTIAL COEFFICIENTS A & B VS EXTRACTION COEFFICIENT E

Fig. 2

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Continuous-Operation Flowsheet

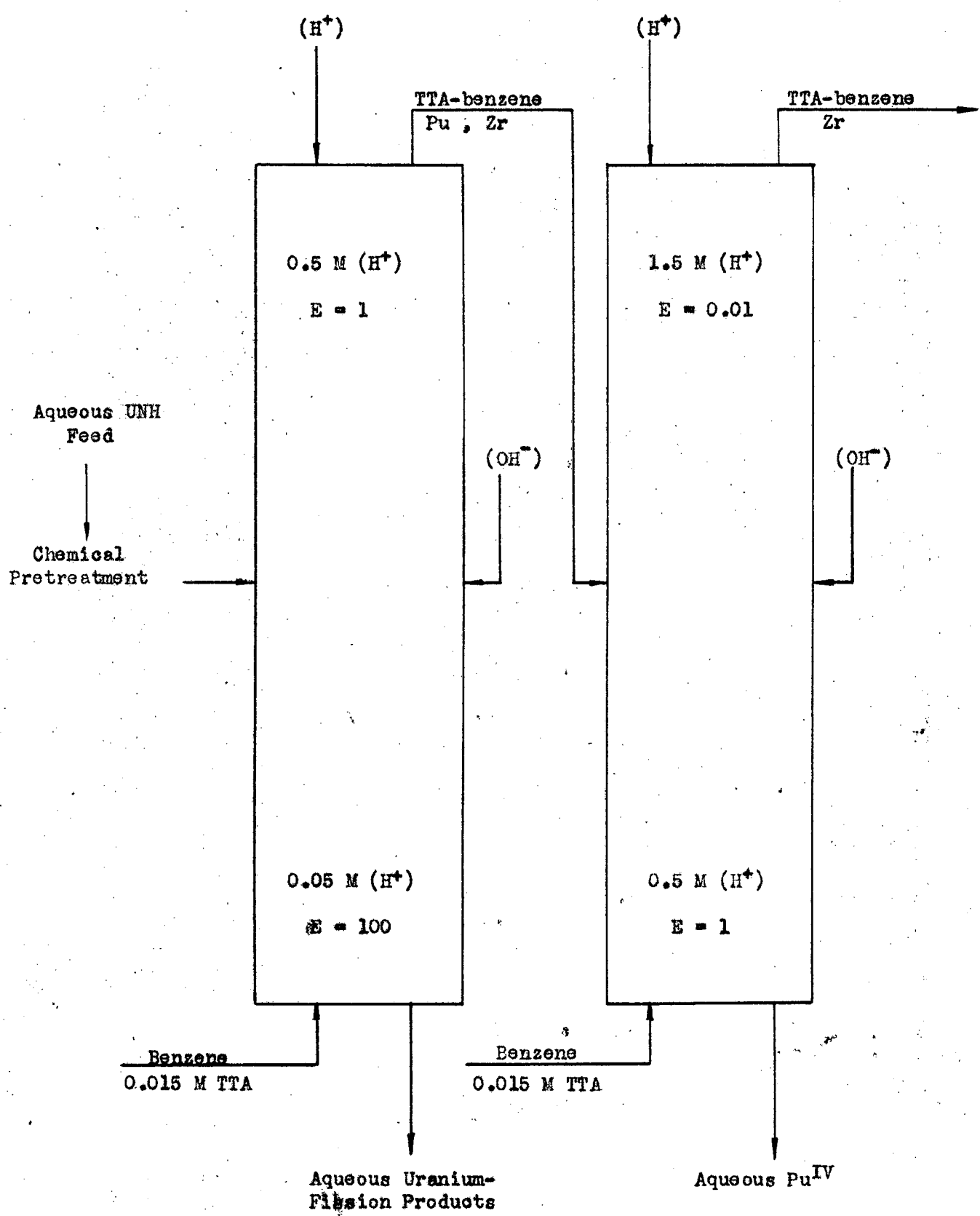
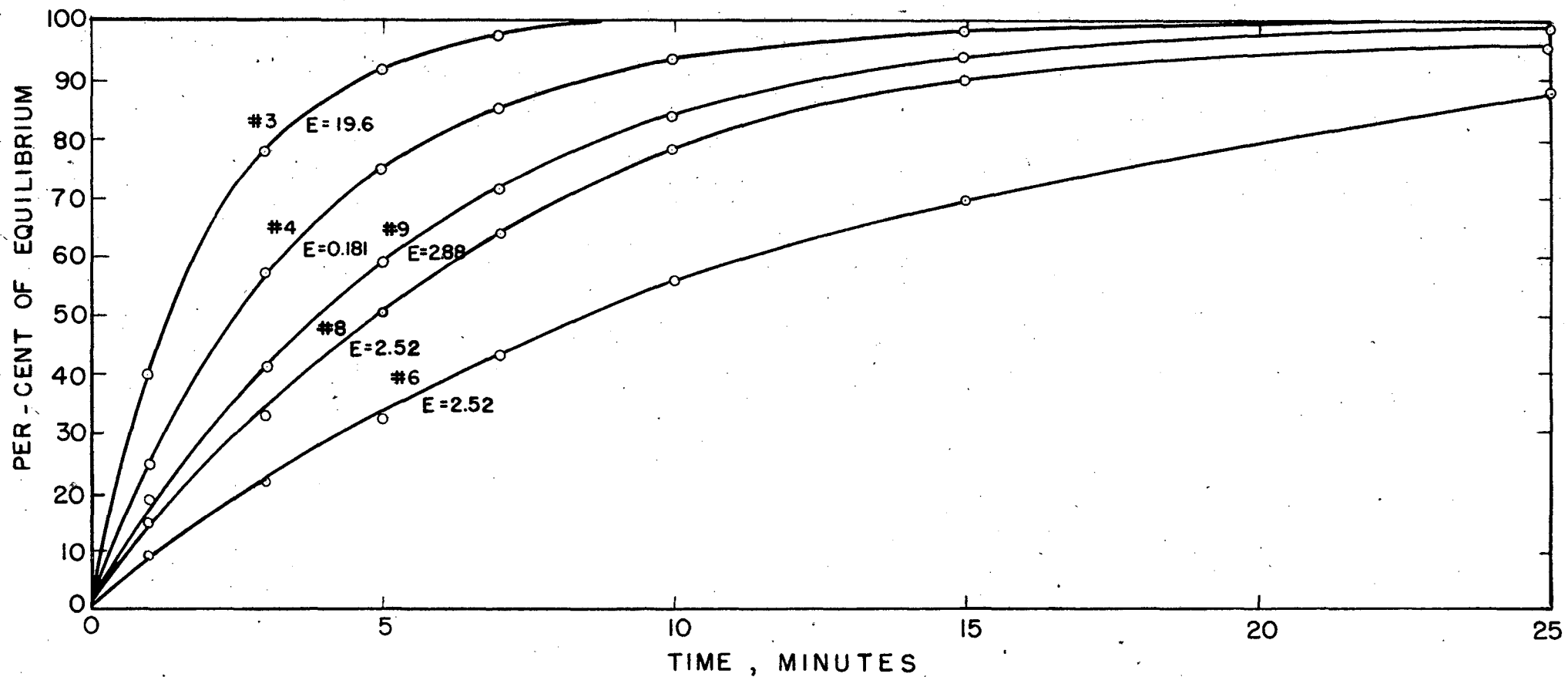
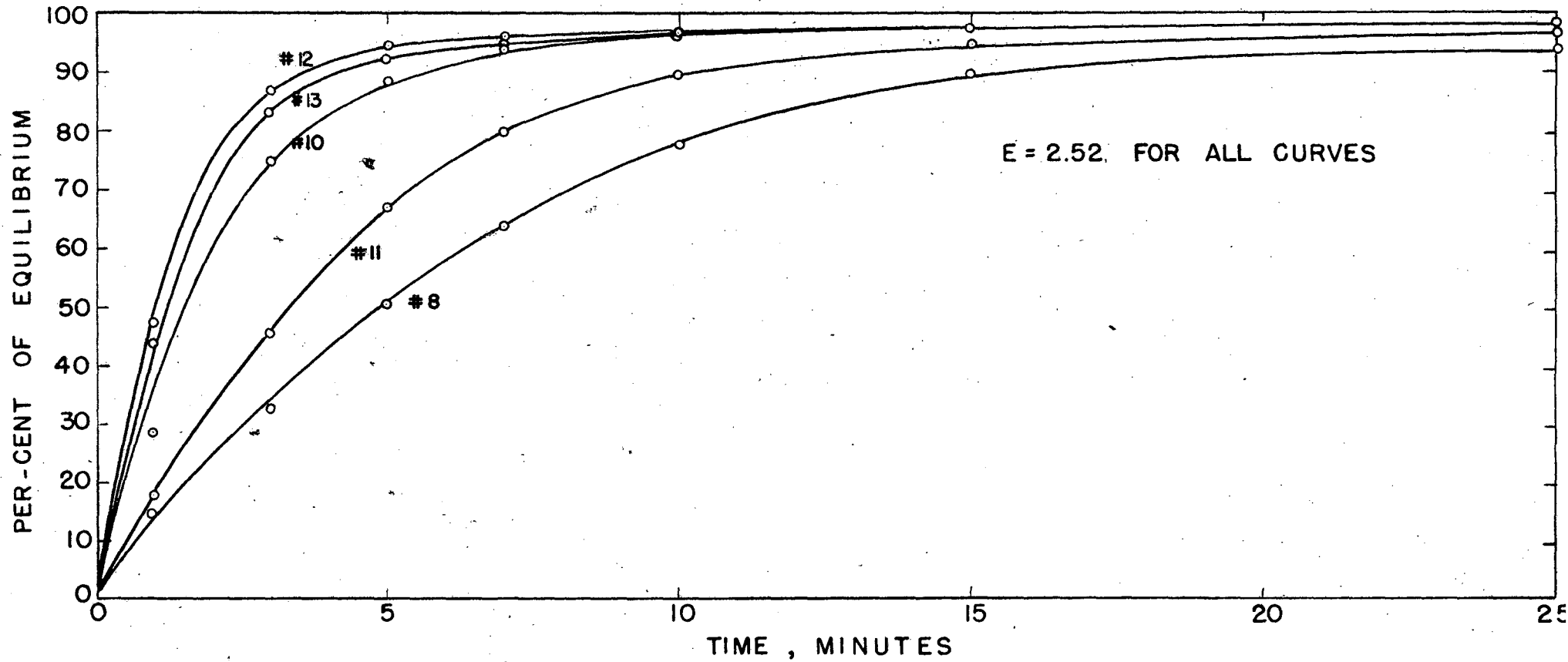


Fig. 3



EFFECT OF E ON RATE OF EXTRACTION

Fig. 4



EFFECT OF STIRRING ON RATE OF EXTRACTION

Fig. 5

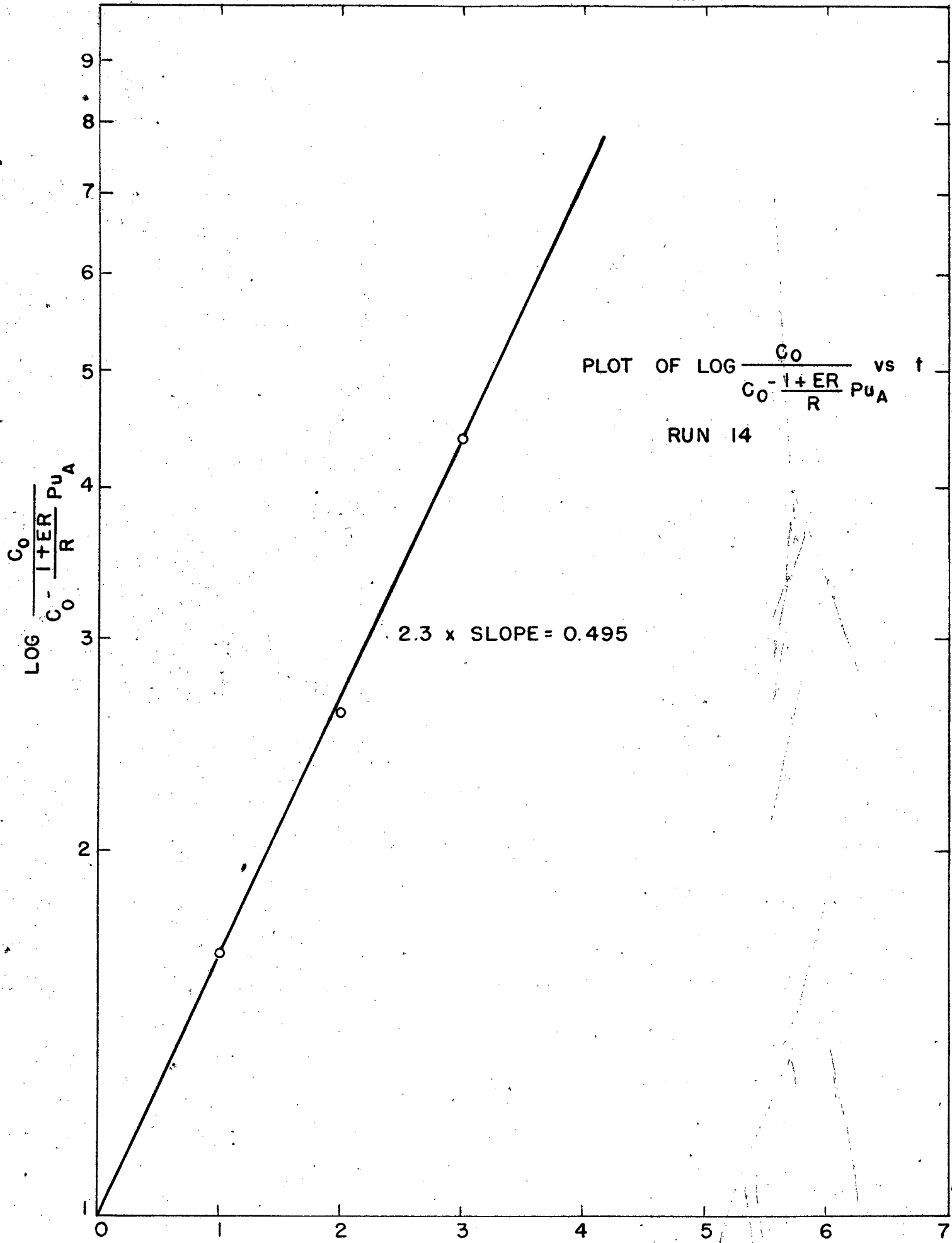


Fig. 6

DETERMINATION OF RATE CONSTANTS

DECLASSIFIED

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