Progress Report for the Period
January 1 - September 30, 1960
ORNL Subcontract No. 1327
EXTRACTION OF FUEL REPROCESSING
METALS WITH ALKYL AMINES
IN NITRATE SYSTEMS
MIT Nuclear Engineering Department

MITNE-6

EQUILIBRIUM EXTRACTION CHARACTERISTICS
of
ALKYL AMINES AND NUCLEAR FUELS METALS
in
NITRATE SYSTEMS

Progress Report for the Period
January 1 - September 30, 1960

Progress Report VII
by
Edward A. Mason
Richard E. Skavdahl
November 1, 1960

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge 39, Massachusetts

Table of Contents

1.0 Summary

During this period, the work by Victor Vaughen has been completed and his final report is currently being finished with regard to typing and reproducing.

Two other programs have been completed: the stainless steel metals extraction studies and the effect of temperature on zirconium extraction. The species studied in the former were iron (III), cobalt (II), nickel (II), and chromium (III). These were in a nitric acid aqueous solution. At a constant. initial aqueous metal concentration of about 50 gm/l and a constant initial amine concentration of about 0.3 molar, the effect of amine type (primary, secondary, and tertiary), hydrogen ion concentration, and nitrate ion concentration on the extraction ratio has been investigated. Four amines were used for the study: (1) Trilauryl amine (TLA), a straight chain tertiary amine; (2) Di (tridecyl) amine (DTDA), a straight chain secondary amine; (3) Amine S-24, a branched chain secondary amine; and (4) Primene JMT, a branched chain primary amine. Toluene was used as the diluent for the entire study.

The results of the study showed that the stainless steel metals are not extracted to any significant degree by the amines considered from aqueous nitrate systems. Extraction ratios of 10^{-5} are typical for these metals.

Experimental work on the temperature effect on zirconium extraction has shown an activation energy of approximately 1 to 2 KCal/mole for S-24 in Amsco or toluene and unpurified TLA in Amsco. The activation energy is about 5 KCal/mole for purified TLA in toluene. Temperature effects are slight. The value of E_A^O being less than a factor of two greater at $50^{\circ}C$ than at $20^{\circ}C$. Severe amine degradation occurs at $50^{\circ}C$ in 8M HNO_3.

The ruthenium program has thus far consisted of an extensive literature search on ruthenium chemistry and solvent extraction, equipment specification and purchase, methods of solution preparation, and a proposed plan of attack.

The literature search yielded conflicting conclusions as to the extractable ruthenium species in nitric acid solution. Two systems, the nitrato-nitrosylruthenium complexes and the nitro-nitrosylruthenium complexes, were chosen as the species to be studied under varying acid, salting, and extractant conditions. Methods of solution preparation for the two systems were found.

Tracer Ru^{106} will be used in the investigations, so a scintillation counting set-up has been specified and purchased. In order to facilitate more rapid and reproducible titrations, a recorder and automatic constant rate burette have been purchased to go along with the existing pH meter.

2.0 Stainless Steel Metals Program

The program covering the extraction studies of the stainless steel metals iron, cobalt, nickel, and chromium has been completed and is described in detail in reference (1). A synopsis, including pertinent graphs, is described in this report.

In general, the program consisted of investigating the equilibrium extraction characteristics of Fe(III), Co(II), Ni(II), and Cr(III) by alkyl amines in nitrate systems using the four different amines JMT, TLA, S-24, and DTDA. Each metal was studied with regard to amine type, nitric acid concentration, and salt concentration. Extraction ratios were determined at initial nitric acid concentrations of approximately 2N, 6N, 8N, and 2N with added $NaNO_3$ to make the total nitrate concentration approximately 7N. To cover the range most important from a process point of view, the acid concentrations used span those in which uranium shows maximum extraction. By adding $NaNO_3$ to one of the 2N acid solutions, the effect of nitrate content at constant acid strength could be studied.

The results of this study show that with the metals cobalt, nickel, and chromium, Primene JMT extracted to a higher degree than the other three amines, reaching values for the extraction ratio of 10^{-4} for cobalt and nickel. With chromium, Primene JMT produced values of E_A^0 of 10^{-5}, whereas the other amines extracted at 10^{-6} or less. In general, an increase in nitrate concentration brought about an increase in the extraction ratio. The data showing the effect of salting with $NaNO_3$ has been plotted in Figure 5.

Following is a description of the extraction results obtained for each individual metal.

1. <u>Iron (III)</u> The results for iron shown in Figure 1 seem to follow the pattern that the order of decreasing extraction was tertiary amine, secondary amine, and primary amine. The highest extraction ratio obtained was 2.3×10^{-5} for TLA at an initial aqueous acid concentration of 6N. A peak extraction occurs in the acid range of 4N to 6N.

The secondary amines seem to follow the same extraction pattern. Maximum extraction ratios obtained for these amines in the acid range of 2N to 8N were 1.4×10^{-5}.

The primary amine exhibited a slight decrease in extraction with increasing acid concentration. Extraction ratios of 0.7×10^{-5} were obtained.

2. <u>Cobalt (II)</u> As shown in Figure 2, all four amines seemed to show a peak extraction in the acid range 4N to 6N. JMT gave an extraction ratio of about 2×10^{-4} at 6N initial acid concentration in the aqueous phase.

Amine S-24 and TLA gave almost the same extraction ratios over the acid range studied, reaching maximum values of E_A^O of 10^{-5}.

DTDA had somewhat lower values with a maximum of 0.7×10^{-5}.

3. <u>Nickel (II)</u> Of the four amines studied, only JMT gave any indication of extracting nickel. See Figure 3. In this case, the value of E_A^O increases steadily over the acid range studied from a value of 0.2×10^{-4} at 2N acid to 2.5×10^{-4} at 8N nitric acid. These results can be expressed by the following empirical equation:
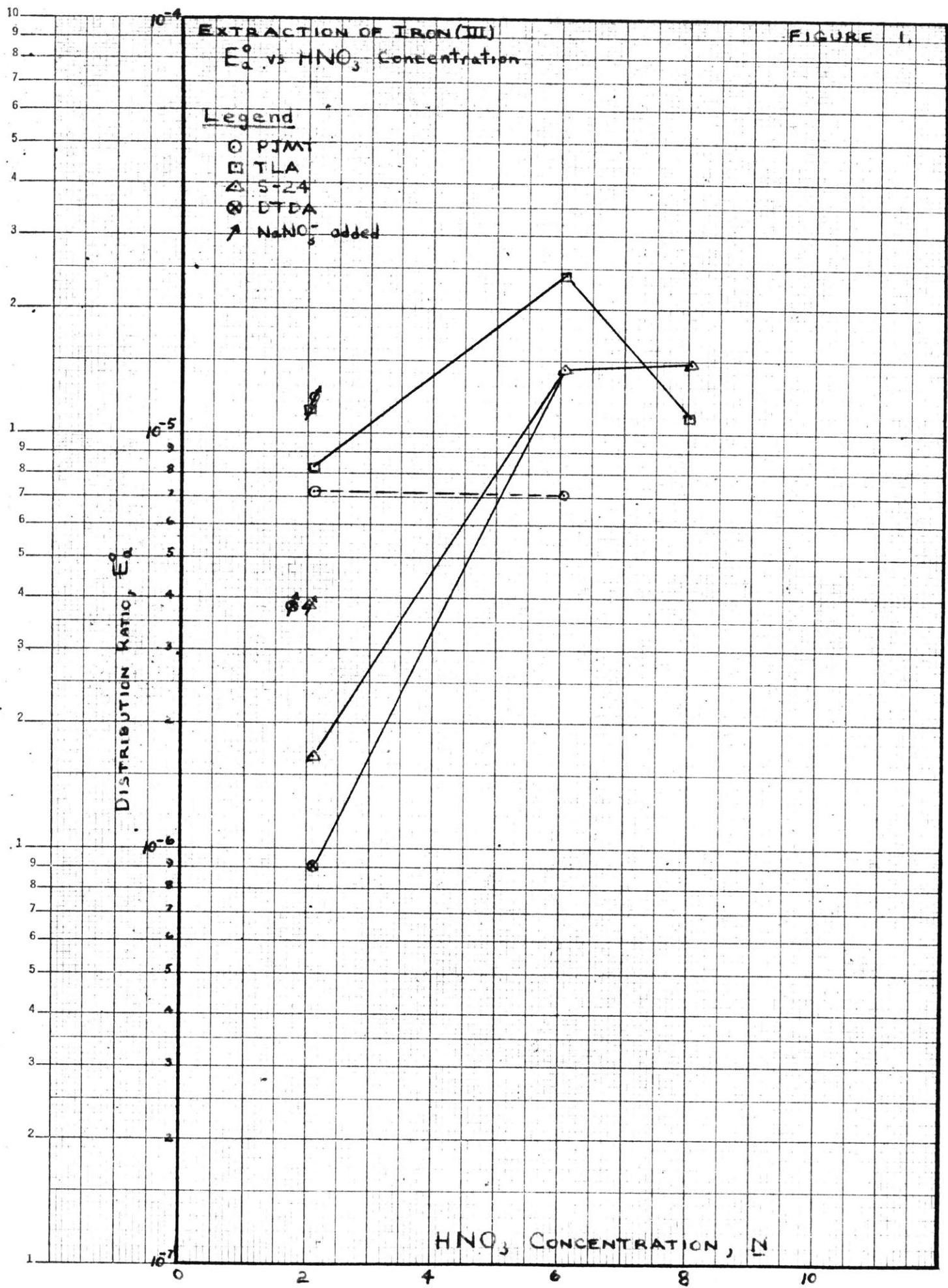
$$E_A^O = 5.32 \times 10^{-6} \; e^{0.21(HNO_3)}$$

where (HNO_3) is the acid normality.

The method for analysis of nickel (dimethylglyoxime method) is sensitive down to about 5 μgm of nickel, which would correspond to an extraction ratio of 6×10^{-6}. However, no trace of nickel could be detected as having been extracted by the secondary and tertiary amines.

4. <u>Chromium (III)</u> This metal was extracted to an order of 10^{-5} by the primary amine with a maximum E_A^O of 2×10^{-5} at 6N HNO_3. See Figure 4. The other three amines gave extraction ratios of less than the secondary amines. All four amines seem to have a peak extraction between the acid concentration of 4N to 6N.

The "Theoretical Curves" in Figure 4 are estimates of the shape of the actual curves since the values were not obtain able at 2N and 8N because of lack of sensitivity of analysis.

All studies were at $25^{\circ}C$, metal concentration of approximately 50 gm/liter, and amine concentration of about 0.3 M.
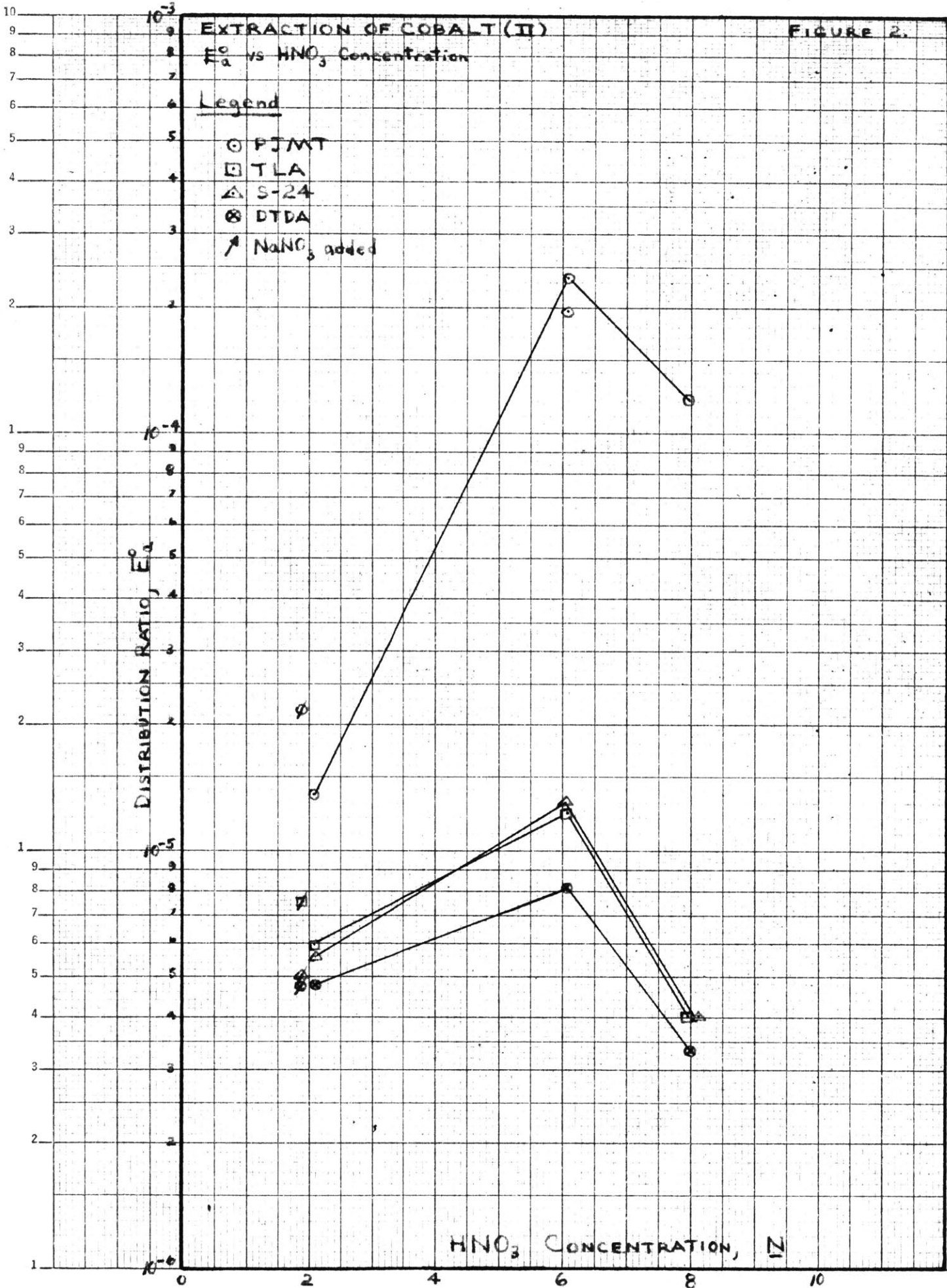
EXTRACTION OF IRON (III)
E_a^o vs HNO_3 Concentration

Legend
⊙ PJMT
□ TLA
△ S-24
⊗ DTDA
➚ NaNO₃ added

FIGURE I.

DISTRIBUTION RATIO, E_a^o

HNO_3 CONCENTRATION, $\underline{N}$

EXTRACTION OF COBALT (II)   FIGURE 2.
E_a^o vs HNO_3 Concentration

Legend

⊙ PJMT
⊡ TLA
△ S-24
⊗ DTDA
⬈ NaNO₃ added

DISTRIBUTION RATIO, E_a^o

HNO₃ CONCENTRATION, N

EXTRACTION OF NICKEL (II)

E_a^o vs HNO_3 Concentration

FIGURE 3.

Legend

⊙ JMT

∅ JMT, $NaNO_3$ added

DISTRIBUTION RATIO, E_a^o

HNO_3 CONCENTRATION, N

EXTRACTION OF CHROMIUM (III)
E_a^o vs HNO_3 Concentration

FIGURE 4.

Legend
⊙ PJMT
□ TLA
△ S-24
⊗ DTDA
↗ NaNO₃ added
---- Theoretical Curve

DISTRIBUTION RATIO, E_a^o

HNO_3 CONCENTRATION, N
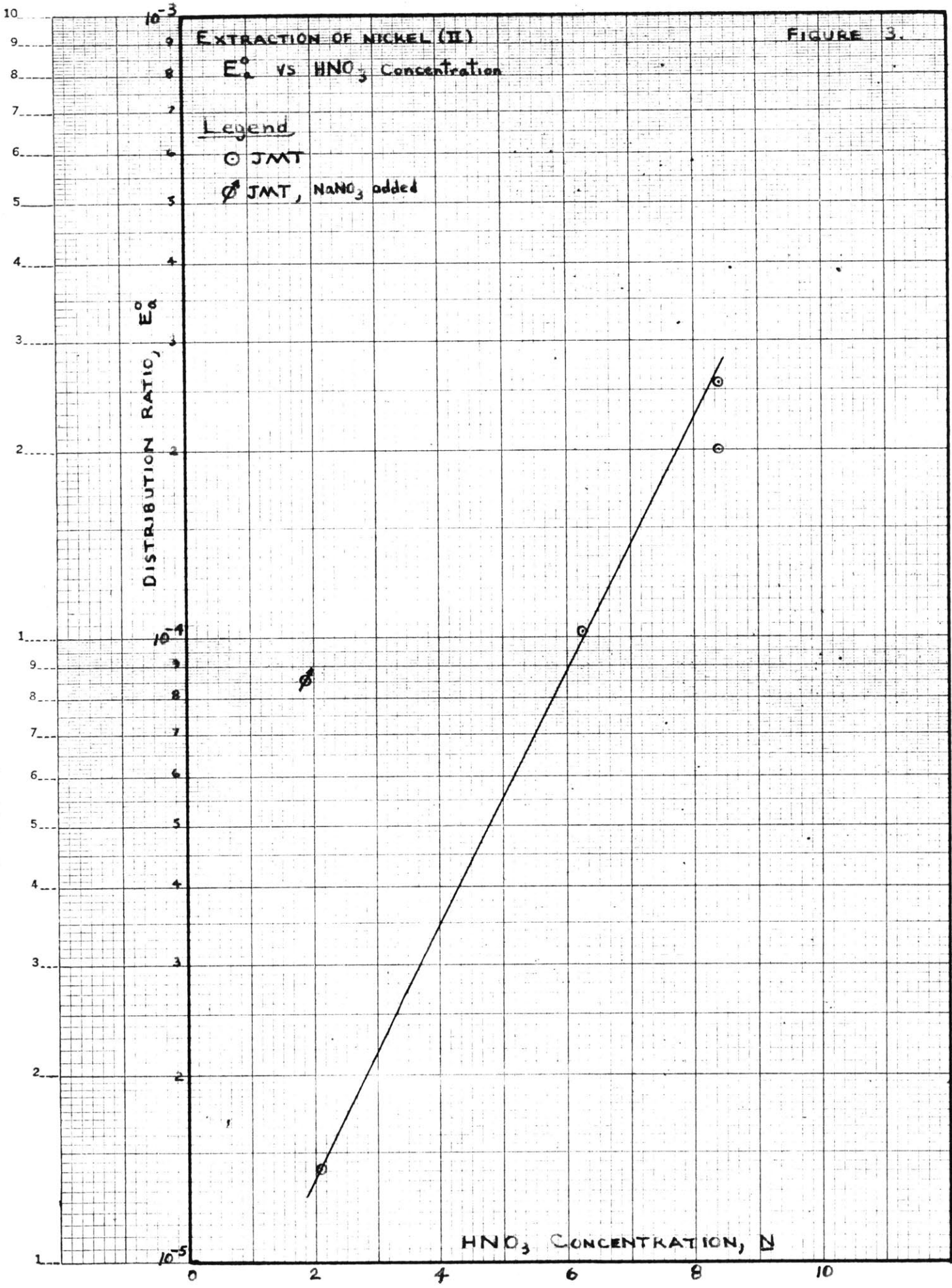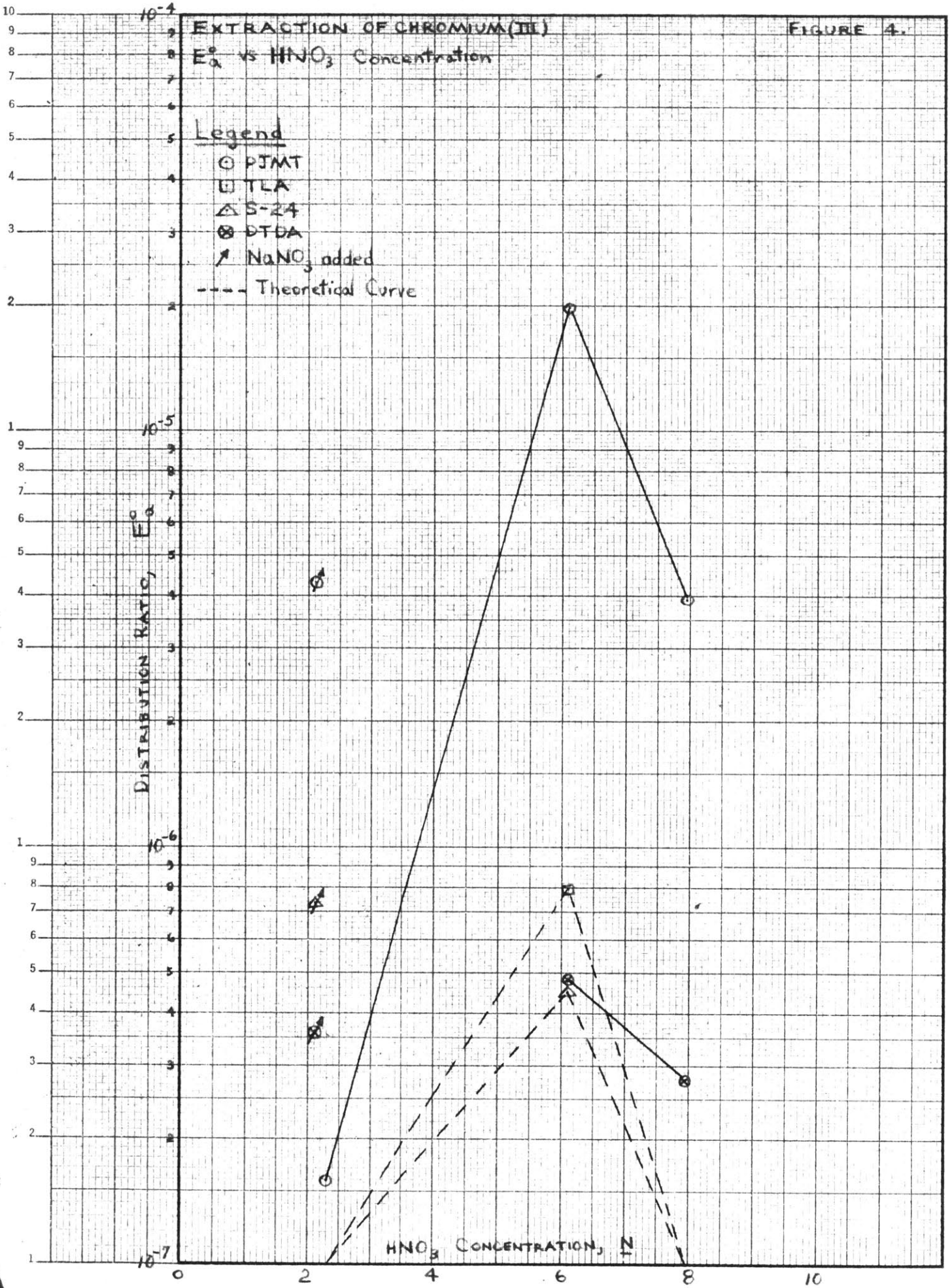
FIGURE 5.

EFFECT OF NITRATE

E_a^o vs NO_3^- Concentration

Legend
○ PJMT
□ TLA
△ S-24
⊗ DTDA

NO_3^- Concentration, M
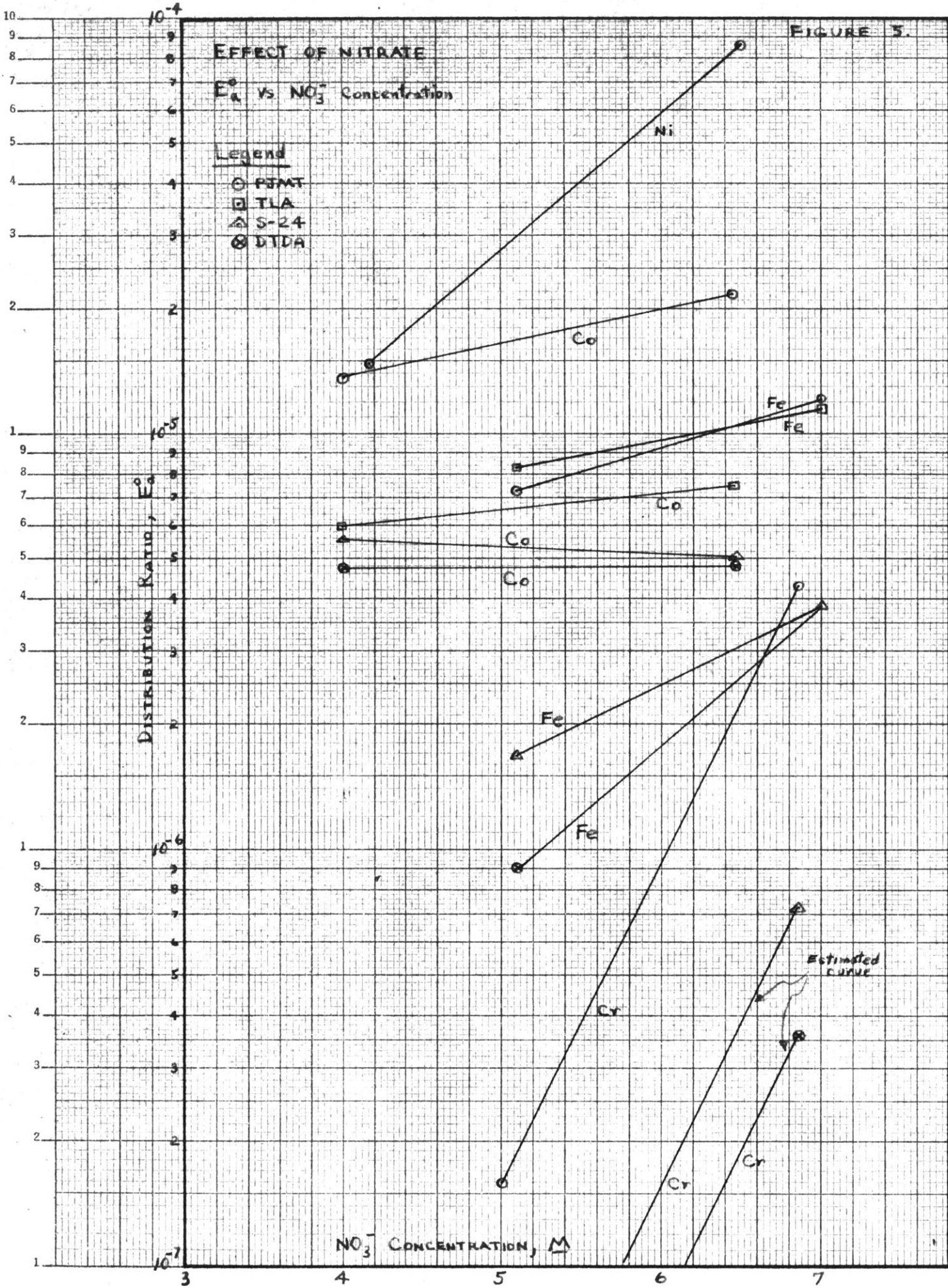
3.0 Effect of Temperature on Zirconium Extraction

The program covering the extraction studies on the temperature effect on zirconium extraction has been completed and is described in detail in reference (2). A summary, including plotted results, is given here.

The general purpose of this program was twofold: (1) to find the dependence of E_A^O on temperature, and (2) to find the effect of temperature on possible amine degradation or interaction with nitric acid.

3.1 The Extraction Ratio

In the first case, extraction studies were carried out on zirconium between the temperatures $25^O C$ and $50^O C$. The extractants used were a secondary amine (S-24) and a tertiary amine (TLA). Two diluents were used, toluene and Amsco. The variable was temperature and the parameter was the extractant-diluent system.

The solutions used were:

Aqueous solution   - 5 gm/l of zirconium in 8N HNO_3

Organic solutions - 0.301 M S-24 in Amsco

                      0.291 M S-24 in toluene

                      0.293 M Technical grade TLA in Amsco

                      0.315 M Purified TLA in toluene

Ten per cent primary decyl alcohol was added in Amsco to prevent third phase formation.

The analysis for zirconium was carried out by an indirect method using a spectrophotometer.

The results of the investigation show little temperature effect on zirconium extraction, the value of E_A^O being less than a factor of two greater at $50^O C$ than at $20^O C$. The results, plotted as E_A^O vs. 1/T, are shown in Figure 6.

Three of the four systems show essentially the same trend, or slope, on the plot, though different absolute magnitudes. The one system that does not follow the pattern is the purified TLA-toluene system. This is thought to be because the purified TLA contains essentially no lower (secondary or primary) amines and that the plot shows the effect of temperature on TLA-toluene-zirconium extraction alone. On the other hand, the TLA-Amsco system also contains small amounts of the lower amines, so is really a plot of a mixture of extractants, not a plot of TLA.

It can be seen that the effect on S-24 is very slight, whereas that on TLA is comparatively larger. Therefore, addition of lower (primary and secondary) amines at the higher temperatures should lower the value of E_A^O and the addition of lower amines at lower temperatures should raise E_A^O. This is qualitatively verified by the graph.

3.2   The Equilibrium Constant

Mason and Vaughen (3) defined the chemical equilibrium constant for zirconium extraction by the following equation:

$$K = \frac{E_A^O}{[A]^{1.6}[H^+]^2[NO_3^-]^2}$$

where $[A]$ = amine molarity in organic phase

$[H^+]$ = hydrogen molarity in aqueous phase

$[NO_3^-]$ = nitrate molarity in aqueous phase

The relation between the equilibrium constant and absolute temperature is written as

$$\frac{\partial \ln K_T}{\partial T} = \frac{+\Delta H^O}{RT^2}$$

Assuming ΔH^O to be constant over a small range of temperature, by integration one obtains

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^O}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

In the above equations, K is based on activity. If K is assumed based on concentration, an analogous relation can be used

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^1}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

By plotting K vs. $\frac{1}{T_1}$ it is possible to obtain a value of ΔH^1, the activation energy. From Figure 7, it is shown that ΔH^1 is about 1 to 2 KCal/mole for S-24 in Amsco and toluene and TLA (unpurified) in Amsco. It is about 5 KCal/mole for purified TLA in toluene.

3.3 Amine Degradation

In order to establish whether or not the amines decomposed during the runs at the higher temperature, extraction samples equilibrated at $55^{\circ}C$ were again shaken at $25^{\circ}C$ and the data were compared with the original $25^{\circ}C$ values. The difference was slight, though noticeable, as can be seen from Figures 6 and 7.

The additional observations were made:

1. The organic phase was colored after it was shaken at $55^{\circ}C$.

2. When the organic samples of (TLA in toluene, shaken at $55^{\circ}C$) and (TLA in toluene, shaken at $55^{\circ}C$ and $25^{\circ}C$) were titrated with sodium hydroxide solution, the color of the solution changed to yellow at the first end point of the titration curve.

This color formation is considered to be the result of the reaction of amine with nitric acid. (4)(5)(6)

FIG 6

Zr Equilibrium Ratio

▲ TLA in Amsco
△ TLA in Toluene
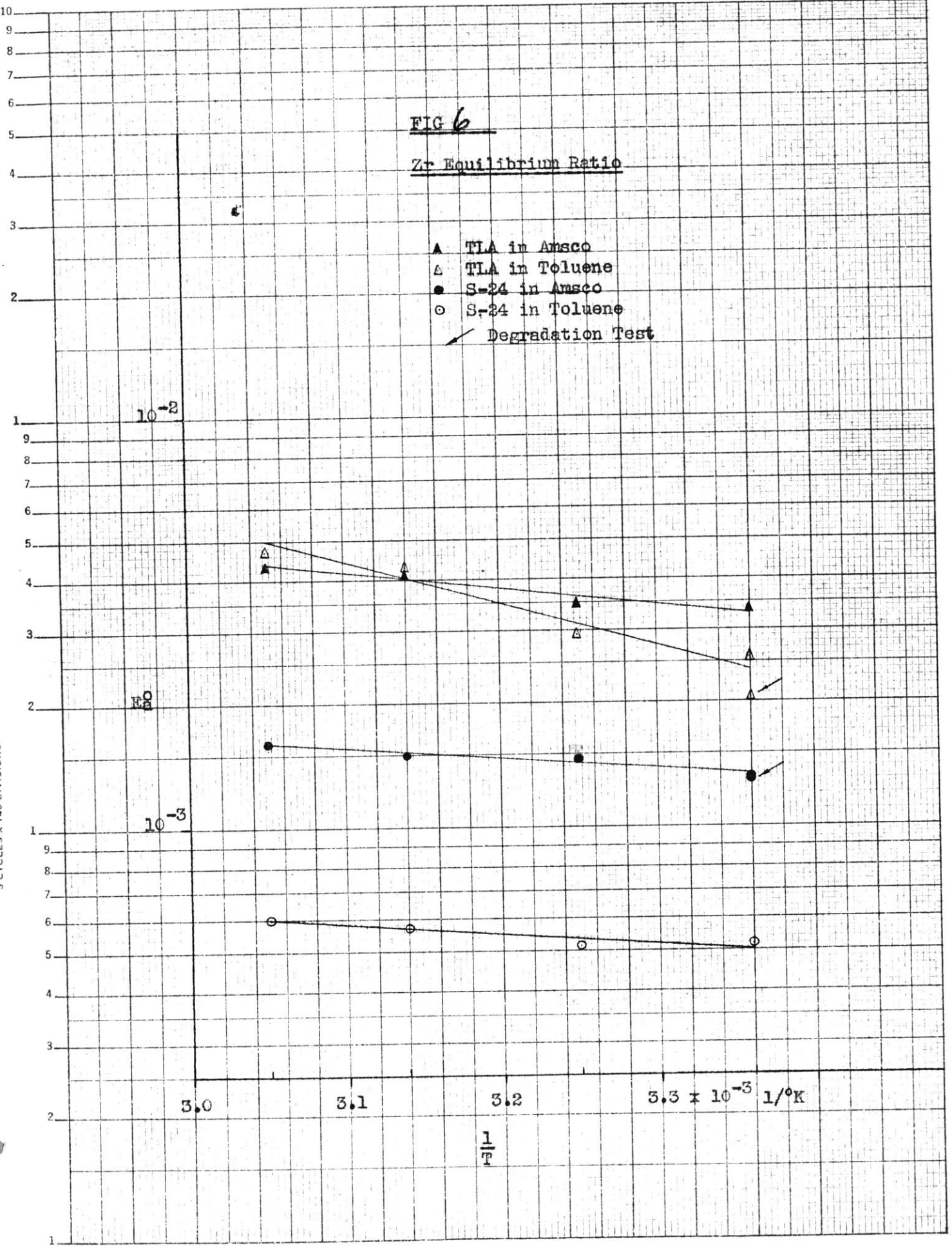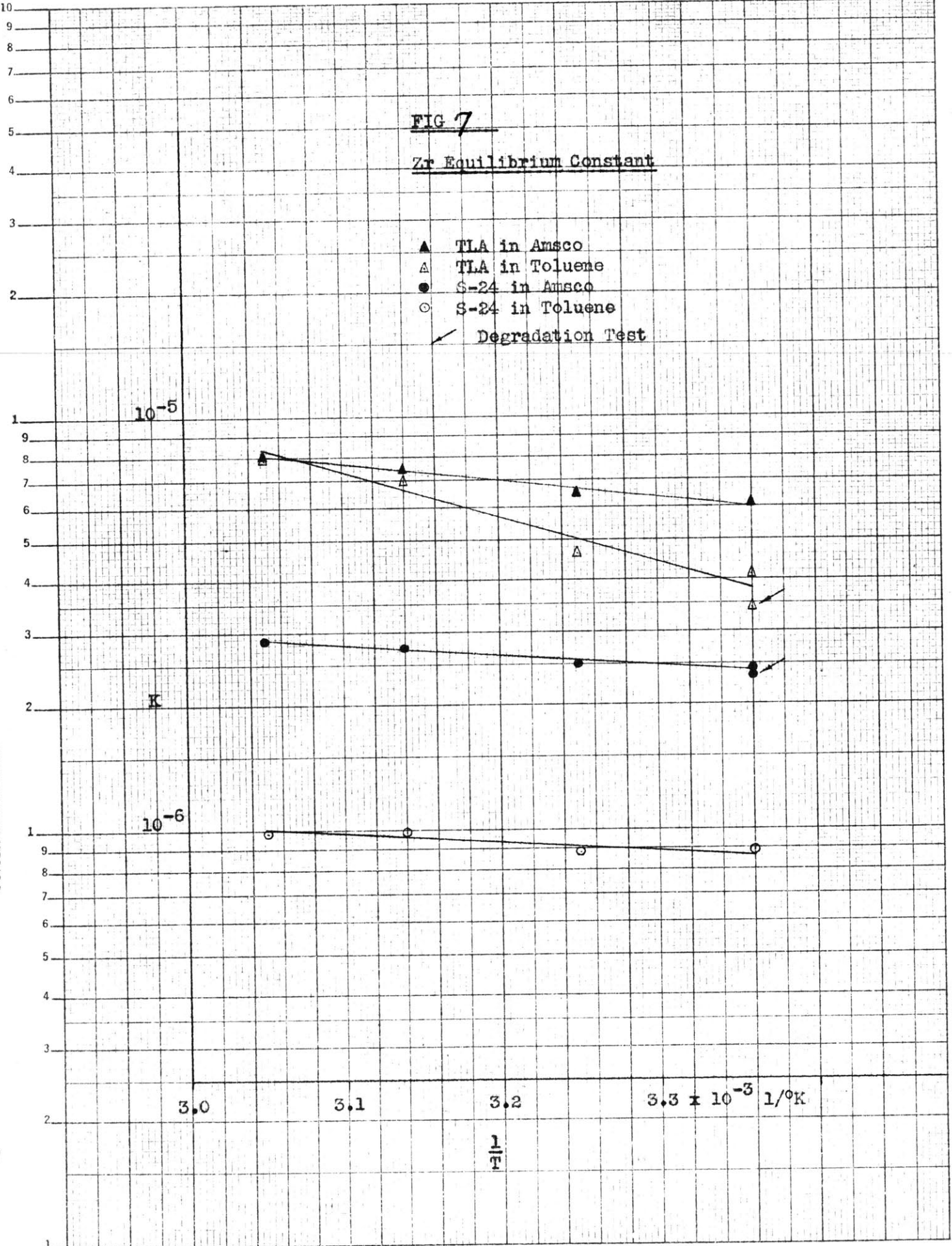● S-24 in Amsco
⊙ S-24 in Toluene
╱ Degradation Test

FIG 7

Zr Equilibrium Constant

▲ TLA in Amsco
△ TLA in Toluene
● S-24 in Amsco
⊙ S-24 in Toluene
╱ Degradation Test

4.0 Ruthenium Progress

The ruthenium program has thus far consisted of an extensive literature search on ruthenium chemistry and solvent extraction, equipment specification and purchase, methods of solution preparation, and a proposed plan of attack.

4.1 Literature Search

The literature search on ruthenium chemistry and solvent extraction has yielded a variety of opinions as to the "extractable" and "non-extractable" forms of ruthenium in nitric acid solution. A thorough study on ruthenium extraction, which includes all known and postulated forms and species of ruthenium complexes, has apparently not been carried out. There is some quantitative data available on the extraction of a selected form of ruthenium and in selected extraction systems. In particular, some work has been done on the extraction into tributyl phosphate (TBP) of tri-valent ruthenium nitrosyl nitrato complexes in nitric acid media (7).

The variety of conclusions in the literature as to the form of the extractable and non-extractable species is evident. Zvyaginsterv (8) says that the extractable form is the bi-valent nitrosyl ruthenium complexes, Brown and co-workers (9) and workers at Savannah River Laboratory (10) say that it is the tri-valent nitrosyl ruthenium complexes, and Bruce (11) says that it is the higher, or tetra-, hexa-, and/or octa-valent states that are extractable.

However, extensive work by Fletcher, Brown, and others at Harwell (12-18) indicate that the important species in nitric acid solution are the nitrato- and nitro-nitrosylruthenium complexes. It is believed that some portion of these species contain the "extractable" form(s) of ruthenium.

The general forms of the complexes are:

$$\text{Nitro-complexes:} \quad \big[\text{RuNO}(\text{NO}_2)_x(\text{OH})_y(\text{H}_2\text{O})_z \big]^{+3-(x+y)}$$
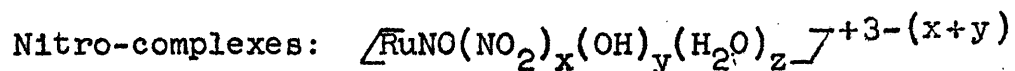
where $(x+y+z) = 5$, since Ru has a coordination number of six.

$$\text{Nitrato-complexes:} \quad \big[\text{RuNO}(\text{NO}_3)_x(\text{OH})_y(\text{H}_2\text{O})_z \big]^{+3-(x+y)}$$
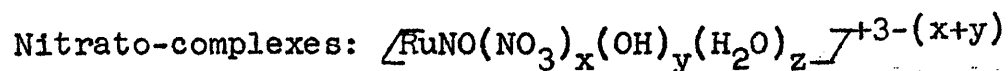
where again $(x+y+z) = 5$.

and a mixture: $[RuNO(NO_2)_w(NO_3)_x(OH)_y(H_2O)_z]^{+3-(w+x+y)}$

where $(w+x+y+z) = 5$.

A plot showing the equilibrium concentration of the nitrato-complexes as a function of nitric acid concentration is given in Figure 8. (18)

The groups A, B, C, and D refer, respectively, to the mono-, di-, tri-, and tetra-plus-penta-complexes; i.e.

$$A = [RuNO(NO_3)(H_2O)_4]^{+2}$$

$$B = [RuNO(NO_3)_2(H_2O)_3]^{+1}$$

$$C = [RuNO(NO_3)_3(H_2O)_2]$$

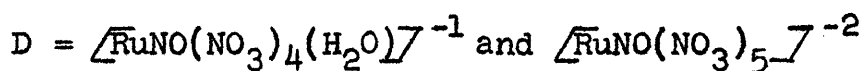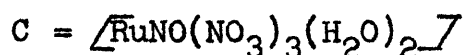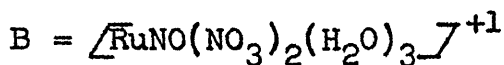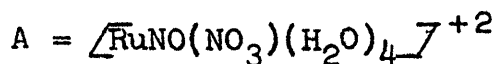$$D = [RuNO(NO_3)_4(H_2O)]^{-1} \text{ and } [RuNO(NO_3)_5]^{-2}$$

Figure 9 gives a breakdown of group D into the tetra- and penta-complexes separately.

Similar plots for the nitro-complexes are not yet available.

4.2 Methods of Solution Preparation

4.2.a Nitrato Complexes

The exact method of preparation of the nitrato-complexes can be found in reference (13). The general method is as follows:

1. Conversion of commercial $RuCl_3$ to nitrosylruthenium chloride by passing an $NO-NO_2$ mixture into a solution of $RuCl_3$.

2. Conversion of $RuNOCl_3$ to $RuNO(OH)_3$ by boiling with addition of NaOH, maintaining pH $\geqslant$ 11

3. Centrifuging at pH 6.4 to remove colloidally-suspended $RuNO(OH)_3$, after aging for several days to allow complete precipitation.

4. After drying, the RuNO(OH)$_3$ is dissolved and boiled in sufficient nitric acid to leave the solution about 8M HNO$_3$. (Boiling with concentrated acid gives slow oxidation to RuO$_4$.)

5. Evaporating solution to dryness at room temperature in a vacuum desiccator over solid caustic soda leaves the trinitrato complex as a dark red mass.

6. Dissolving in nitric acid at desired molarity and againg for several days gives the equilibrium concentrations shown in Figure 8 at the desired molarity.

4.2.b Nitro Complexes

The exact method of preparation of these complexes are given in references (13) and (17). The general method is as follows.

1. Conversion of commercial RuCl$_3$ to RuNOCl$_3$ by passing an NO-NO$_2$ mixture into a solution of RuCl$_3$.

2. Conversion of RuNOCl$_3$ to Na$_2$[RuNO(NO$_2$)$_4$OH] by adding slowly additional NaNO$_2$ at 80° C and pH~7.

3. Conversion of Na$_2$[RuNO(NO$_2$)$_4$(OH)] to [RuNO(NO$_2$)$_2$(OH)(H$_2$O)$_2$] by addition of dilute acid.

4. Conversion of (RuNO) nitrato complexes to [RuNO NO$_2$(NO$_3$)$_2$(H$_2$O)$_2$] and [RuNO(NO$_2$)$_3$(H$_2$O)$_2$] by evaporation in vacuo of solutions formed in nitric acid by the action of oxides of nitrogen (NO+NO$_2$) on (RuNO) nitrato complexes.

4.3 Proposed Plan of Attack

The general approach in the forthcoming studies of ruthenium extraction by amine-type reagents will be to consider initially the nitrato-complexes and then the nitro-complexes. Other species may be investigated, though it does not appear at this time that the other species are of importance.

Solutions of the complexes will be prepared varying in acid concentration from about 0.1M to 12M, varying in salting concentration from zero to saturation, and varying in ruthenium concentration. These will be extracted with an organic phase which will be varied with regard to amine type (primary, secondary, tertiary, and/or quaternary), amine concentration, and possibly diluent type.

The extractions may also be varied with respect to shaking, or contact, time, especially in the case of the nitrato complexes, where rearrangement to equilibrium concentrations is faster than in the nitro-complexes.
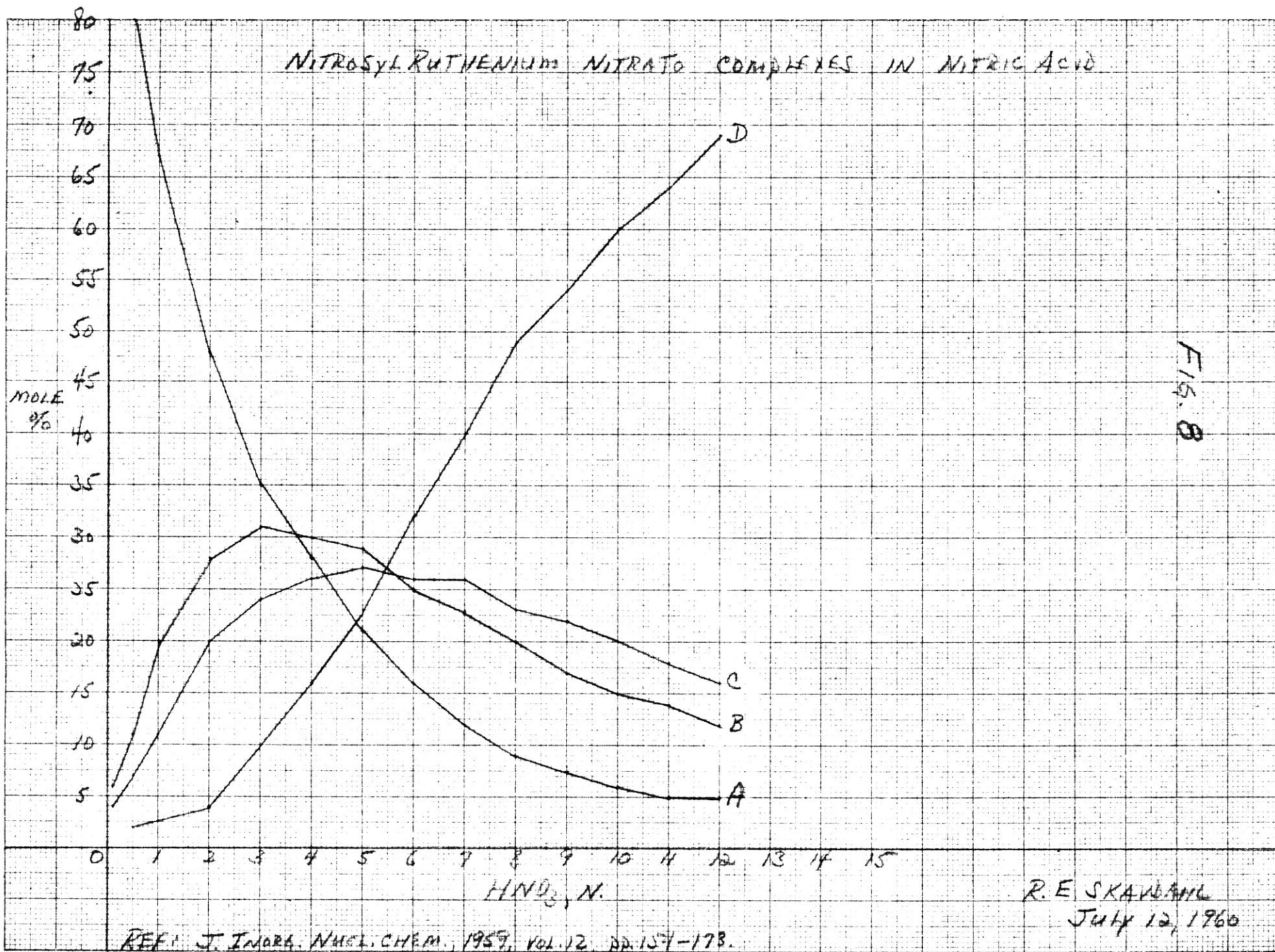
The desired result is the knowledge of the extractable and non-extractable forms of ruthenium, the method or mechanism of extraction, and the quantitative data regarding extraction ratios of the individual species and the amount of species in solution.

The application of this knowledge would be in the prediction of the behavior of ruthenium under various process conditions and to facilitate adjusting the conditions to meet a specific purpose. For instance, one application of this work would be the specification of optimum scrubbing conditions for ruthenium decontaimination.

4.4 Equipment Specification and Purchase

It is planned to use tracer Ru^{106} along with macro-amounts of carrier Ru in the extraction studies. The values of E_A^O will be determined by the ratio of counting rates of equal portions of organic and aqueous phase. In order to accomplish this, a well-type scintillation counting set-up was procured.

To enable faster and more reproducible titrations, an automatic constant rate burette and a recorder for the existing pH meter has been obtained.

NITROSYL RUTHENIUM NITRATO COMPLEXES IN NITRIC ACID

FIG. 8

MOLE %

HNO₃, N.

REF: J. INORG. NUCL. CHEM. 1959, VOL 12, pp. 157-178.

R.E. SKAVDAHL
July 12, 1960

NITROSYL RUTHENIUM NITRATO COMPLEXES IN NITRIC ACID

FIG. 9

REF: J. INORG. NUCL. CHEM., 1959, VOL. 12, PP. 154 - 173.
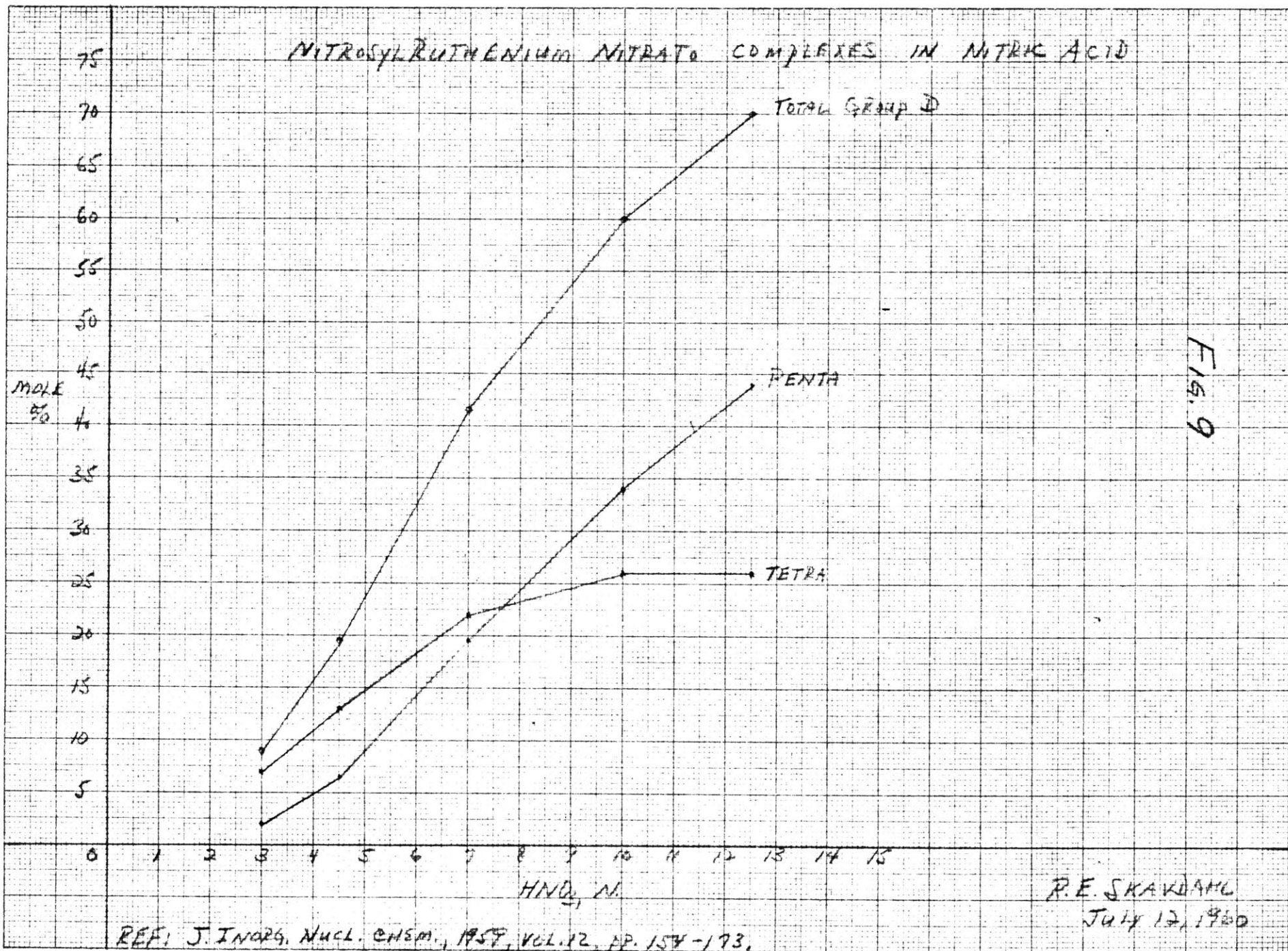
R. E. SKAVDAHL

July 12, 1960

5.0 References

(1)   Sosnoski, Donald M., "Solvent Extraction of the
       Stainless Steel Metals Iron, Cobalt, Nickel, and
       Chromium with Alkyl Amines," S.M. Thesis, Department
       of Nuclear Engineering, M.I.T., August 1960.

(2)   Tamai, Kujoshi, "Effect of Temperature on the
       Extraction of Zirconium from Nitrate Solutions by
       Alkyl Amines," Report of work on a 10:90 Project,
       Chemical Engineering Department, M.I.T.; submitted
       to Prof. E. A. Mason, Nuclear Engineering Department,
       M.I.T., September 1960.

(3)   Mason, E. A., and Vaughen, V. C., "Equilibrium
       Extraction Characteristics of Alkyl Amines and Nuclear
       Fuels Metals in Nitrate Systems," Progress Report VI,
       M.I.T. Nuclear Engineering Department, 1959.

(4)   Degering, E. F., Bordenca, C., and Gwynn, B. H., "An
       Outline of Organic Nitrogen Compounds," John S. Swift
       Co., Inc., 1942, p. 89.

(5)   Hickinbottom, W. J., "Reactions of Organic Compounds,"
       Longmans, Green and Co., 1938, p. 280.

(6)   Richter, C. H., "Textbook of Organic Chemistry,"
       2nd Edition, John Wiley and Sons, Inc., 1944, p. 246.

(7)   Brown, K. B., Chemical Technology Division, Chemical
       Development Section C, Progress Report for April-May
       1960, ORNL-CF-60-5-114.

(8)   Zvyagintsev, O. E., "The Chemistry of Ruthenium,"
       Proceedings of the International Conference on the
       Peaceful Uses of Atomic Energy, Geneva, 1955, vol. 7,
       pp. 169-170.

(9)   Brown, P. G. M., et al, "The Significance of Certain
       Complexes of Ruthenium, Niobium, Zirconium, and Uranium
       in Plant Processes," Proceedings of the 2nd
       International Conference on the Peaceful Uses of Atomic
       Energy, Geneva, 1958, vol. 17, p. 118, also A/CONF.15/P/31.

(10)   "Nuclear Magnetic Resonance Spectra of N-14 in
       Ruthenium Nitrosyl Complexes," DP-391.

(11)   Bruce, F. R., "Solvent Extraction Chemistry of the
       Fission Products," Proceedings of the International
       Conference on the Peaceful Uses of Atomic Energy,
       Geneva, 1955, vol. 7, p. 100.

(12) Anderson, J. S., and McConnell, J. D. M., "Ruthenium (IV) Nitrates," Journal of Inorganic and Nuclear Chemistry, vol. 1, No. 6, December 1955, pp. 371-7.

(13) Fletcher, J. M., et al, "Nitrato and Nitro Complexes of Nitrosylruthenium," Journal of Inorganic and Nuclear Chemistry, vol. 1, No. 6, December 1955, pp. 378-401.

(14) Fletcher, J. M., "Complexes Derived from (RuNO) III and Ru IV," Journal of Inorganic and Nuclear Chemistry, vol. 8, 1958, pp. 277-87.

(15) Fletcher, J. M., "Chemical Principles in the Separation of Fission Products from Uranium and Plutonium by Solvent Extraction," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, vol. 9, pp. 459-63.

(16) Fletcher, J. M., Progress in Nuclear Energy, Series 3, Process Chemistry, vol. 1, pp. 105-121, (1956).

(17) Brown, P. G. M., "Nitro Complexes of Nitrosylruthenium," Journal of Inorganic and Nuclear Chemistry, vol. 13, pp. 73-83 (1960).

(18) Fletcher, J. M., et al, Journal of Inorganic and Nuclear Chemistry, vol. 12, p. 154 (1959).