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URANIUM PHASE EQUILIBRIA IN THE TBP PROCESS

by

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URANIUM PHASE EQUILIBRIA IN THE TBP PROCESS

INTRODUCTION

The development of uranium phase equilibrium data for the tributyl phosphate (TBP) process for waste metal recovery has proceeded at an accelerated pace since initial studies at Oak Ridge in 1949. Early studies covering some simple batch equilibrations for the process are reported in Document ORNL-260.

Early work by the Hanford Works Chemical Research Section resulted in the development and experimental confirmation of a theoretical equation (see Equation (1), below) expressing the phase equilibrium relationship for uranium between aqueous solutions and TBP solutions⁽⁸⁾. Additional equilibrium data for the TBP process, based on a number of batch counter-current type equilibrium runs at various proposed flowsheet conditions, are reported in Chemical Research Section Monthly Reports (see references 1, 2, 3, and 4 in the attached bibliography).

A series of batch equilibrium studies reported in Documents HW-17339⁽⁷⁾ and HW-17179⁽⁶⁾ by the Process Chemistry Group, Chemical Development Section, Hanford Works, supplied additional equilibrium data for the RA and RC Column systems.

OBJECTIVES

The objective of the studies reported in this document was to correlate the RA and RC Column uranium equilibrium data presented in the reports cited in the Introduction, above. The correlations were originally made for use in analyzing pilot-plant column data obtained at Hanford Works. The results are being reported in the belief that they may be useful to others.

It should be noted that the accuracy of equilibrium data required for the evaluation of TBP-process RA Column run results is less than required for the Redox-process IA Column since (a) the equilibrium X-Y curve for TBP (see Figures 8, 9 and 10) has a larger curvature (i. e., greater distance between operating and equilibrium lines) than for the Redox system; and (b) unlike the Redox IA curve, the TBP RA equilibrium curve exhibits no pronounced deflection (concave downward) at the dilute end of the curve. Both of these factors mean that less accuracy is required in locating an equilibrium curve for a TBP-

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type run in order to obtain a given accuracy in calculating H. T. U. (height of a transfer unit) or H. E. T. S. (height of a theoretical stage) values.

SUMMARY AND CONCLUSIONS

A. General

Correlations have been prepared for uranium equilibria in RA and RC type columns (TBP process) and are presented under their respective headings in this report. Correlation of RC equilibrium data was much simpler than that of RA equilibrium data since in the RC system HNO₃ and UNH are the only solutes present in significant amounts, while the RA system also contains H₃PO₄, H₂SO₄, NaNO₃ and ferrous sulfamate.

The final equilibrium correlations for TBP-HW #4 Flowsheet conditions indicate that approximately 3.5 equivalent stages are required in both the RA Column extraction section and the RC Column to reduce uranium losses below 0.5% of the feed uranium in the waste stream from each column. The corresponding number of transfer units is approximately 7.0 for both columns ("overall water-film" basis for the RA extraction section, and "overall organic-film" basis for the RC Column).

B. Uranium Phase Equilibria in the RA Column

Based chiefly on 30 batch equilibrium points reported in Document HW-17339⁽⁷⁾ with supplementary data from ORNL-260⁽⁵⁾, six major variables affecting uranium equilibrium in RA type columns have been correlated graphically on the basis of the "constant" K in the equation⁽⁸⁾:

$$E_a^0 = K(\text{NO}_3^-)^2 (\text{TBP} - 2\text{UN})^2 \dots \dots \dots (1)$$

(see table of nomenclature in the Appendix)

The final correlation has furnished RA Column equilibrium data required for H. T. U. and H. E. T. S. calculations suitable for design specifications. Data appear to be within engineering accuracy for RA Columns operating within the range of conditions represented by the TBP-HW #2, 3, 4, or 5 Flowsheets (see Table I, attached).

The major variables affecting uranium equilibrium in terms of K from Equation (1) above are listed below. Effects of each variable on the distribution ratio, E_a⁰, which are not given below for the sake of brevity, are altered and sometimes even reversed from the effects on K because the variable also appears

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in Equation (1). The numerical value of E_a^0 can be calculated by substituting proper numerical values of the terms in Equation (1), the value of K being obtained from $K^{1/2}$ as read from Figure 7.

<u>Variable</u>	<u>Effect on the "Constant" K</u>
1. H_3PO_4	Addition of H_3PO_4 from 0 to 0.44 <u>M</u> decreases K by a factor of about 10, presumably because of the complexing action of H_3PO_4 on uranium in aqueous solution.
2. H_2SO_4	Addition of H_2SO_4 from 0 to 0.44 <u>M</u> decreases K by a factor of about 2, also presumably because of a complexing action, exerted by H_2SO_4 , on uranium.
3. HNO_3	Addition of "free" HNO_3 (as defined later) increases K to a maximum at about 1 <u>M</u> HNO_3 (with H_2SO_4 present), after which further addition of HNO_3 gradually decreases K.
4. $NaNO_3$	Addition of $NaNO_3$ from 0 to 5 <u>M</u> decreases K by a factor of about 2.
5. UNH	Increasing the concentration of UNH from 10 to 150 g. UNH/l. (in the equilibrated aqueous phase) increases K by a factor of 1.5.
6. TBP	Changes in TBP concentration (10, 12.5, and 15 volume per cent in hydrocarbon diluent) cause only minor effects upon K, the more dilute TBP solutions resulting in slightly higher K values.

Variables having little or no effect on uranium equilibria were found to be ferrous sulfamate and solvent diluent. In the concentration range 0 to 0.02 M, no measurable effect was noted for ferrous sulfamate. Random data using as diluents Deobase, Shell Deodorized Spray Base, Shell Cleaning Solvent (Stoddard type), Varsol, and hexane indicated no significant change in K attributable to these different diluents.

The equilibrium correlations presented in this report were originally developed for the TBP-HW #3 Flowsheet. Subsequent developments have shown

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that the correlations also apply within engineering accuracy to TBP-HW #2, 4, and 5 Flowsheets.

For comparison, nominal compositions for TBP-HW #2, 3, 4, and 5 Flowsheets are tabulated below together with an estimated range over which this correlation applies.

Aqueous Phase, RA Extraction Section	Nominal Flowsheet Conditions				Estimated Range Over Which Correlations Apply
	TBP #2	TBP #3	TBP #4	TBP #5	
H ₃ PO ₄ , M	0.22	0.18	0.18	0.13	0 to 0.5
H ₂ SO ₄ , M	0.22	0.18	0.18	0.13	0 to 0.5
"Free" HNO ₃ , M*	2.4 to 2.7	3.0 to 3.3	1.6 to 1.8	1.2 to 1.4	0.5 to 4
NaNO ₃ , M	3.4	2.8	2.8	2.1	1 to 5
UNH, g./l.	0 to 110	0 to 100	0 to 100	0 to 75	1 to 150
Vol. % TBP in RAX	15	12.5	12.5	12.5	10 to 15

* Basis: Species in solution assumed as NaNO₃, UNH, H₃PO₄, H₂SO₄, and "free" HNO₃.

The correlations presented here are expected to be useful during TBP plant operation. This is because changes in feed composition resulting from variable sludge and supernate compositions and from changing sludge to supernate volume ratios may require day-to-day minor changes in operating conditions in order to realize maximum processing capacity and maximum chemical costs consistent with acceptable uranium losses in the RAW (waste) stream.

C. Uranium Phase Equilibria in the RC Column

A series of batch equilibrations conducted at Hanford Works by the Process Chemistry Group⁽⁶⁾ and some counter-current batch equilibrations performed by the Chemical Research Section^(1,2) are the basis for the RC equilibrium diagrams presented in this report. Sufficient data were obtained at 15 volume per cent TBP to permit drawing uranium equilibrium curves with parameters of HNO₃. Use of data from a limited number of 10 and 12.5

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volume per cent TBP batch equilibrations permitted the construction of a general correlation of a 10, 12.5, and 15 volume per cent TBP equilibrium diagram (Figures 11 and 12). Three figures (Figures 13, 14, and 15 for 10, 12.5, and 15 volume per cent TBP respectively) to be used for run calculations were constructed from the general correlation.

Because the RC system involves only uranium and nitric acid as diffusing components and is therefore simpler than the RA system, RC data were correlated directly on phase equilibrium diagrams instead of in terms of K as was done for RA. Therefore the following summary statements apply to E_a^0 instead of K .

1. Increasing the concentration of HNO_3 increases the uranium distribution ratio E_a^0 . At 10 grams UNH/liter in the equilibrated aqueous phase, E_a^0 is increased by a factor of almost a hundred when the nitric acid concentration is raised from 0 to 30 g./l.

2. Increasing the concentration of TBP in the solvent increases E_a^0 . At 100 grams UNH/liter in the equilibrated aqueous phase and with no nitric acid present, E_a^0 is increased by a factor of about 2 when the TBP concentration in the organic phase is increased from 10 to 15 volume per cent.

3. Below about 30 grams UNH/liter in the aqueous phase, a plot of $\log Y$ vs. $\log X$ (see table of nomenclature, attached) results in essentially straight lines for any given HNO_3 concentration in the aqueous phase. Above about 30 grams UNH/liter in the equilibrated aqueous phase, the slope of the $\log Y$ vs. $\log X$ plot begins to decrease because of an approach towards 100 per cent saturation of the TBP with uranium. At 100 grams UNH/liter in the equilibrated aqueous phase, the percentage saturation of the equilibrated TBP solvent increases from about 22 to 29 when the TBP concentration is increased from 10 to 15 volume per cent.

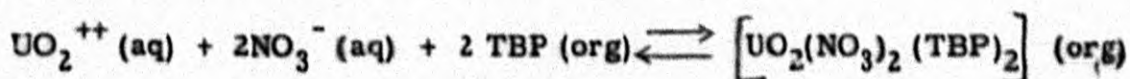
DISCUSSION: URANIUM PHASE EQUILIBRIA IN THE RA COLUMN

A. Origin of Correlations

The equilibrium correlations presented in this report are based primarily upon data from Document HW-17339⁽⁷⁾ as reported by F. Clagett of the Process Chemistry Group, Chemical Development Section, Hanford Works. Supplementary data contained in ORNL-260⁽⁵⁾ helped in determining the effects of "free" nitric acid and sodium nitrate.

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Equation (1) above, developed by R. L. Moore, of the Chemical Research Section, Hanford Works, was of particular value as a starting point. As discussed in Document HW-15230, Equation (1) has been derived on the basis of the following assumed reaction for the extraction:



The equation was developed on the basis of experiments with an aqueous phase containing only UNH and HNO_3 . However, by using Equation (1) as a starting point, it has been possible to correlate data for systems also containing H_2SO_4 , H_3PO_4 , and NaNO_3 in the aqueous phase and varying concentrations of TBP in the organic phase. This was accomplished by expressing the equilibrium "constant" K as an empirical function of the concentrations of the several constituents.

Variables were in general correlated, on the basis of K from the equation above, by holding all concentrations constant except the particular variable being investigated. Since the "constant" K changes rather slowly and continuously with change in any one variable, it was found possible to extend rather limited data over fairly wide ranges by plotting K against the single variable (with other experimental conditions held constant).

B. Effect of H_2SO_4 on K (From Equation (1), Above)

A plot of $\log K$ vs. $\frac{M}{\Delta} (\text{SO}_4^{=})$ (with other variables held constant) based on four points from HW-17339⁽⁷⁾ is shown on Figure 1. The plot forms approximately a straight line with a slope $\frac{\Delta \log K}{\Delta (\text{SO}_4^{=})}$ of about -0.25, the $\text{SO}_4^{=}$ concentration being in moles per liter.

C. Effect of H_3PO_4 on K

A plot of $\log K$ vs. $\frac{M}{\Delta} (\text{PO}_4^{=})$ (with other variables held constant) based on four points from HW-17339⁽⁷⁾ is also shown on Figure 1. The plot forms approximately a straight line with a slope of about -0.8. The ratio of the two slopes ($0.8/0.25 = 3.2$) indicates that the complexing action of H_3PO_4 is about 3 times as strong as the action of H_2SO_4 .

D. Combined Effect of H_2SO_4 Plus H_3PO_4 on K

The 3-to-1 ratio of $\log K$ vs. H_3PO_4 and H_2SO_4 slopes suggested a plot of $\log K$ vs. $(\text{SO}_4^{=} + 3 \text{PO}_4^{=}) \frac{M}{\Delta}$ and this is shown in Figure 2. The

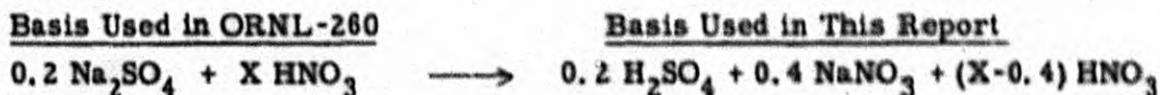
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validity of the 3-to-1 ratio was checked by preparing separate plots (not presented here) based on arbitrarily assumed 3-to-2 and 6-to-1 ratios for the effects of the concentrations of PO_4^{3-} and SO_4^{2-} on $\log K$. The plot originally prepared on the basis of the 3-to-1 ratio proved to be a much better correlation of the data than either of the other two plots. The effects of ferrous sulfate and TBP concentrations shown on Figure 2 will be discussed later in the report.

E. Effect of HNO_3 and NaNO_3

Data from HW-17339⁽⁷⁾ and ORNL-260⁽⁵⁾ were plotted as $\log K$ vs. HNO_3 concentration on Figure 3 with parameters of $(\text{SO}_4^{2-} + 3 \text{PO}_4^{3-}) \text{ M}$ as well as NaNO_3 . The basis, selected chiefly for convenience, of using H_2SO_4 , H_3PO_4 , NaNO_3 , and HNO_3 as the form of the separate species in solution causes the curve for 0.2 M SO_4^{2-} concentration (ORNL-260 data) to exhibit a HNO_3 deficiency of approximately 0.4 M at the low-acid end of the curve. Conversion between the two bases for expressing solution compositions is as follows:



The curves as plotted on Figure 3 from Oak Ridge data also are based on NaNO_3 as parameters in concentrations stoichiometrically equivalent to the amount of $\text{Na}_2\text{SO}_4 + \text{Na}_3\text{PO}_4$ originally added to the respective solutions.

Expressing the sulfate and phosphate on an "all acid" basis in this report was arbitrarily adopted, since the individual ionization constants for the mixture of acids and salts in solution are not known. However, if the ionization constant for each species in solution by itself is assumed to apply for the mixture of acids and salts in the RA extraction section, it is concluded that the sulfate and phosphate are more nearly represented by the molecular acid forms (H_2SO_4 and H_3PO_4) than by the completely neutralized salt forms (Na_2SO_4 and Na_3PO_4). For this reason, and because the ionic equilibria in solution shift anyway with changes in concentration, the use of the above "all-acid" basis is believed justified for simplicity.

Reference to Figure 3 shows that the lines at fixed values of the parameter $(\text{SO}_4^{2-} + 3 \text{PO}_4^{3-}) \text{ M}$ bear a definite relationship to each other, as to

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general shape, maxima, and position relative to each other. Curves representing solutions of different $(\text{SO}_4^{2-} + 3 \text{PO}_4^{3-}) \text{ M}$ concentrations are uniformly lower as this parameter is increased. Also, the curves representing solutions containing H_2SO_4 all show a maximum at about 1 M free HNO_3 .

The drop in K below 1 M HNO_3 concentration roughly corresponds to the acid region in which the first hydrogen of sulfuric acid is ionized. If the complexing action of sulfuric acid involves the $(\text{HSO}_4)^-$ ion in the mechanism, this decrease in K would be explained. Further support for this hypothesis is furnished by the curve representing a solution containing 0.1 M PO_4^{3-} but no sulfate, which curve does not show a decrease in K at low acid concentrations. Since the first hydrogen from H_3PO_4 in a water solution does not ionize significantly until the hydrogen ion concentration is less than 0.1 M, a decrease in K due to complexing by phosphate might also be expected, but only at "free" HNO_3 concentrations of less than 0.1 M. The curve for a solution containing neither H_2SO_4 nor H_3PO_4 does not go through a maximum, and hence is also in agreement with the hypothesis that the drop in K below 1 M HNO_3 concentration involves the $(\text{HSO}_4)^-$ ion.

Except for the falling off of the value of K below 1 M HNO_3 noted in the paragraph above, increasing the concentration of HNO_3 gradually decreases the values of K . This drop, for all curves, is assumed to be due to a decrease in the activity coefficient of the nitrate salting agent.

The effect of NaNO_3 upon K is further elucidated in Figure 4 by cross-plots of data from Figure 3. Values of K from ORNL-260⁽⁵⁾ data have been converted to the same $(\text{SO}_4^{2-} + 3 \text{PO}_4^{3-}) \text{ M}$ basis as data from HW-17339⁽⁷⁾ by the use of Figure 2. By reference to Figure 4, it would be possible to place other parameters of NaNO_3 (at constant $(\text{SO}_4^{2-} + 3 \text{PO}_4^{3-}) \text{ M}$) on Figure 3.

Comparison of the curves from Figure 3 with those of Figure 4 shows that the general shapes and slopes of the two sets of curves are different. The curves on Figure 4 (NaNO_3) differ from those of Figure 3 (free HNO_3) in exhibiting (a) no maxima, and (b) a slightly different slope. The decrease in the value of K with increase in concentration for both NaNO_3 and HNO_3 is presumably due to increased association to form the molecular species, which has the effect of lowering the effective nitrate ion concentration in solution (i. e., a decrease in the nitrate ion activity coefficient). In the case of nitric acid, this

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association effect is modified (at the lower concentrations) because of the specific interaction of the sulfate and phosphate ions with the dissociated hydrogen ions. Therefore the salting effect of NaNO_3 differs quantitatively from that of HNO_3 although it is qualitatively similar.

If, as in Figure 5a, $\log K$ is plotted against total nitrate concentration instead of free HNO_3 (as in Figure 3), maxima of the curves do not all occur at the same value of total (NO_3^-) . Moreover, as would be expected from a comparison of Figures 3 and 4, the curve describing constant HNO_3 does not coincide with the curve for constant NaNO_3 but exhibits a different slope and appears to be approaching a maximum at a different location. For these reasons, plotting K against free HNO_3 , as on Figure 3, was considered more useful for the present study.

Figure 5b shows the effect of nitrate ion upon the uranium distribution ratio, E_a^0 . The curves of E_a^0 show a broad maximum which is reasonably constant over a range of total nitrate concentration from about 3.5 to 7 M. From Equation (1), E_a^0 should increase continuously with increasing (NO_3^-) concentration if K remains constant. The decrease in E_a^0 at high values of (NO_3^-) occurs because the decrease in K (as shown in Figures 3, 4, and 5a) has overcome the $(\text{NO}_3^-)^2$ term in Equation (1).

F. Effect of UNH Concentration

Figure 6 shows the effect of UNH concentration on K over the range 10 to 150 g. UNH/l. in the aqueous phase, based on data from HW-17339⁽⁷⁾. In these experiments, the concentration of HNO_3 in the aqueous phase varied with the individual equilibration. Since the uranium distribution is dependent upon the HNO_3 concentration in the aqueous phase it was necessary to correct for the effect of HNO_3 in determining the effect of UNH alone. This correction was made by dividing experimental values of K by K -values at the particular HNO_3 concentration of the experiment as determined from Figure 7b. As shown on Figure 6, K increases about 50% when the UNH concentration in the aqueous phase is raised from 10 to 150 g. /l. Throughout this report, no correction has been applied for the small effect of organic-phase uranium concentration on organic-phase density, and hence on TBP concentration. The effect of this correction is to increase K slightly as the uranium concentration increases (about 10% higher at 100 g. UNH/l. in the aqueous phase). This

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correction is in the wrong direction to account for the increase in K with UNH concentration shown by the data on Figure 6.

Because of analytical difficulties mentioned in HW-17339⁽⁷⁾, no attempt was made to extend the correlation on Figure 6 below 10 g. UNH/l. The only data available at the time this correlation was carried out ⁽¹⁾, ⁽²⁾, ⁽³⁾, ⁽⁴⁾ indicate variations on the order of $\pm 50\%$ from the assumed mean value of K at uranium concentrations below 10 g. /l. probably as a result of analytical difficulties.

Fortunately, because of the steep slope of the equilibrium line, (approximately 7) together with the mild slope of the operating line (approximately 0.7), small errors in K in this dilute region do not introduce significant errors in the calculation of H. T. U. values for RA extraction column runs.

Rather than prepare a separate K-correction plot for the UNH concentration variable, the correction has been incorporated into the RA phase equilibrium diagrams by a method which is illustrated in Exhibit A shown in the Appendix.

The following factors are taken into account in the method of calculation shown in Exhibit A:

- (a) the change of K with UNH concentration (as read from Figure 6),
- (b) the change of uranium equilibria with total nitrate concentration, and
- (c) the change in aqueous volume due to the partial molal volume of UNH.

G. Effect of Ferrous Sulfamate and TBP Concentration

The effect of ferrous sulfamate and TBP concentration on K is shown graphically in Figure 2, which is based on data presented in Document HW-17339⁽⁷⁾. For concentrations up to 0.02 M, the effect of ferrous sulfamate on uranium equilibrium appears to be negligible within the analytical error. There does appear to be a definite effect corresponding to the concentration of TBP however; and, the lines for 10 and 15 volume per cent TBP included on Figure 7 have been sketched in parallel to the 12.5 volume per cent TBP curve through averages of the equilibrium points mentioned above.

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H. Integrated Correlation

An integrated correlation of the variables discussed above with K is shown in Figure 7. The corresponding equilibrium curves are presented in Figures 8, 9, and 10. Figure 7 was formed from the foregoing curves in the following manner. Figure 2 was plotted directly on Figure 7a as $\log K_1$ vs. $(\text{SO}_4^{2-} + 3 \text{PO}_4^{3-}) \text{ M}$, except that K_1 has been plotted as the square root of K (from Figure 2). The curve from Figure 3 representing a solution containing 3.4 M NaNO_3 was then plotted on Figure 7b as $\log K_2$ vs. HNO_3 with NaNO_3 as a parameter, except that K_2 has been plotted as the square root of K (from Figure 3). As a matter of convenience, the curves for K_2 have been displaced slightly downward so that the product of $K_1 K_2$ equals $K^{1/2}$ in the equation:

$$E_a^0 = (K^{1/2} \text{NO}_3^-)^2 (\text{TBP-2UN})^2 \dots \dots \dots (2)$$

The only difference between Equation (2) and Equation (1) given previously is the algebraic form of the $(K) (\text{NO}_3^-)^2$ factor. The use of the square root of K rather than K allows direct substitution into the parameters of $(K^{1/2} \text{NO}_3^-)$ shown in Figure 8, 9, and 10, which are based on Equation (2), above. The positions of the $(K^{1/2} \text{NO}_3^-)$ equilibrium lines (Figures 8, 9, and 10) differ slightly from Equation (2) because of the inclusion of a correction term for increase in K with increase in UNH concentration and a small correction for the partial molal volume of UNH, as previously discussed. Since this effect of UNH concentration on K was taken into account in locating the equilibrium line parameters, the correction is made automatically when a value of $(K^{1/2} \text{NO}_3^-)$ is determined at the dilute (10 g. UNH/l. or less, aqueous phase) end of the extraction section for the RA Column.

The curves of Figures 8, 9, and 10 agree closely with direct experimental data for $K^{1/2} = 1$, but for $K^{1/2}$ values of 0.5 or 2, the error in Y is about 5% at an X value of 100 g. UNH/l., since the effect of the NO_3^- ion in UNH is not properly allowed for when $K^{1/2} \neq 1$. This error drops to zero per cent below an X value of 10 g. UNH/l. and may be neglected in most run calculations since the major part of the calculation involves the range below 50 g. UNH/l. in the aqueous phase. Furthermore, the numerical value of $K^{1/2}$ is not normally greatly different from 1 for the RA extraction section processing Hanford underground waste containing PO_4^{3-} and SO_4^{2-} ($K^{1/2}$ is approximately 1.4 for the TBP-HW #4 Flowsheet).

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For organic solutions which differ slightly from the 10, 12.5, and 15 volume per cent TBP concentrations used on Figures 8, 9, and 10, percentage errors in H. E. T. S. are approximately equal to the percentage error in volume per cent TBP. Percentage errors in H. T. U. are very approximately one-half of the percentage error in volume per cent TBP. For an accurate equilibrium diagram at a TBP concentration other than 10, 12.5 or 15 volume per cent, it is suggested that a new diagram be prepared from a cross-plot of the 10, 12.5 and 15 volume per cent values.

DISCUSSION: URANIUM PHASE EQUILIBRIA IN THE RC COLUMN

A. Origin of Correlations

Due to the complexity of the RA system, it proved expedient to relate the uranium equilibria to a theoretical equation in order to extrapolate limited data over the wide range of possible operating conditions. However, in the RC system only UNH and HNO_3 solutes are present in significant concentrations so that uranium equilibrium lines with an HNO_3 parameter may be drawn and H. E. T. S. and H. T. U. calculations may be carried out by estimating the acid concentration of each stage. In order to reduce the analytical work load, complete equilibrium data were obtained only for 15 volume per cent TBP in the solvent, while data for 10 and 12.5 volume per cent TBP were only spot-checked. The variables in Equation (1) were then rearranged to act as a guide in establishing a correlation of all of the available experimental data.

Based on the rearranged equation, a suitable correlation of the data was obtained by plotting (UNH/TBP) (org.) as the ordinate vs. (UNH) aq. $(\text{TBP})^{1/2}$ org. as the abscissa, both on logarithmic scales. Derivation of this generalized RC Column equilibrium correlation is carried out on Exhibit B, attached. The equilibrium points for 10, 12.5, and 15 volume per cent TBP (with HNO_3 concentration held constant) all fell very close to the best line through the points as may be seen from Figures 11 and 12.

The equilibrium lines presented on Figure 11 (UNH/TBP) (org.) vs. (UNH) aq. $(\text{TBP})^{1/2}$ (org.) extend over the concentration ranges covered by the experimental data presented in Document HW-17179⁽⁶⁾. The uranium equilibrium line for 0 M HNO_3 in the aqueous phase was drawn somewhat higher in the dilute uranium region than the corresponding line drawn in HW-17179⁽⁶⁾. Both correlations represent the data adequately within the accuracy of analytical

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results. For RC Column operation at TBP process conditions, the slight difference between these two correlations has no significant effect on the accuracy of calculated H. T. U. values.

B. Final Correlation

Figures 13, 14, and 15 are uranium phase-equilibrium diagrams similar to the RC Column run calculation sheets used by the Chemical Development Section at Hanford Works for calculating H. T. U. and H. E. T. S. values. These three figures were prepared from an original large-scale plot of UNH/TBP (org.) vs. (UNH) aq. $(TBP)^{1/2}$ org. similar to Figures 11 and 12. Figures 13, 14, and 15 were constructed for 10, 12.5, and 15 volume per cent TBP respectively, using log-log scales because of the 10,000-fold range of numerical values covered. The slopes of the equilibrium lines on the log-log plots decrease from about 3 to about 1 when the nitric acid concentration is increased from 0 to 30 g./l. in the aqueous phase. The slope of each equilibrium line also decreases noticeably above approximately 30 g. UNH/l. in the aqueous phase. For example, the equilibrium line at 12.5 volume per cent TBP in the organic phase and zero HNO_3 in the aqueous phase decreases in slope from about 2.7 to about 1.7 when the uranium concentration (equilibrated aqueous) is increased from 10 to 100 g./l. This is quantitatively in agreement with the known fact that the equilibrium lines must approach zero slope as the TBP approaches 100% saturation with uranium.

At any given uranium concentration in the aqueous phase (X), increased volume percentages of TBP result in increased concentrations of uranium in the organic phase (Y). At 100 g. UNH/l. in the equilibrated aqueous phase and with no nitric acid present, E_a^0 with 10, 12.5 and 15 per cent TBP in the organic phase is 1.9, 3.0, and 4.0, respectively.

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NOMENCLATURE

E_a^0	Uranium distribution ratio <u>g. UNH/l. (organic)</u> g. UNH/l. (aqueous).
g./l.	grams/liter.
H. E. T. S.	Height Equivalent to a Theoretical Stage.
H. T. U.	Height of a Transfer Unit.
K	Constant, in Equations (1) and (2).
<u>M</u>	Concentration, molar.
(NO_3^-)	in Equations (1) and (2), total nitrate concentration, including that from UNH, aqueous phase, molar.
TBP	Tributyl phosphate; in Equations (1) and (2), concentration, organic phase, molar.
UN	Uranyl nitrate; in Equations (1) and (2), concentration, organic phase, molar.
UNH	Uranyl nitrate hexahydrate ($UO_2(NO_2)_2 \cdot 6H_2O$).
X	Grams UNH/Liter (Aqueous phase).
Y	Grams UNH/Liter (Organic phase).

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D. P. Granquist

D. P. Granquist

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E. T. Merrill

DPG:ETM:lb

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APPENDIX

EXHIBIT A
METHOD OF CALCULATION FOR $K^{1/2} \text{NO}_3$ PARAMETERS PLOTTED

ON EQUILIBRIUM DIAGRAMS, FIGURES, 8, 9, and 10

The following numerical example is presented as an illustration of how points were calculated which form the basis for the equilibrium line parameters presented in Figures 8, 9, and 10. The following points are calculated for the $5 \text{ M } K^{1/2} \text{NO}_3$ line using 12.5 volume per cent TBP. Points for the other curves were calculated in an identical manner.

	UNH (Aq.)		$K^{1/2(1)}$	A ⁽²⁾	$K^{1/2}A$	KA^2	KA^2X	UNH (Org.) ⁽³⁾	
	g./l.	$M = (X)$						$M = Y$	g./l.
10	0.01991		1	5.0353	5.0353	25.3542	0.5048	0.0584	29.3
25	0.04978		1.032	5.0871	5.2499	27.5618	1.3720	0.0961	48.3
40	0.07965		1.070	5.1395	5.4992	30.2416	2.4087	0.1179	59.2
65	0.1294		1.121	5.2267	5.8591	34.3289	4.4422	0.1398	70.2
90	0.1792		1.162	5.3140	6.1749	38.1290	6.8327	0.1535	77.1
105	0.2091		1.180	5.3664	6.3324	40.0993	8.3848	0.1595	80.1

(1) Increase in K with increasing aqueous UNH concentration read from Figure 6.

(2) A is defined as:

$$\frac{\text{NO}_3^-}{(1 + 0.05 X)} + 2X$$

where the factor $(1 + 0.05 X)$ is a correction term for the partial molal volume of UNH and $2X$ represents the molar nitrate contribution of UNH in the aqueous phase.

(3) Y is calculated from equation (1) (see text) modified as follows:

$$Y = (KA^2X) (\text{TBP} - 2Y)^2$$

or in this case

$$Y = (KA^2X) (0.20885 - 1.828Y + 4Y^2)$$

EXHIBIT B
DERIVATION OF THE GENERALIZED RC COLUMN
EQUILIBRIUM CORRELATION

Equation (1),

$$E_a^0 = \frac{UN}{(UNH)_{aq.}} = K (NO_3^-)^2 (TBP - 2UN)^2 \quad (1)$$

(for terms, See Table of Nomenclature,
 Page 18) may be rearranged as follows

$$\frac{UN}{TBP} = K (NO_3^-)^2 (UNH)_{aq.} (TBP) \left(1 - \frac{2UN}{TBP}\right)^2 \quad (3)$$

$$NO_3^- = HNO_3 + 2(UNH)_{aq.}$$

$$\text{When } HNO_3 = 0, NO_3^- = 2(UNH)_{aq.}$$

From Equation (3),

$$\frac{UN}{TBP} = 4K \left[(UNH)_{aq.} (TBP)^{1/3} \right]^3 \left(1 - \frac{2UN}{TBP}\right)^2 \quad (4)$$

Now let

$$X_o \doteq (UNH)_{aq.} (TBP)^{1/3}$$

$$\text{and } Y' \doteq \frac{UN}{TBP}$$

Then, Equation (4) may be expressed as

$$Y' = 4K X_o^3 (1 - 2Y')^2$$

$$\text{or } \frac{Y'}{(1 - 2Y')^2} = 4K X_o^3 \quad (5)$$

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Thus at $\text{HNO}_3 = 0$ if K were actually constant, it would be possible to correlate the uranium concentration in the two phases uniquely by Equation (5). While it was found that the experimental data did not lend themselves to adequate correlation in terms of X_0 and Y' , a satisfactory correlation in the 10 to 15 volume per cent TBP range was obtained by a plot of Y' against the variable X' , defined as $(\text{UNH})_{\text{aq.}} (\text{TBP})^{1/2}$. The correlation in terms of X' and Y' was found to be applicable not only at $\text{HNO}_3 = 0$, but also at aqueous-phase nitric acid concentrations of 10, 20, and 30 g./l. This correlation is shown in Figures 11 and 12.

The semi-theoretical, semi-empirical basis of this correlation calls for caution against extrapolation from the experimentally established plots. The partial theoretical basis of the correlation gives rise to considerable doubt about the validity of any extrapolation on the 20 and 30 g. HNO_3 /l. curves toward lower uranium concentrations, hence higher $\text{HNO}_3/(\text{UNH})_{\text{aq.}}$ ratios.

TABLE I

TBP PROCESS FLOWSHEET COMPOSITIONS

TBP-HW #2 Flowsheet (Abstracted from HW-15507)

Stream	Flow Ratio (RAF = 100)	Compositions						
		UNH M	SO ₄ ⁼ M ⁴	PO ₄ ⁼ M ⁴	NO ₃ ⁻ M ³	Na ⁺ M	H ⁺ M	TBP Vol. %
RAS	50	0	0	0	5.0	0	5.0	0
RAF	100	0.33	0.32	0.32	6.5	4.97	3.13	0
RAX	250	0	0	0	0	0	0	15
R CX	250	(Water only)						

TBP-HW #3 Flowsheet (Abstracted from HW-15987)

RAS	50	0	0	0	5.0	0	5.0	0
RAF	100	0.27	0.26	0.26	6.5	4.05	3.78	0
RAX	200	0	0	0	0	0	0	12.5
R CX	160	(Water only)						

TBP-HW #4 Flowsheet (Abstracted from HW-18169)

RAS	50	0	0	0	2.0	0	2.0	0
RAF	100	0.27	0.26	0.26	5.71	4.07	2.96	0
RAX	250	0	0	0	0	0	0	12.5
R CX	200	0	0	0	0.01	0	0.01	0

TBP-HW #5 Flowsheet (Abstracted from HW-18232)

RAS	34	0	0	0	2.0	0	2.0	0
RAF	100	0.18	0.18	0.18	3.89	2.78	2.01	0
RAX	170	0	0	0	0	0	0	12.5
R CX	136	0	0	0	0.01	0	0.01	0

in the equation $E_a^0 = (K)(NO_3^-)^2(TBP-2UH)^2$

E_a^0 = uranium distribution ratio, $\frac{K \cdot U_{NH} / l. (Org.)}{g. U_{NH} / l. (Aq.)}$

K = an empirical "constant"

NO_3^- = total nitrate ion concentration including U_{NH}, aqueous phase, M

TBP = concentration of TBP, organic phase, M

UH = concentration of uranyl nitrate, organic phase, M

Data plotted are from HW-17339. Concentrations (aqueous phase) before equilibration with TBP in Shell deodorized base were as follows:

Component	Concn. M
U _{NH}	0.1
NaNO ₃	3.4
HNO ₃	2.5
H ₂ SO ₄ and H ₃ PO ₄	Variable

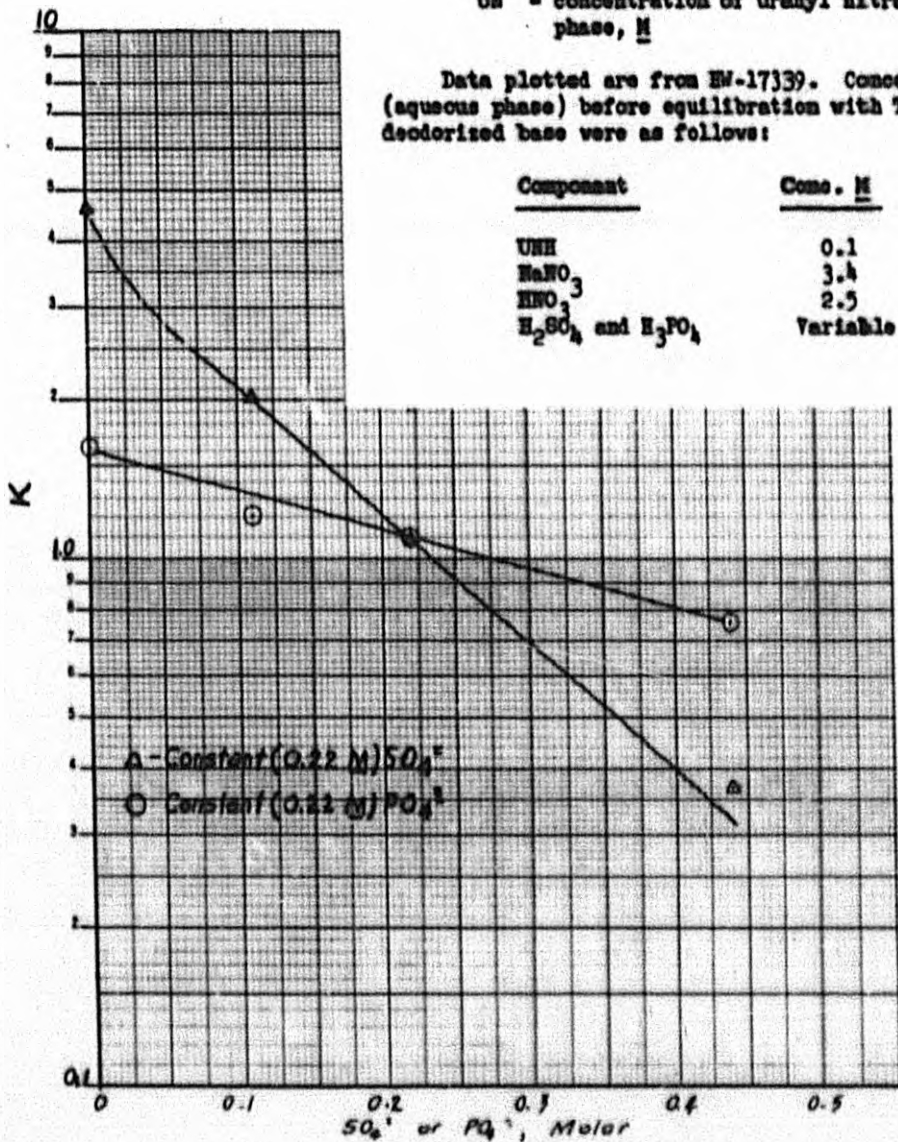


FIGURE 1

EFFECT OF SO_4^{2-} OR PO_4^{3-} UPON K FROM THE EQUATION $E_a^0 = K(NO_3^-)^2(TBP-2UH)^2$

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Symbol	Tributyl Phosphate (TBP) Vol. %	Ferrous Sulfamate M
△	10	0.0
□	10	0.02
○	12.5	0.0
◇	12.5	0.02
◇	15.0	0.0
○	15.0	0.02

In the equation $E_a^c = (K)(NO_3^-)^2(TBP-2UN)^2$

E_a^c = uranium distribution ratio, $\frac{g.UNH/l.(Org.)}{g.UNH/l.(Aq.)}$

K = an empirical "constant"

NO_3^- = total nitrate ion concentration including UNH, aqueous phase, M

TBP = concentration of TBP, organic phase, M

UN = concentration of uranyl nitrate, organic phase, M

Data plotted are from HW-17339. Concentrations (aqueous phase) before equilibration with TBP in Shell deodorized base were as follows:

Component	Conc. M
UNH	0.1
NaNO ₃	3.4
HNO ₃	2.5
H ₂ SO ₄ and H ₃ PO ₄	Variable

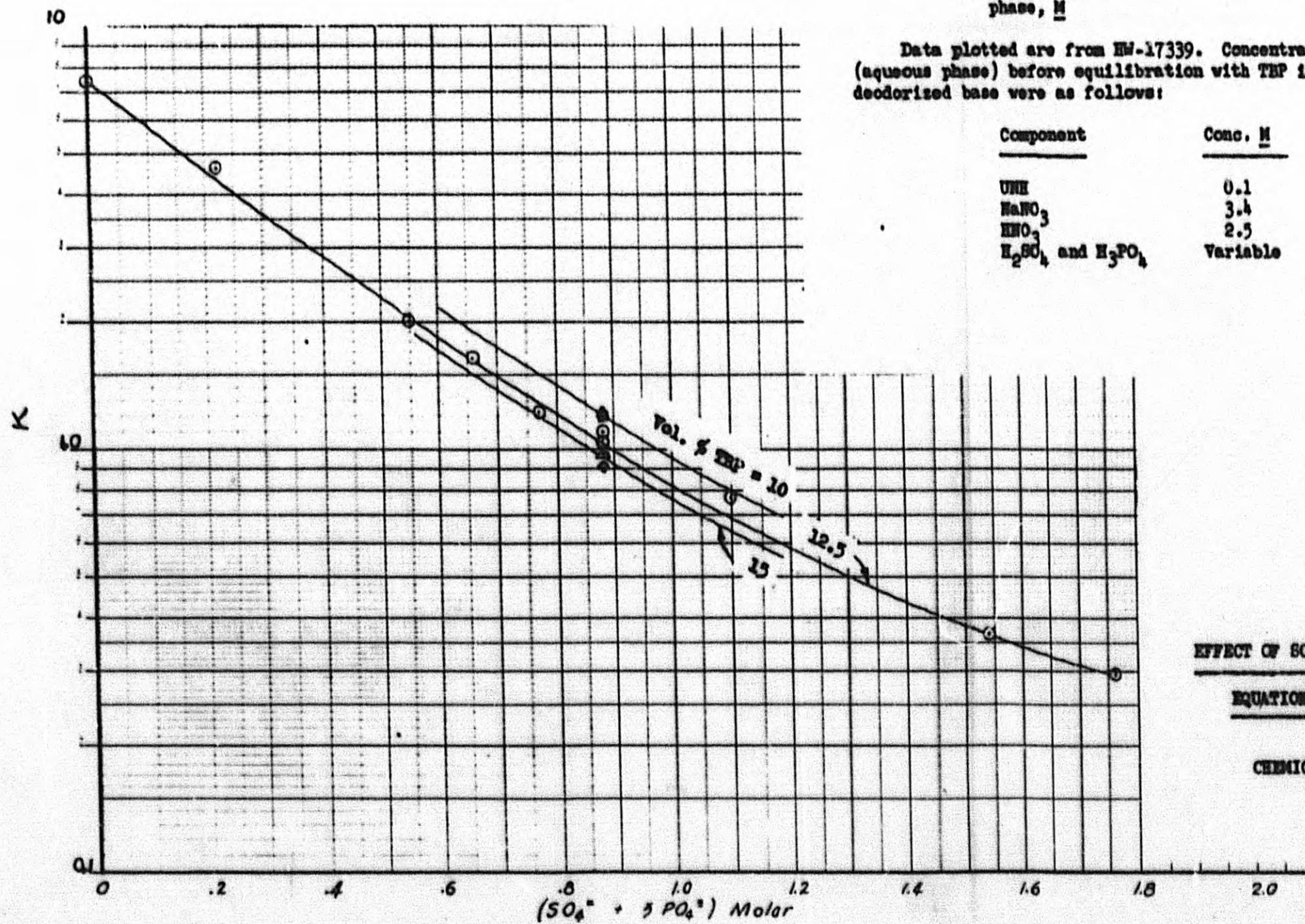


FIGURE 2
EFFECT OF SO_4^{2-} AND PO_4^{3-} UPON K FROM THE
EQUATION $E_a^c = K(NO_3^-)^2(TBP-2UN)^2$

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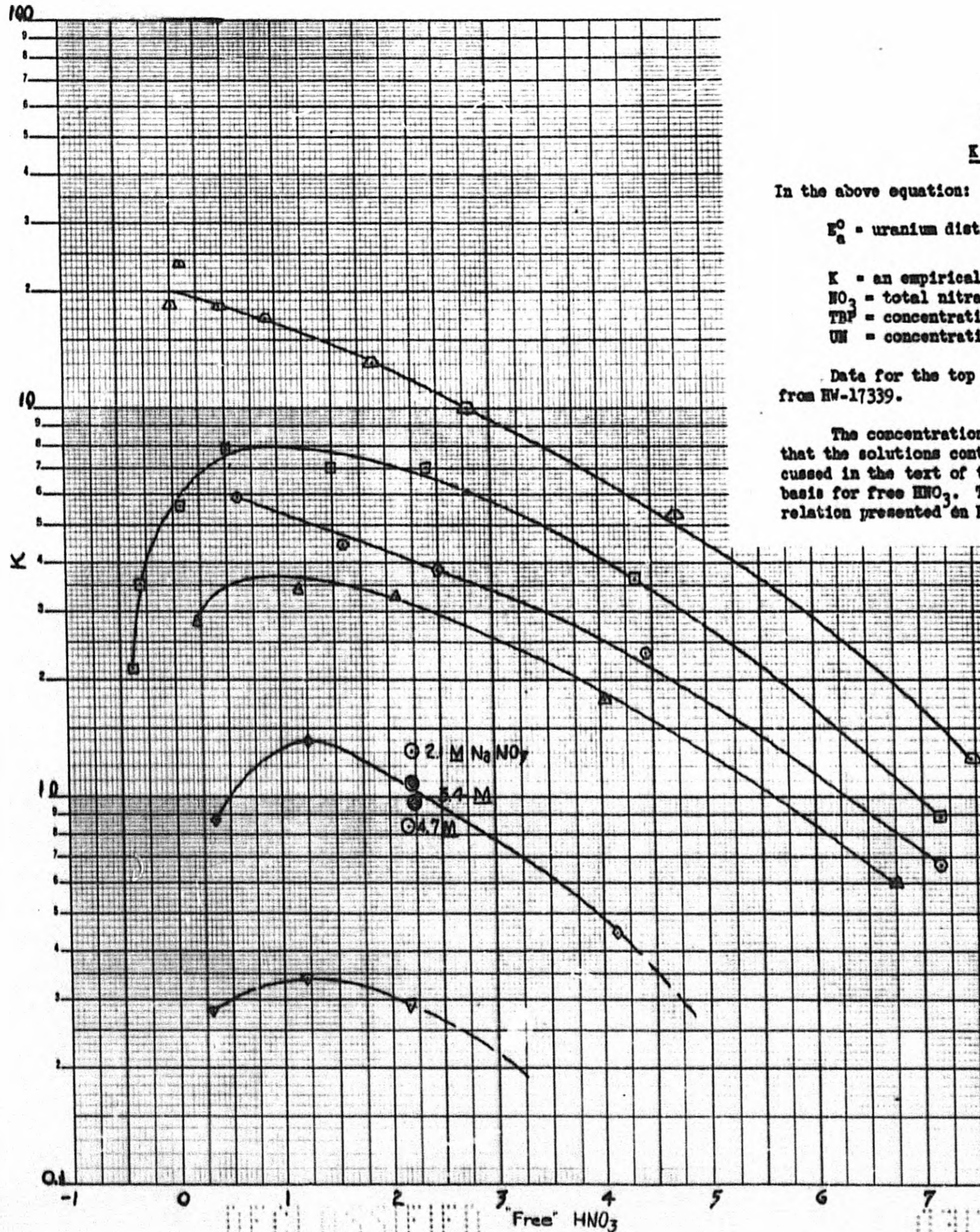


FIGURE 3

PLOT TO DETERMINE EFFECT OF HNO_3 UPON
 K IN THE EQUATION $E_a^0 = K(\text{NO}_3^-)^2(\text{TBP} - 2\text{UH})^2$

In the above equation:

E_a^0 = uranium distribution ratio, $\frac{\text{g. UH}/\text{l. (Org.)}}{\text{g. UH}/\text{l. (Aq.)}}$

K = an empirical "constant"

NO_3^- = total nitrate ion concentration including UH, aqueous phase, M

TBP = concentration of TBP, organic phase, M

UH = concentration of uranyl nitrate, organic phase, M

Data for the top four lines are from ORNL 260; and for the bottom two curves, from HW-17339.

The concentration of free HNO_3 was calculated based on the arbitrary assumption that the solutions contained UH, NaNO_3 , H_2SO_4 , H_3PO_4 , and "free" HNO_3 . As discussed in the text of this report, the ORNL 260 data were recalculated to the above basis for free HNO_3 . The use of $(\text{SO}_4^{2-} + 3\text{PO}_4^{3-})_{\text{M}}$ as a parameter is based on the correlation presented in Figure 2.

Symbol	Aqueous Phase Concentration			Value of Parameter ($\text{SO}_4^{2-} + 3\text{PO}_4^{3-}$) M
	NaNO_3 M	H_2SO_4 M	H_3PO_4 M	
Δ	0	0	0	0
\square	0.4	0.2	0	0.2
\circ	0.3	0	0.1	0.3
\triangle	0.7	0.2	0.1	0.5
\diamond	3.4	0.22	0.22	0.88
\circ	2.1 to 4.7	0.22	0.22	0.88
∇	3.4	0.44	0.44	1.76

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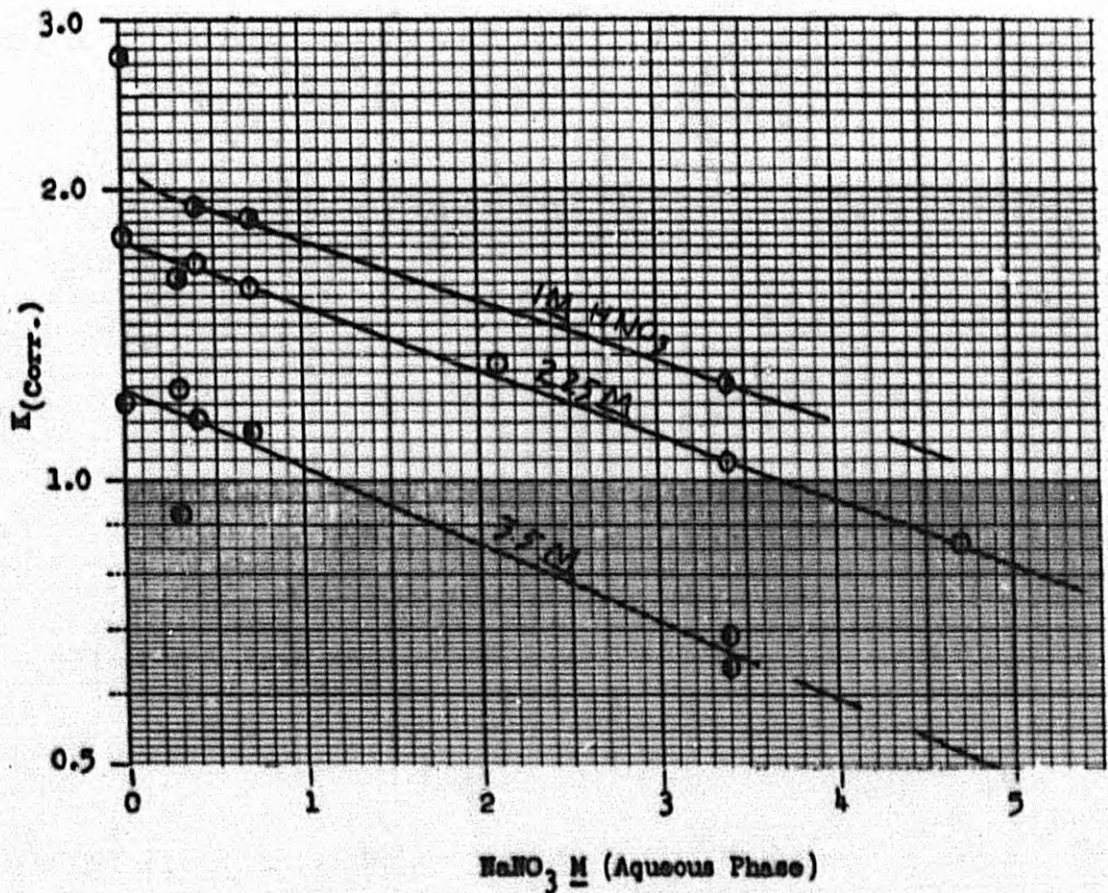
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FIGURE 4

CROSS-PLOT OF FIGURE 3 TO DETERMINE EFFECTOF NaNO₃ UPON K IN THE EQUATION

$$E_a^0 = K(\text{NO}_3^-)^2 (\text{TBP} - 2\text{OH})^2$$

Data at dilute NaNO₃ concentrations (below 1 M) are from ORNL-260. The experimental K values from ORNL-260 have been modified to a common (SO₄ + 3PO₄)_M basis to agree with HW-17339 concentrations by using Figure 2. Points at higher NaNO₃ concentrations are directly from HW-17339 and represent solutions containing 0.22 M H₃PO₄ and 0.22 M H₂SO₄ as well as URE, HNO₃, and NaNO₃.



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FIGURE 5

EFFECT OF TOTAL NITRATE (EQUILIBRATED AQUEOUS PHASE) CONCENTRATION UPON URANIUM EQUILIBRIA

Legend:

Symbol	Source	Aqueous Phase Concentrations Before Equilibration					Organic Phase Concentrations	
		HNO_3 M	H_2SO_4 M	H_2O_2 M	H_2O_2 M	OH M	Vol.% Diluent	
△	ORNL 260	0.02 to 8.0	0	0	0	0.12	15	Hexane
□	ORNL 260	0.02 to 8.0	0.4	0.2	0	0.12	15	Hexane
○	ORNL 260	0.02 to 8.0	0.3	0	0.1	0.12	15	Hexane
△	ORNL 260	0.02 to 8.0	0.7	0.2	0.1	0.12	15	Hexane
◇	HW-17339	0.5 to 4.5	3.4	0.22	0.22	0.05 to 0.1	12.5	Shell Decolorized Spray base
○	HW-17339	2.5	2.1 to 4.7	0.22	0.22	0.05 to 0.1	12.5	
▽	HW-17339	0.5 to 2.5	3.4	0.44	0.44	0.05 to 0.1	12.5	
○	Estimated from Fig. 7	1.6	2.2	0.18	0.18	0.001	12.5	

(Point corresponds approximately to an RW Solution from RW-TSP #4 Flowheet)

Figure 5a

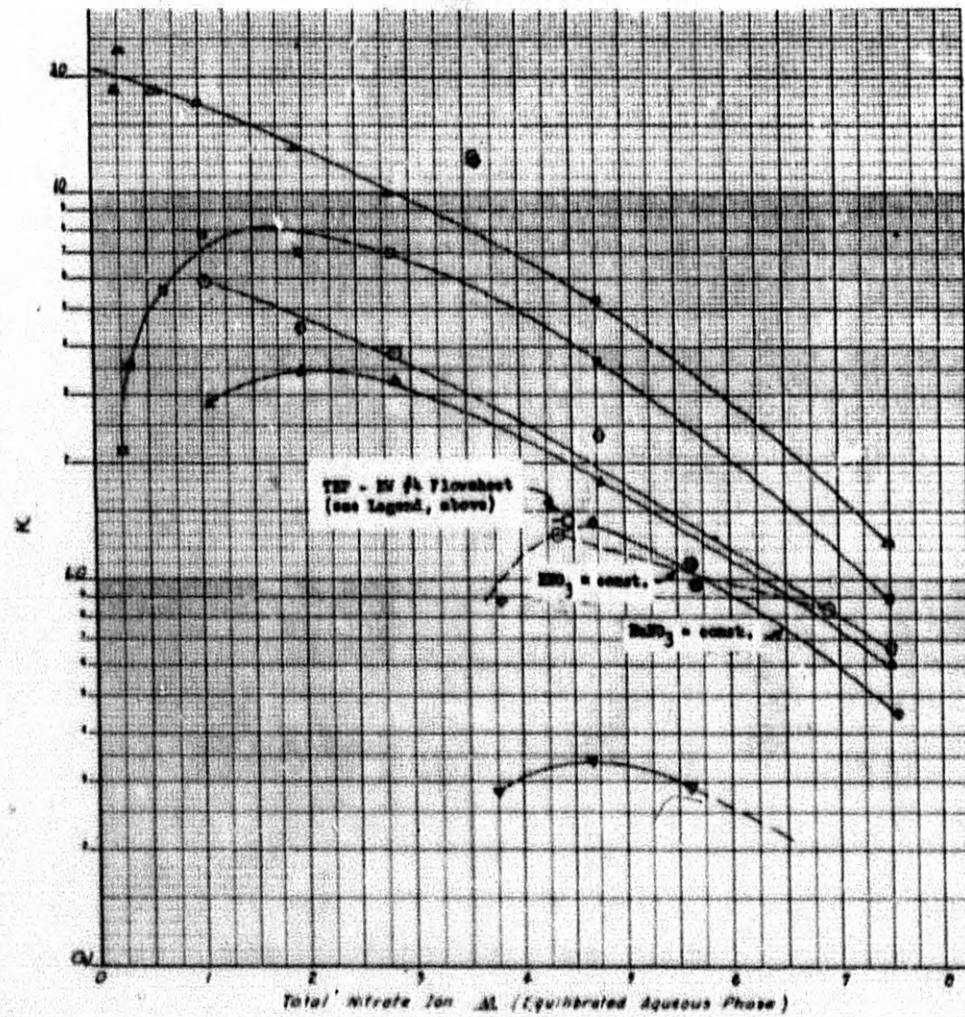
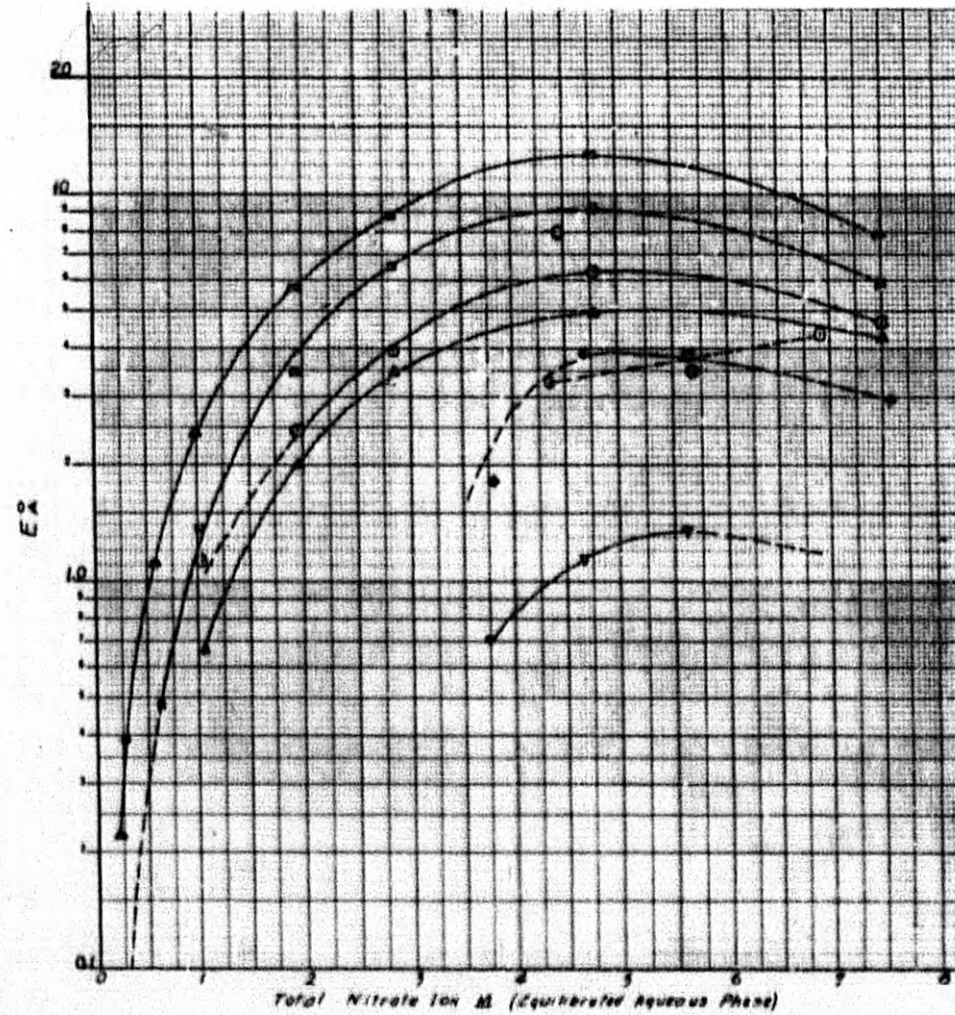


Figure 5b



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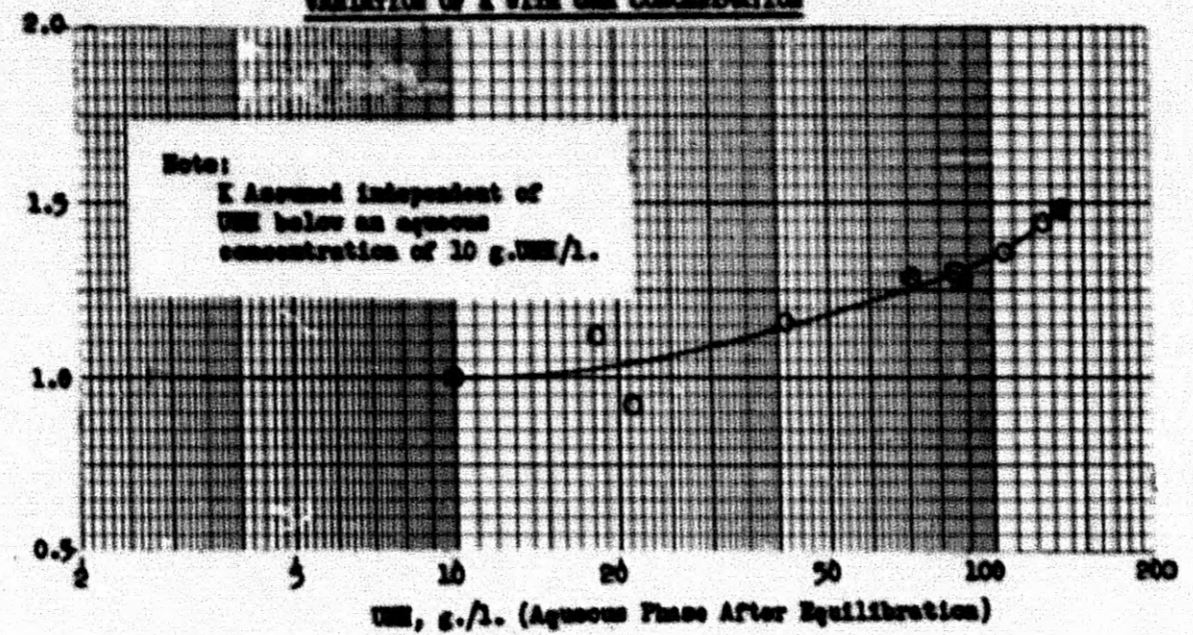
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RATIO OF $\frac{K}{K'} \left(\frac{M_{H_2O}}{M_{H_2O} + M_{H_2SO_4}} \right)$

FIGURE 6
VARIATION OF K WITH URE CONCENTRATION



Nominal Aqueous Phase Compositions

Symbol	Component	Concentration \underline{M}
All Points	H_2SO_4	0.22
	H_3PO_4	0.22
	HNO_3	3.4
○	HNO_3	2.5
●	HNO_3	1.0

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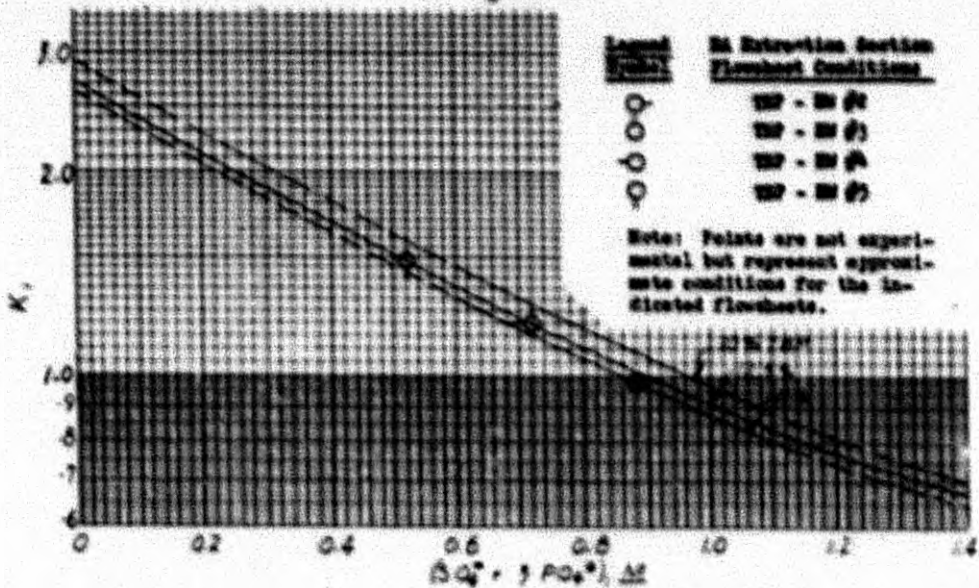
FIGURE 7

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CHART FOR DETERMINING VALUE OF $E^{1/2}$ FOR USE WITH K_2 EQUILIBRIUM CORRELATIONS

BASED ON FIGURES 8, 9, AND 10.

Figure 7a



Directions for Use:

1. Determine K_1 from Figure 7a at correct TBP concentration for conditions of run.
2. Determine K_2 from Figure 7b at correct HNO_3 concentration assuming the following compounds in solution: HNO_3 , $UO_2(NO_3)_2 \cdot 6H_2O$, H_2PO_4 , H_2PO_3 and "Free HNO_3 ".
3. $E^{1/2}$ for the equation $K_1^2 = \frac{(E^{1/2}(NO_3^-))^2 (TBP-ORG)^2}{E^{1/2} - K_2}$

where K_2 = uranium distribution ratio $\frac{g. UO_2 / l. (Org.)}{g. UO_2 / l. (Aq.)}$

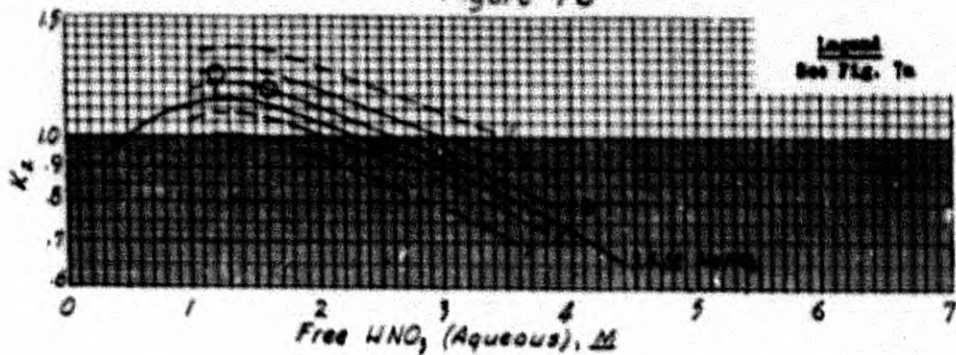
NO_3^- = Total nitrate concentration, MAM, Molar

TBP = Tri-butyl phosphate conc., MAM, Molar

OR = Oranyl nitrate conc., (Org.), Molar

4. Use this value of $E^{1/2}$ in conjunction with Figures 8, 9, and 10 for uranium phase equilibrium data at conditions approximating the TBP-OR #0, 3, 4 or 5 flowcharts.

Figure 7b



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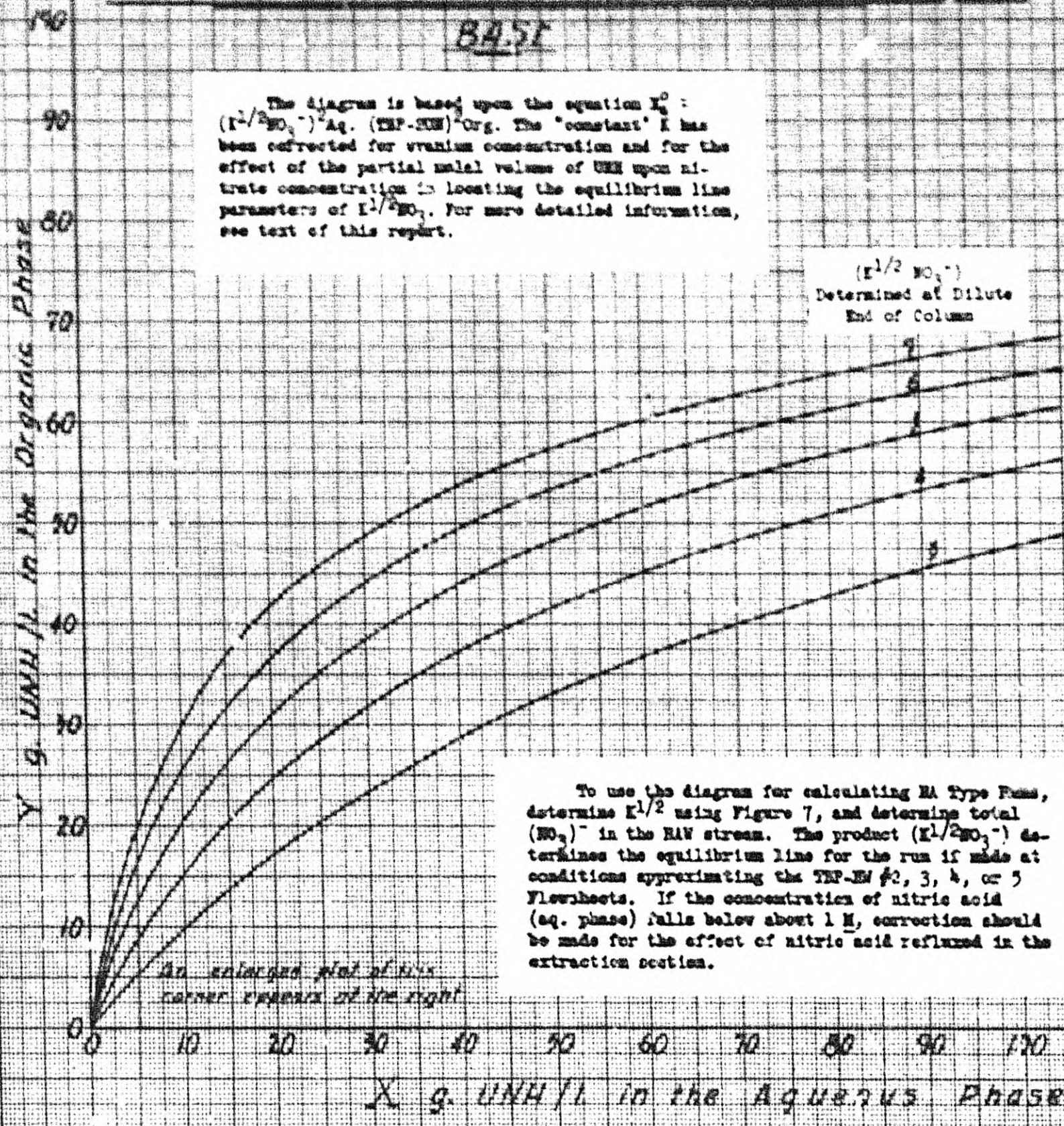
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FIGURE 8

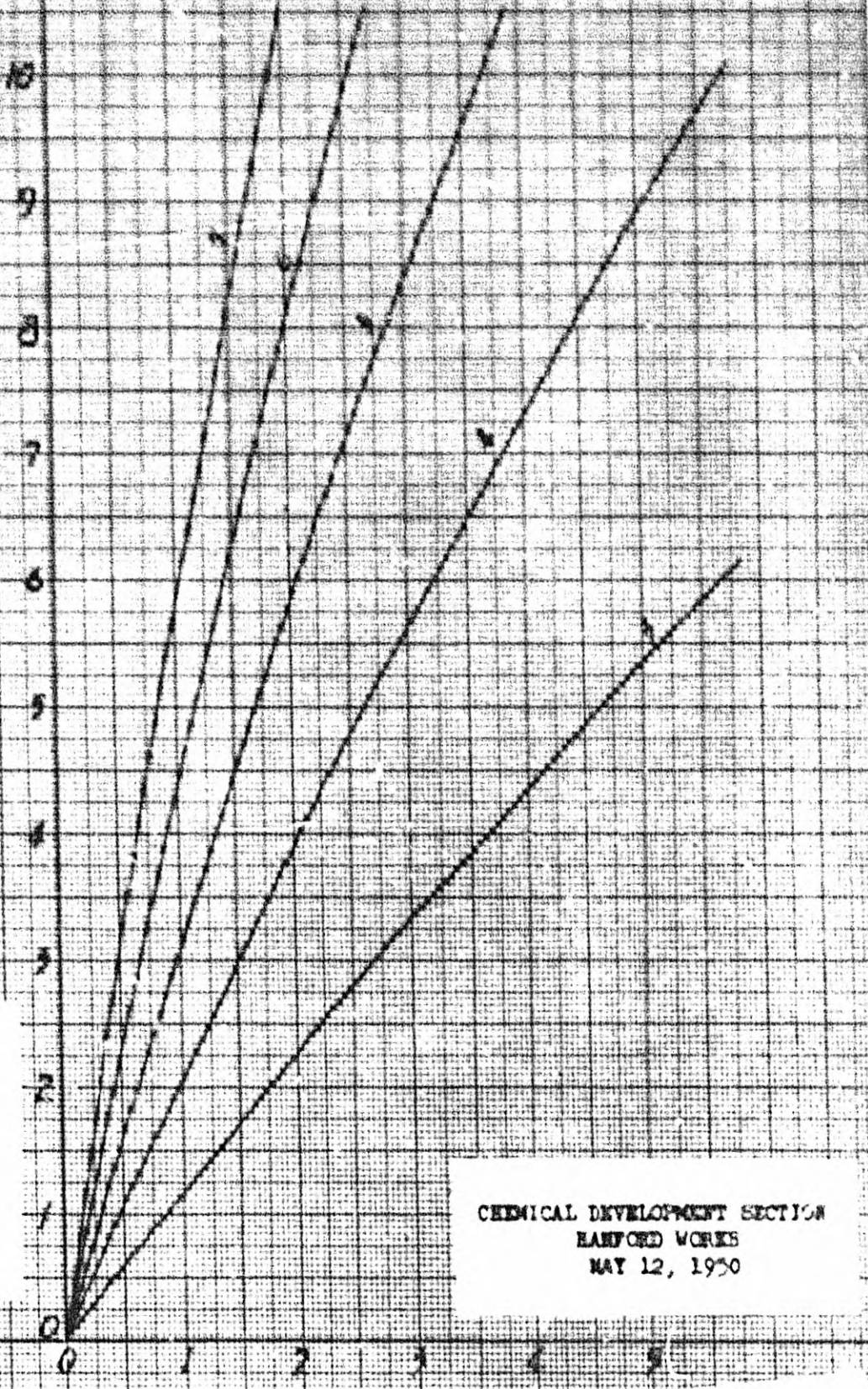
RA COLUMN PHASE EQUILIBRIUM DIAGRAM FOR
10% (BY VOLUME) TBP IN 5MILL DIODORIZED SPRAY
BASE

The diagram is based upon the equation $K_d^0 = (E^{1/2}NO_3^-)_{Aq.} (TBP-UUU)_{Org.}$. The "constant" K has been corrected for uranium concentration and for the effect of the partial molal volume of UUU upon nitrate concentration in locating the equilibrium line parameters of $E^{1/2}NO_3^-$. For more detailed information, see text of this report.

$(E^{1/2} NO_3^-)$
Determined at Dilute
End of Column



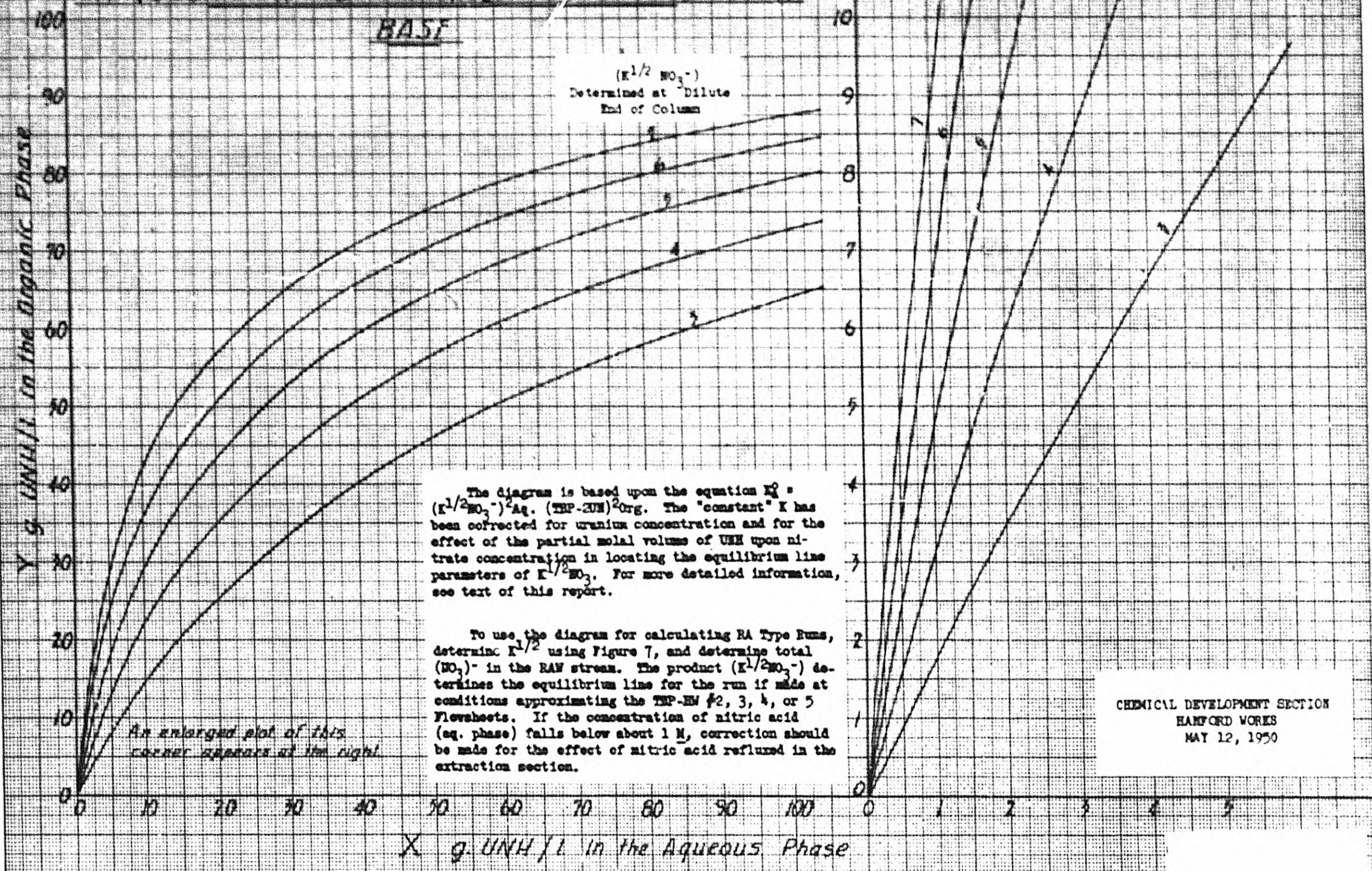
To use the diagram for calculating RA Type Runs, determine $E^{1/2}$ using Figure 7, and determine total (NO_3^-) in the RAW stream. The product $(E^{1/2}NO_3^-)$ determines the equilibrium line for the run if made at conditions approximating the TBP-UU #2, 3, 4, or 5 Flow sheets. If the concentration of nitric acid (aq. phase) falls below about 1 M, correction should be made for the effect of nitric acid refluxed in the extraction section.



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Figure 9

RA COLUMN PHASE EQUILIBRIUM DIAGRAM FOR
12.5 VOLUME % TBP IN SHELL DEODORIZED SPRAY
BASF

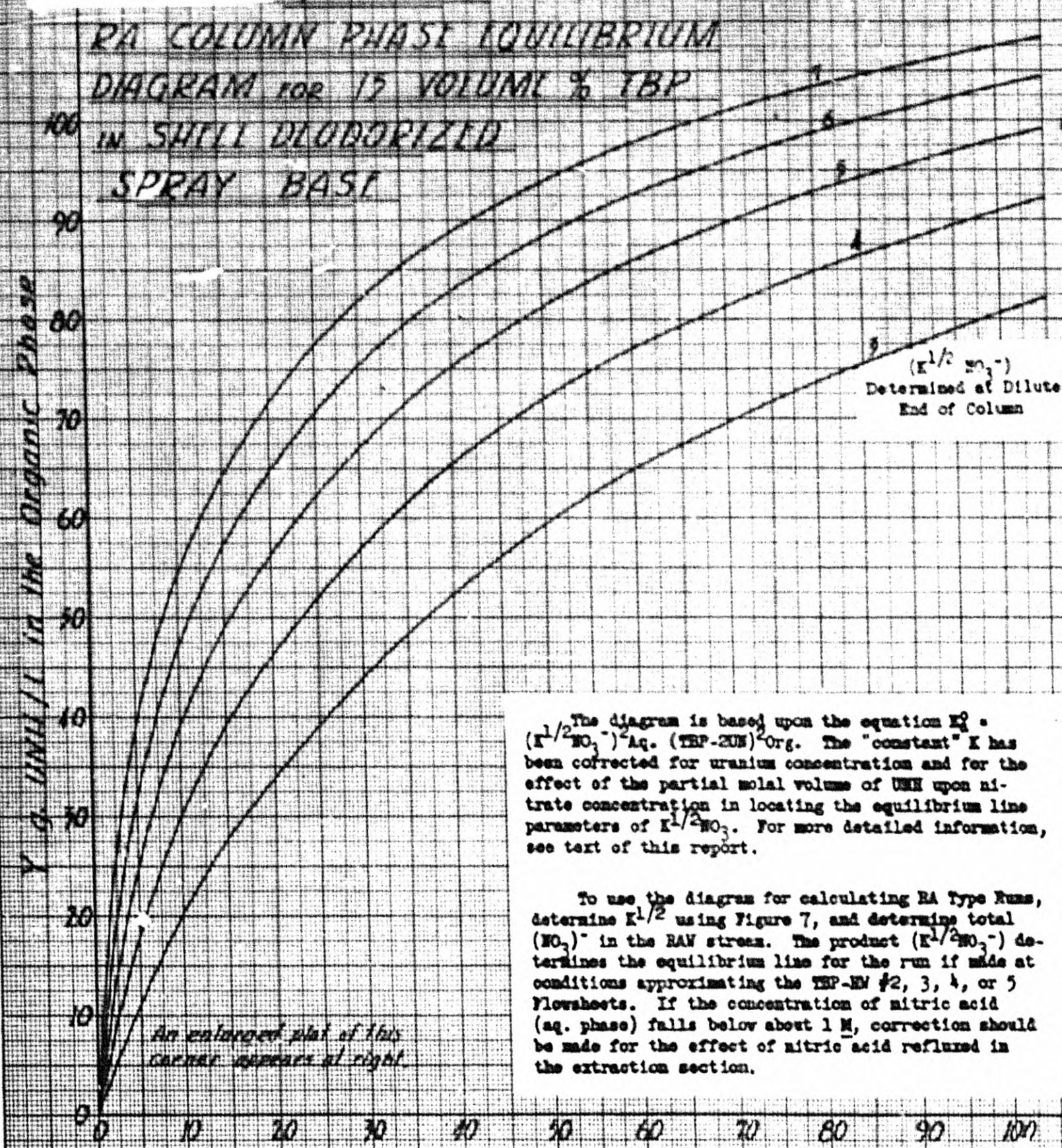


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Figure 10

RA COLUMN PHASE EQUILIBRIUM
DIAGRAM FOR 17 VOLUME % TBP
IN SULL DIBORATED
SPRAY BAST

Y g. UNH/l in the Organic Phase

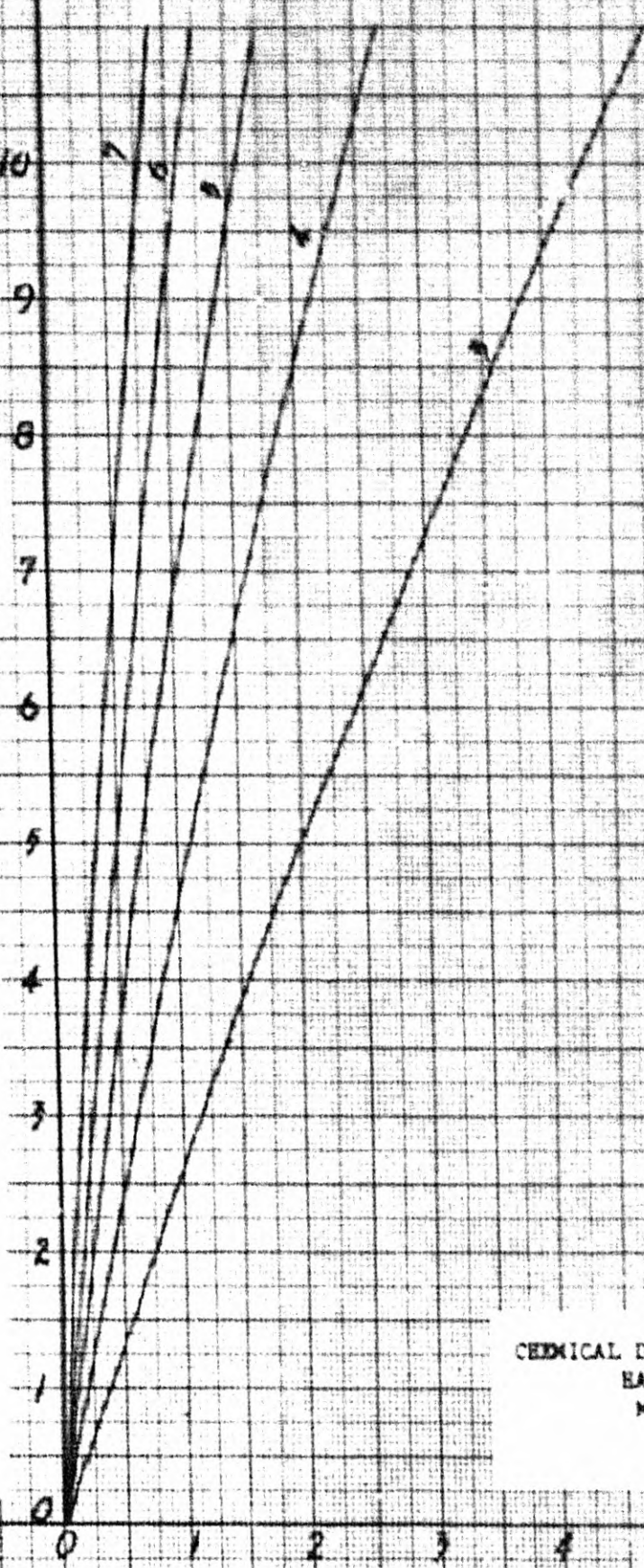


($K^{1/2} \text{NO}_3^-$)
Determined at Dilute
End of Column

The diagram is based upon the equation $K^{1/2} = \frac{(\text{K}^{1/2} \text{NO}_3^-)_{\text{Aq.}} (\text{TBP-2UH})_{\text{Org.}}}{(\text{NO}_3^-)_{\text{Aq.}}}$. The "constant" K has been corrected for uranium concentration and for the effect of the partial molal volume of UH₂ upon nitrate concentration in locating the equilibrium line parameters of $K^{1/2} \text{NO}_3^-$. For more detailed information, see text of this report.

To use the diagram for calculating RA Type Runs, determine $K^{1/2}$ using Figure 7, and determine total (NO_3^-) in the RAW stream. The product $(K^{1/2} \text{NO}_3^-)$ determines the equilibrium line for the run if made at conditions approximating the TBP-EV #2, 3, 4, or 5 Flowsheets. If the concentration of nitric acid (aq. phase) falls below about 1 M, correction should be made for the effect of nitric acid refluxed in the extraction section.

An enlarged plot of this corner appears at right



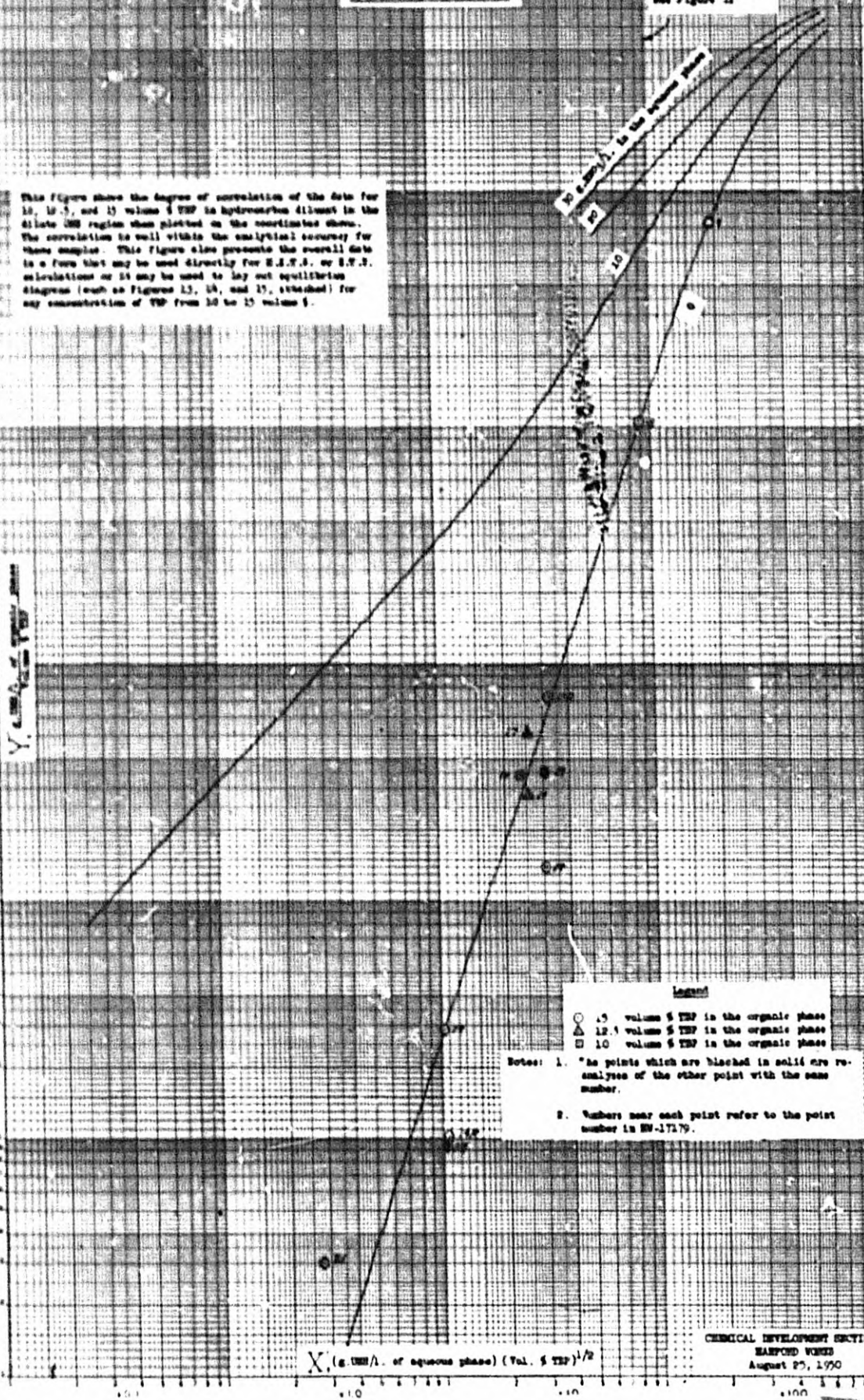
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X g. UNH/l in the Aqueous Phase

FIGURE 11
IN COLUMN EQUILIBRIUM DATA

For an enlarged
plot of this region
see Figure 12

This figure shows the degree of correlation of the data for 10, 12.5, and 15 volume % TBP in hydrocarbon diluent in the dilute (III) region when plotted on the coordinates shown. The correlation is well within the analytical accuracy for these samples. This figure also presents the overall data in a form that may be used directly for H.S.T.S. or S.T.S. calculations or it may be used to lay out equilibrium diagrams (such as Figures 13, 14, and 15, attached) for any concentration of TBP from 10 to 15 volume %.



Legend

- 15 volume % TBP in the organic phase
- △ 12.5 volume % TBP in the organic phase
- 10 volume % TBP in the organic phase

Notes: 1. "No points which are bisected in solid are re-analyses of the other point with the same number.
2. Numbers near each point refer to the point number in HW-17279.

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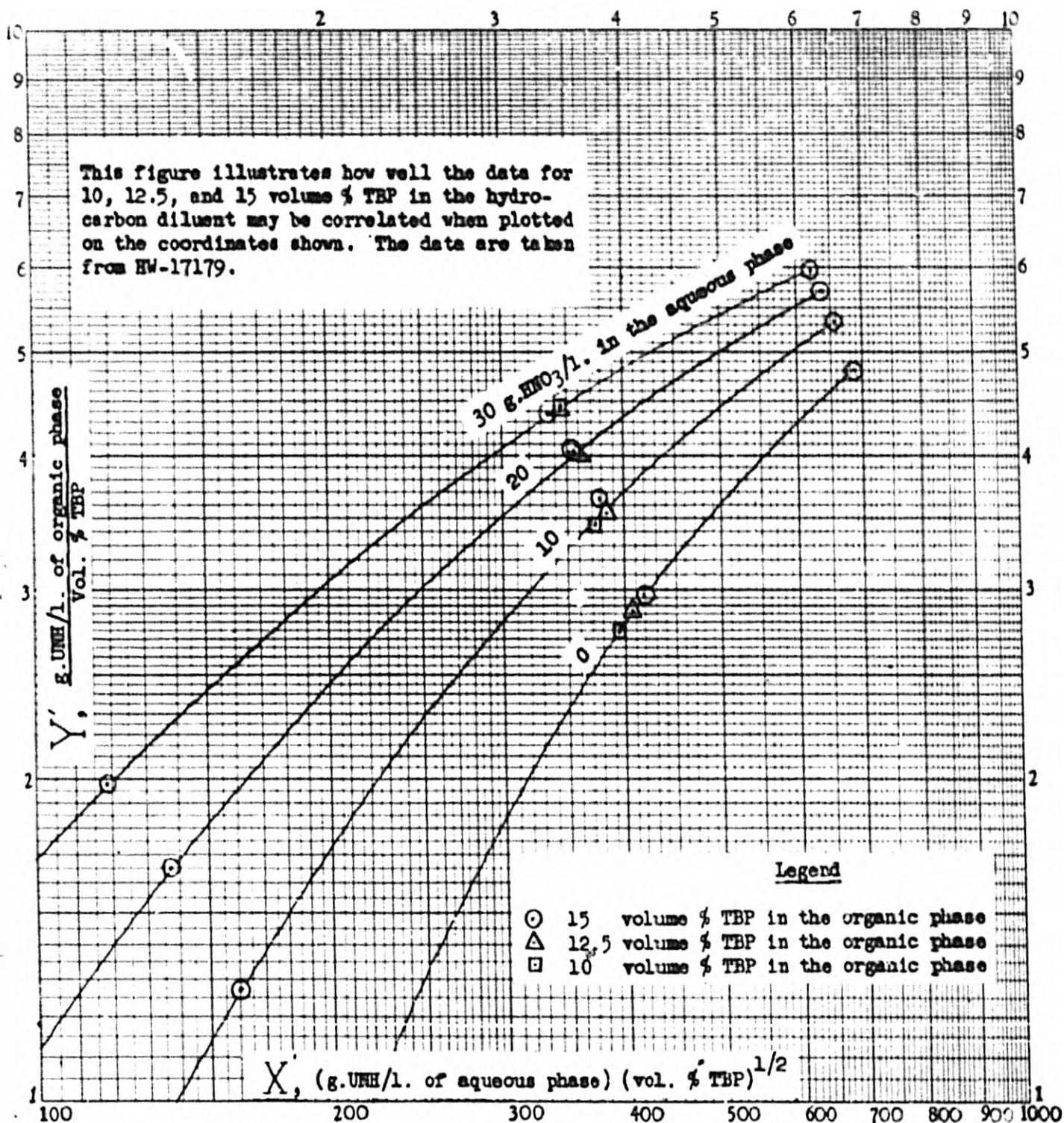
X, (g. TBP/l. of aqueous phase) (Vol. % TBP)^{1/2}

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FIGURE 12

RC COLUMN EQUILIBRIUM DATA
CONCENTRATED UNH REGION



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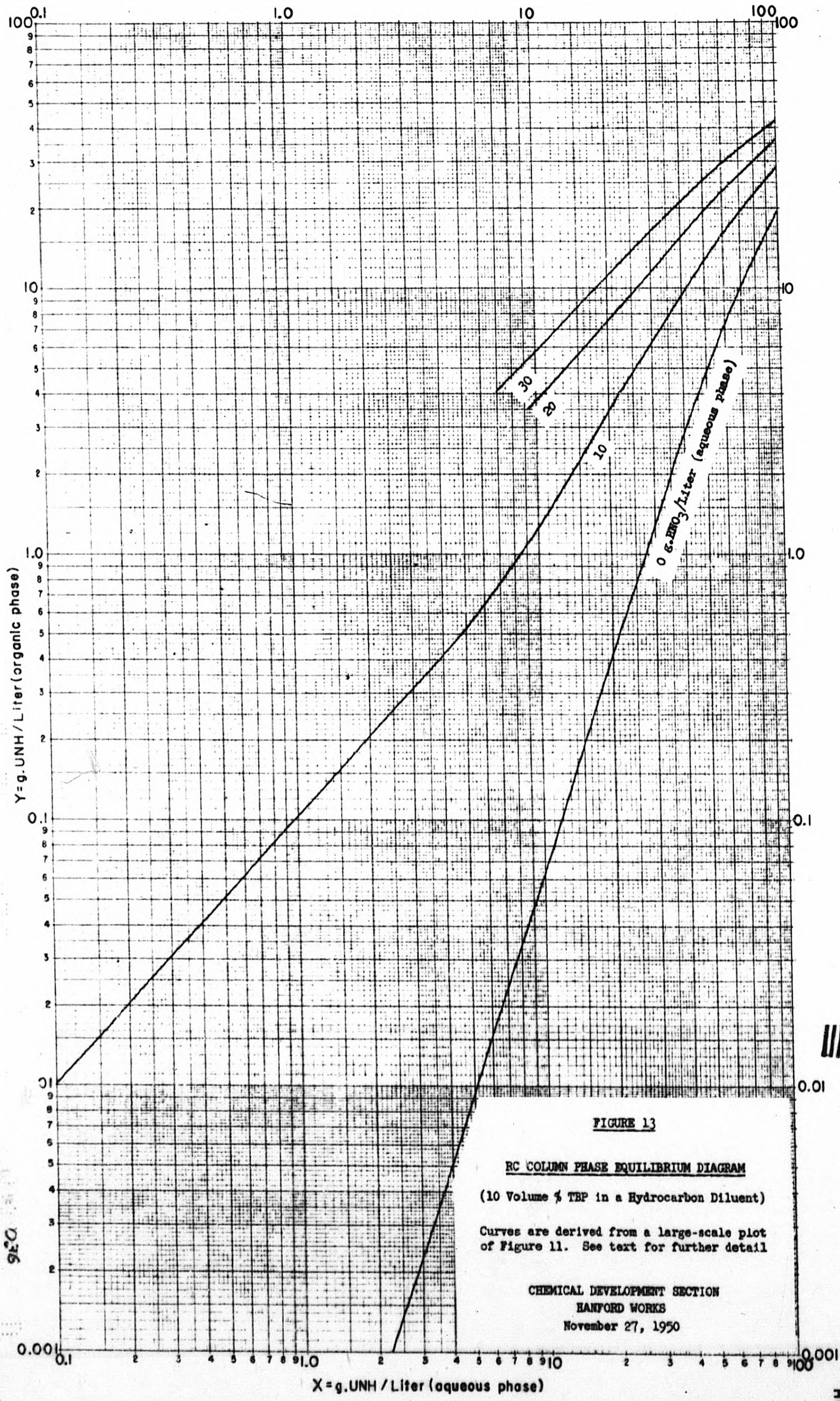


FIGURE 13

RC COLUMN PHASE EQUILIBRIUM DIAGRAM

(10 Volume % TBP in a Hydrocarbon Diluent)

Curves are derived from a large-scale plot of Figure 11. See text for further detail

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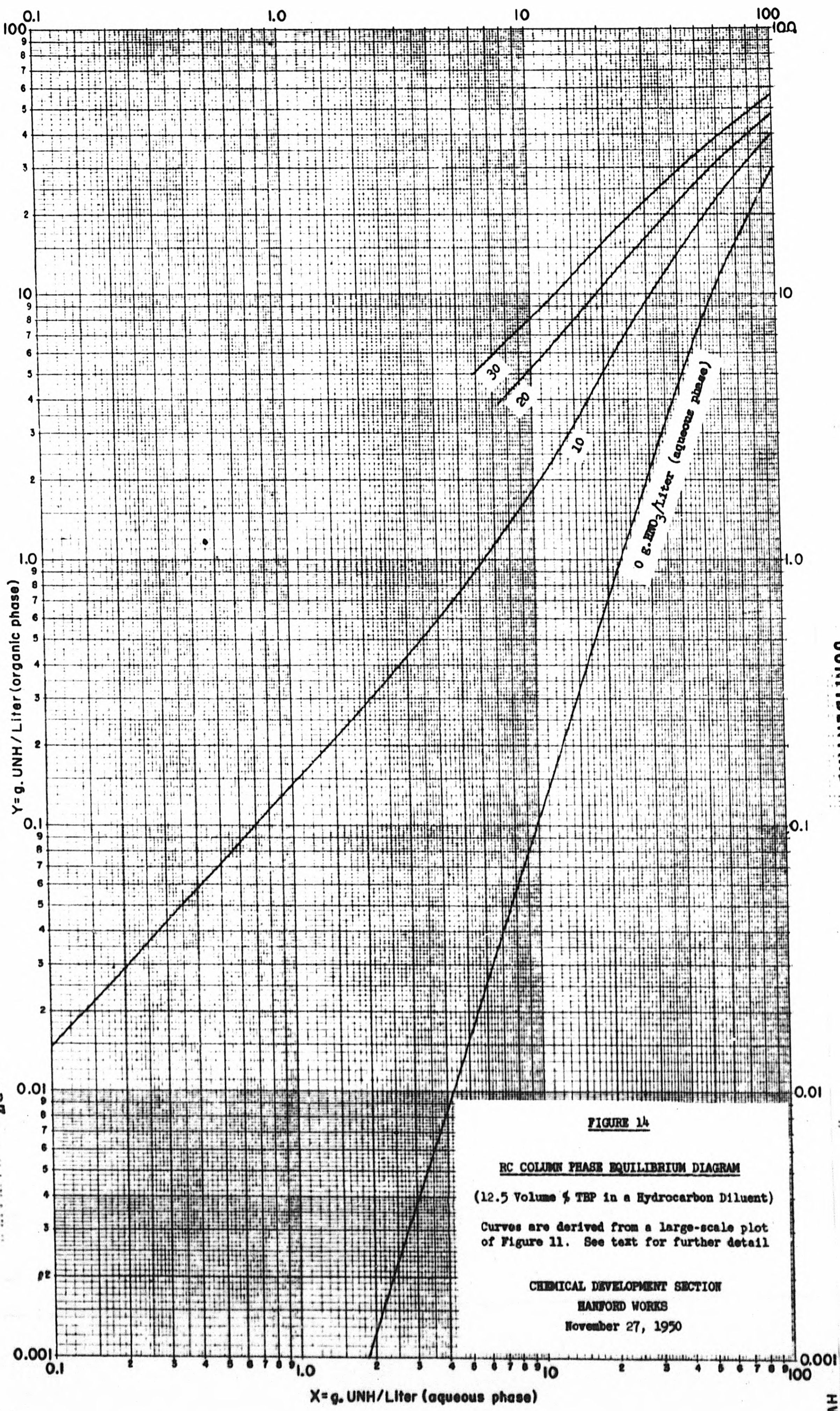


FIGURE 14

RC COLUMN PHASE EQUILIBRIUM DIAGRAM

(12.5 Volume % TBP in a Hydrocarbon Diluent)

Curves are derived from a large-scale plot of Figure 11. See text for further detail

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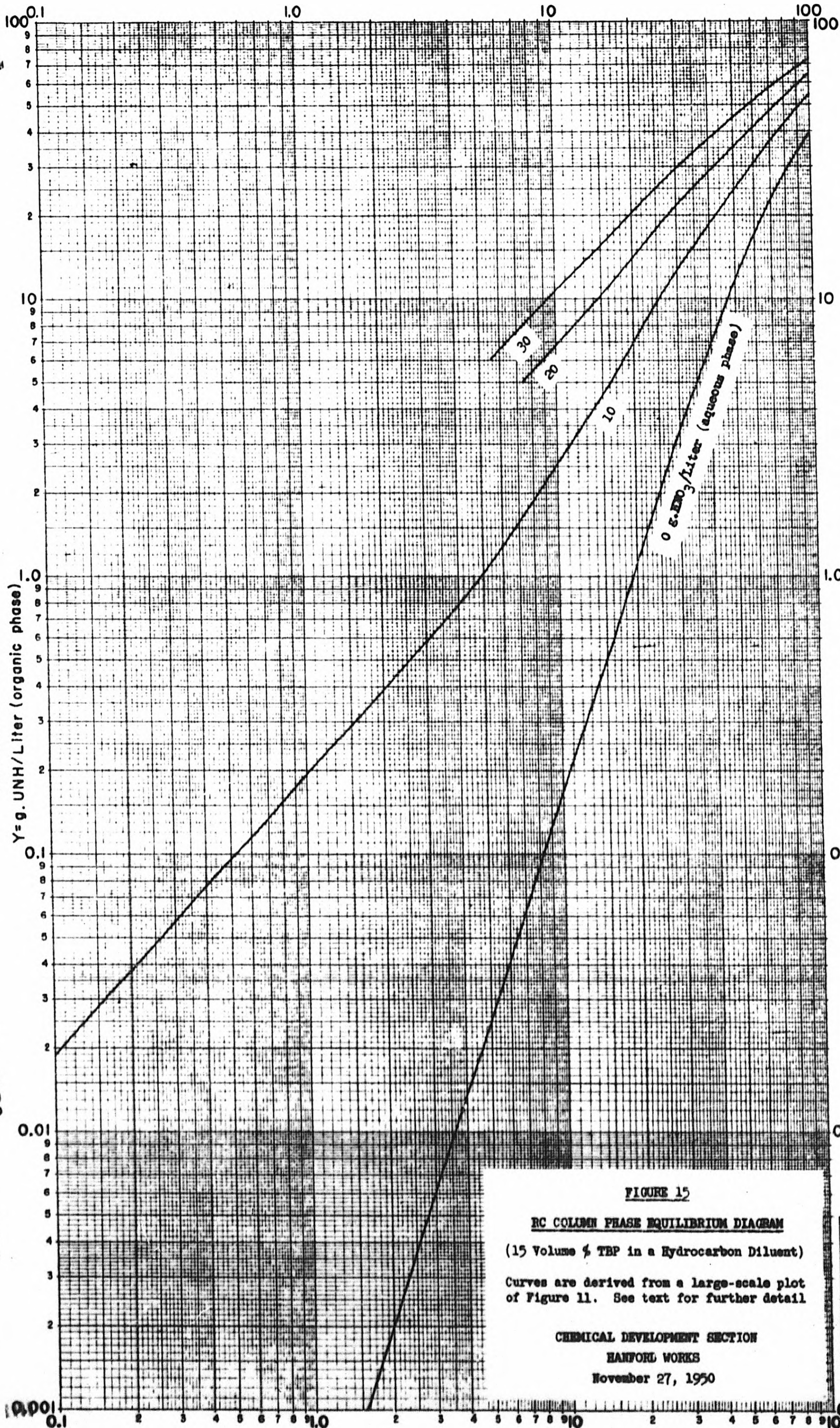
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FIGURE 15
RC COLUMN PHASE EQUILIBRIUM DIAGRAM
 (15 Volume % TBP in a Hydrocarbon Diluent)
 Curves are derived from a large-scale plot of Figure 11. See text for further detail
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END

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