THE SIMULTANEOUS TRANSFER OF URANYL NITRATE AND

NITRIC ACID ACROSS THE WATER-TRIBUTYL

PHOSPHATE INTERFACE

By

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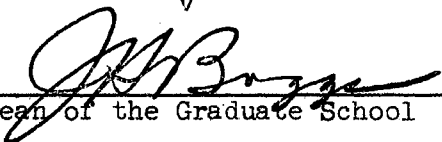for the degree of
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Thesis Approved:

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PREFACE

Although liquid-liquid extraction has been applied industrially for many years, fundamental studies of the actual mass transfer processes involved have been somewhat neglected until recent times.

Recently, Bush (5) made a fundamental study of the mass transport processes of uranyl nitrate transferring across the water-tributyl phosphate (TBP) interface. The purpose of this present work was to extend the work of Bush (5) to the case of simultaneous transfer of uranyl nitrate and nitric acid.

I wish to express my appreciation to Dr. John B. West for his advice and help throughout this study. Appreciation is also expressed to Mr. Dale Bush for sharing his invaluable experience and advice in performing the experimental work and to Mr. Eugene McCroskey for his help in securing needed materials. I thank my wife, Barbara, for her help, patience, and encouragement throughout this study. I also thank Barbara's and my parents for their support and instilling a desire to seek further knowledge.

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CHAPTER I

INTRODUCTION

"Liquid-liquid solvent extraction processes are currently the most widely used aqueous separation processes for reactor fuels." (27)[1]

One of the more common of the solvent extraction processes is the Purex Process. The Purex Process utilizes solvent extraction to separate and purify uranium and plutonium from dissolved, "spent" reactor fuels. A thirty-volume-percent solution of tributyl phosphate in kerosene is used as the solvent. For a salting agent, nitric acid is used. Because of the extractability of uranyl nitrate and the relative inextractability of fission products, a separation can be accomplished.

Several studies have been made of the fundamental transport properties involved in the Purex Process. Sato (22) studied the effects of nitric acid concentration, uranyl nitrate concentration, and temperature on the equilibrium distribution in order to determine optimum extraction conditions. He found that greater than ninety-seven percent extraction was obtained when solutions containing less than ten grams per liter of uranyl nitrate and six molar nitric acid were extracted with nineteen percent tributyl phosphate in kerosene at a temperature of less than twenty

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[1]Note: ( ) refers to Selected Bibliography.

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degrees Centigrade. McKay and Rees (16) investigated the rate of transfer of nitrates between water and tributyl phosphate in falling drops. They found molecular diffusion to be a quite significant factor. Murdock and Pratt (17) studied the extraction of uranyl nitrate in a wetted-wall column and found that transfer was partly diffusion controlled and partly dependent on interfacial resistance. The extraction of uranyl nitrate in packed columns was studied by Smith, Thornton, and Pratt (25), who found in this case that turbulent transfer had replaced molecular diffusion. They found no evidence of interfacial resistance. Hahn (12) investigated the mechanism of uranium extraction from tributyl phosphate. His was a strictly diffusion-controlled experiment. Lewis (14) observed the build up of an interfacial resistance in the uranyl nitrate system. He used a small stirred extraction cell in his study.

Of great interest to this study are the works of Burger (3) and Bush (5). Burger studied the transfer of uranyl nitrate and nitric acid across the tributyl phosphate-water interface using a small extraction cell. He investigated several variables including stirring rates, concentration of reactants and salting agents, and temperatures.

Bush studied the transfer of uranyl nitrate across the tributyl phosphate-water interface under both steady-state and unsteady-state conditions. The effects of stirring rate, driving force, and concentration level were studied by Bush. The results of Bush's and Burger's work are compared with the results of this work and discussed in greater detail in Chapter V.

Olander and Reddy (19) studied the effect of concentration driving force on the mass transfer coefficient of nitric acid transferring across

the tributyl phosphate-water interface. They found that transfer from the organic phase to the aqueous phase was unstable. The overall mass transfer coefficient increased by as much as a factor of four as the driving force was increased. In some systems, the overall mass transfer coefficient went through a maximum and then returned to a stable value as the driving force was increased.

The purpose of this work was to extend the work of Bush (5) to include the simultaneous transfer of nitric acid and uranyl nitrate across the water-tributyl phosphate interface.

In this study, mass transfer coefficients were determined for uranyl nitrate transferring in both directions across the water-tributyl phosphate interface while nitric acid was also transferring in the same direction. The runs were made under steady state conditions. Various concentration levels of uranyl nitrate and nitric acid were studied.

In general, the presence of nitric acid caused a decrease in the mass transfer coefficients of uranyl nitrate when transfer was from the organic phase into the aqueous phase. Transfer in the opposite direction was apparently not affected by the presence of nitric acid.

CHAPTER II

THEORY OF INTERPHASE MASS TRANSFER

In mass transfer work, the mass transfer coefficient defined
by

$$N_A = k \, \triangle c_A,$$ (1)

where: N_A = rate of transfer of component A (moles/sec-cm^2),

   k = mass transfer coefficient (cm/sec),

   $\triangle c_A$ = concentration difference (moles/liter),

is often utilized. $\triangle c_A$ is the concentration difference between the
beginning and the end of the diffusion path. The mass transfer coef-
ficient includes all of the other factors affecting mass transfer.
Various attempts have been made to interpret mass transfer coefficients.
The most common interpretations of mass transfer coefficients are those
derived from film theory, penetration theory, and surface renewal theory.

Film theory is the outgrowth of ideas presented by Lewis and Whitman
(15). Film theory is based on the assumption that molecular diffusion
through a laminar film is the basic mechanism of mass transfer. The
effect of turbulence is merely to reduce the film thickness. Thus,
the greater the turbulence, the shorter the diffusion path and, hence,
the greater the rate of mass transfer. Film theory predicts

$$k \propto \frac{D}{\delta}$$ (2)

where: D = Diffusion coefficient (cm^2/sec).

δ = Film thickness (cm).

Penetration theory, first presented by Higbie (12), assumes the transferring solute penetrates a stagnant liquid by molecular diffusion. If the time of exposure is short, the solute penetrates only a short distance and integration of Fick's second law yields

$$N_A = \sqrt{\frac{4D}{\pi\Theta}}\,\Delta c_A \tag{3}$$

where Θ = time (sec).

Danckwerts (7) extended penetration theory to apply to turbulent systems. He suggested that eddies were continually being swept to the surface where they remained for a short time while the solute penetrated the liquid. The eddies were then swept away and replaced by others. This theory is known as surface renewal theory. Surface renewal theory predicts

$$N_A = \sqrt{Ds}\,\Delta c_A \tag{4}$$

where   s = average fractional rate of production of new surface (sec^{-1}).

Often in liquid-liquid extraction processes a solute is transferred between two immiscible liquids. To interpret the process, the simultaneous diffusion of the solute in the two phases must be considered together with the equilibrium distribution of the solute in the two phases.

The concentration gradients that are present near the liquid-liquid interface are shown by Figure 1. In order for mass transfer to occur, there must be a concentration drop from the bulk of the raffinate, Phase A,
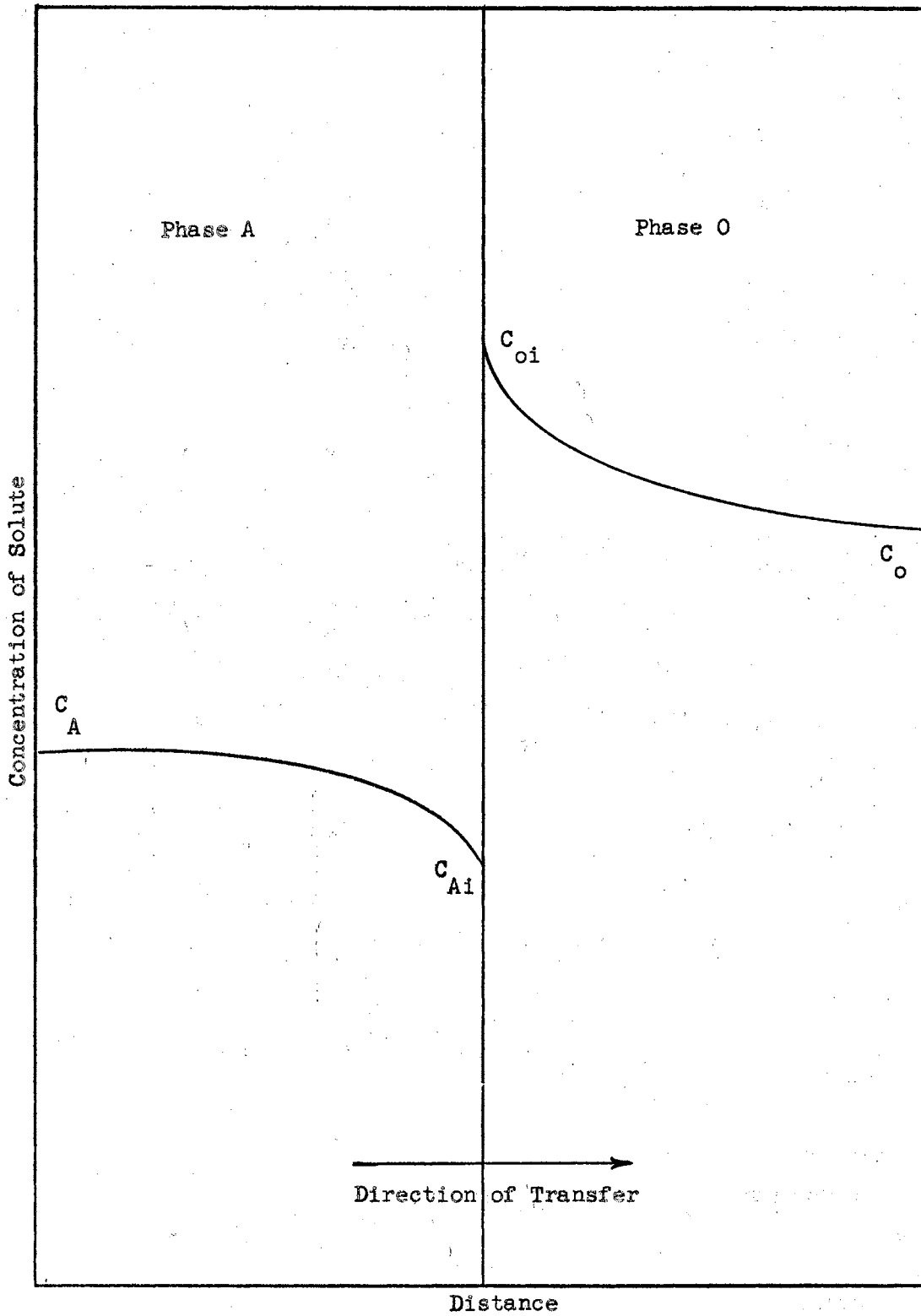
Figure 1. Concentration Gradients in Interphase Mass Transfer (28).

and a corresponding concentration drop in the extract, Phase O. However, it is possible for C_O to be greater than C_A and still have transfer occur, if C_O represents a lower chemical potential than C_A.

In a two phase system, $(C_A - C_O)$ does not represent the driving force of Equation (1) for transfer between the two phases. Therefore, Equation (1) cannot be applied directly to the two phase system. However, the rate equation can be written for each phase.

$$N_A = k_A(C_A - C_{Ai}) \tag{5}$$

$$N_A = k_o(C_{oi} - C_o) \tag{6}$$

Obviously, it is not possible to measure C_{Ai} and C_{oi}. Whitman (30) overcame this problem by proposing that C_{Ai} and C_{oi} were in equilibrium and that resistances to mass transfer between the phases were additive. The assumption of equilibrium conditions at the interface implies that there is no resistance to mass transfer at the interface. This is the so called two-resistance theory which is not only applicable to film theory but to penetration theory and surface renewal theory as well. The significance of this theory can be shown by referring to Figure 2.

Point B represents the bulk phase concentration and I represents the corresponding equilibrium concentration.

If steady-state conditions exist, Equations (5) and (6) are equal and can be rearranged to yield

$$\frac{\triangle C_o}{\triangle C_A} = \frac{C_{oi} - C_o}{C_{AI} - C_A} = -\frac{k_A}{k_o} \tag{7}$$
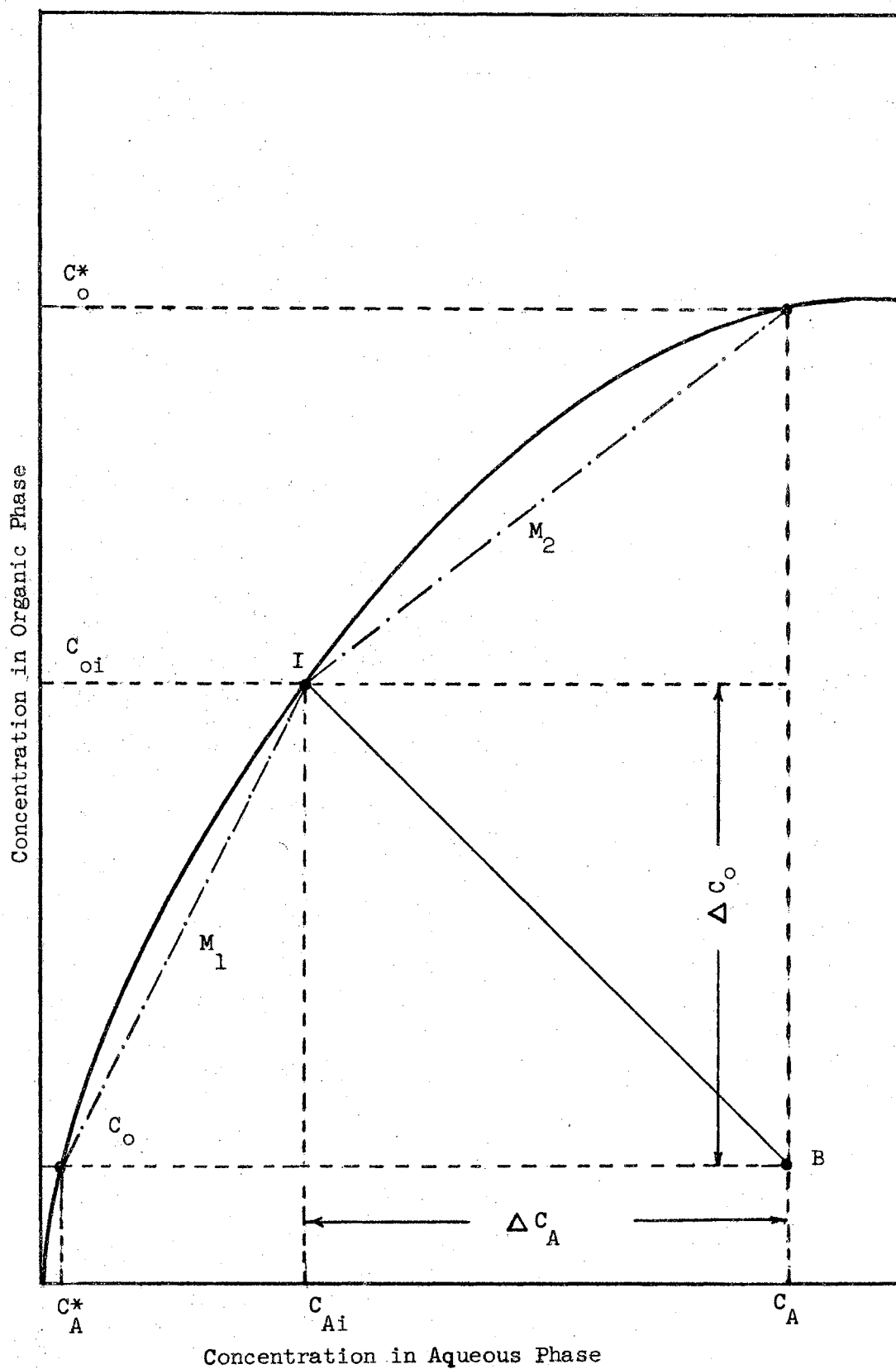
Figure 2. Equilibrium Distribution Curve (28).

It is readily seen that the slope of the line $\overline{IB}$ is equal to $-\dfrac{k_A}{k_O}$.

If the distribution of the solute between the two phases is known, C_O^* can be used as a measure of C_O. Therefore, the rate equation for transfer between the two phases can be written in the form

$$N_A = K_O(C_O^* - C_O) \tag{8}$$

or

$$N_A = K_A(C_A - C_A^*). \tag{9}$$

K_O and K_A are called overall mass transfer coefficients.

From Figure 2 it can be seen that

$$C_O^* - C_O = \Delta C_O + m_2 \Delta C_A \tag{10}$$

or

$$\frac{N_A}{K_O} = \frac{N_A}{k_O} + \frac{m_2 N_A}{k_A} . \tag{11}$$

Therefore,

$$\frac{1}{K_O} = \frac{1}{k_O} + \frac{m_2}{k_A} . \tag{12}$$

Similarly

$$\frac{1}{K_A} = \frac{1}{k_A} + \frac{1}{m_A k_O} . \tag{13}$$

Equations (12) and (13) represent the principle of additivity of resistances.

Gordon and Sherwood (11) in a study using a stirred transfer cell confirmed the additivity of resistances and indirectly the existence of equilibrium at the interface. However, the existence of equilibrium at the interface has been questioned by several workers (8, 24, 29, 30) who have reported a resistance to mass transfer at the interface. Davies (8) encountered interfacial resistance in the water-nitrobenzene system while studying the passage of salts through a plasma membrane. Interfacial resistance was encountered by Sinfelt and Drickamer (24) in their diffusion studies of molecular sulfur crossing a liquid-liquid interface. Tung and Drickamer (29) found resistance in the interface to be quite significant compared with the resistance to ordinary diffusion in the SO_2-n-heptane system. They also studied the phenol-sulfuric acid-water system and found a significant interfacial resistance. They concluded that resistance to motion in the interface must be important in many, if not all, partially miscible systems and that it was certainly not safe to assume equilibrium at the interface for such systems. They felt that with polar molecules, a high degree of orientation was necessary in order to pass through the interface. On the other hand, Ward and Brooks (30) found no interfacial resistance when they used the Lamm scale method to study the diffusion of carboxylic acid across the water-toulene interface. However, they stated that their type of experiment would not detect a barrier at the interface unless it was very high.

Treybal (28) points out several factors that Equations (12) and (13) do not consider, yet which cannot be neglected. Among the factors mentioned by Treybal (28) are temperature changes at the interface, interfacial resistance due to absorbed trace substances, interfacial turbulence, and

chemical reactions.

Temperature changes at the interface are due to the solute having different heats of solution in the two phases or due to the heat of reaction of a chemical reaction at the interface. Treybal (28) mentions that heat effects are usually small but refers to the study of Searle and Gordon (23) where it was estimated that there was an eleven degree Centigrade temperature rise when acetic acid was transferred from isobutanol to water containing sodium hydroxide.

Treybal (28) points out that trace substances adsorbed at the interface may affect the rate of mass transfer by blocking the interface, reducing surface motion and interaction with the solute. Lewis (14) reported that rigid protein films caused a retardation of transfer, probably due to damping of interfacial turbulence. Burger (3) reported surface active agents reduced the rate of transfer and attributed it to mechanical blocking of the interface.

Interfacial turbulence is usually attributed to concentration gradients along the surface of the interface. This phenomenon, usually attributed to the Marangoni effect , has been studied extensively by Sternling and Scriven (26). Their theory stated that the origin of the interfacial turbulence is the local variation of interfacial tension with solute composition. Treybal (28) suggests that interfacial turbulence may be promoted by the following conditions.

1. Transfer of a solute out of a liquid of higher viscosity.

2. Transfer of solute out of the liquid in which its diffusivity is lower.

3. Large differences in the kinematic viscosity
   and the diffusivity for the two liquids.

4. Large concentration gradients near the interface.

5. Low viscosities and diffusivities in both
   phases.

6. Strong variation of surface tension with con-
   centration.

7. Absence of surface active agents that increase
   surface viscosity.

8. Highly dispersed systems with large surface
   area.

Olander and Benedict (18) in studying the extraction of nitric acid
with tributyl phosphate observed that the transfer process was greatly
accelerated by interfacial turbulence at high acid levels and attributed
it to the Marangoni effect.

In some systems, the transferring component may undergo a chemical
reaction at the interface. If the reaction is slow, it may be the con-
trolling factor in the mass transfer process. In some cases, the re-
action may simply be a dimerization or solvation.

To account for all of the above mentioned added resistances, ad-
ditional terms are usually added to Equations (12) and (13). However, the
assumption of additivity of resistances has recently been challenged by
Abrazon and Ostrovskii (1). They reviewed much of the literature and
pointed out that much of the experimental data contradicts the assumption
that resistances are additive. They concluded that the rate of the
overall process is determined by only one stage, the slowest stage, which

corresponds to the highest energy barrier.

It is obvious from the foregoing discussion that the theory of interphase mass transfer is not complete and that many questions are yet to be answered.

CHAPTER III

EXPERIMENTAL APPARATUS

The experimental apparatus for this work consisted of a small
stirred extraction cell and its flow lines, and temperature control
equipment (See Figures 3 and 4 and Plates I and II). Auxiliary
equipment consisted of a Beckman DU Spectrophotometer and a Beckman
Expanded Scale pH meter.

The stirred extraction cell, shown in Plate II and Figure 4, was
patterned after those used by Lewis (14) and Burger (3). The cell was
the identical cell that was used by Bush (5). The cell was constructed
of heavy wall glass tubing and was four inches high and had an internal
diameter of two and one-eighth inches. The top and bottom plates were
machined from one-fourth inch stainless steel. The plates were fitted
with Swagelok fittings for holding the flow lines. The transfer area
was formed by a baffle ring and a center baffle both made of teflon.
The annulus thus formed had an inner diameter of three-fourths inches
and an outer diameter of one and one-eighth inches. The interface was
maintained in the center of the annulus by raising or lowering the lower
phase outlet tube. To prevent swirling, the cell was baffled by three one-
fourth inch teflon rods. The two phases were stirred by paddle stirrers.
The rectangular paddles were made from thin stainless steel sheets and
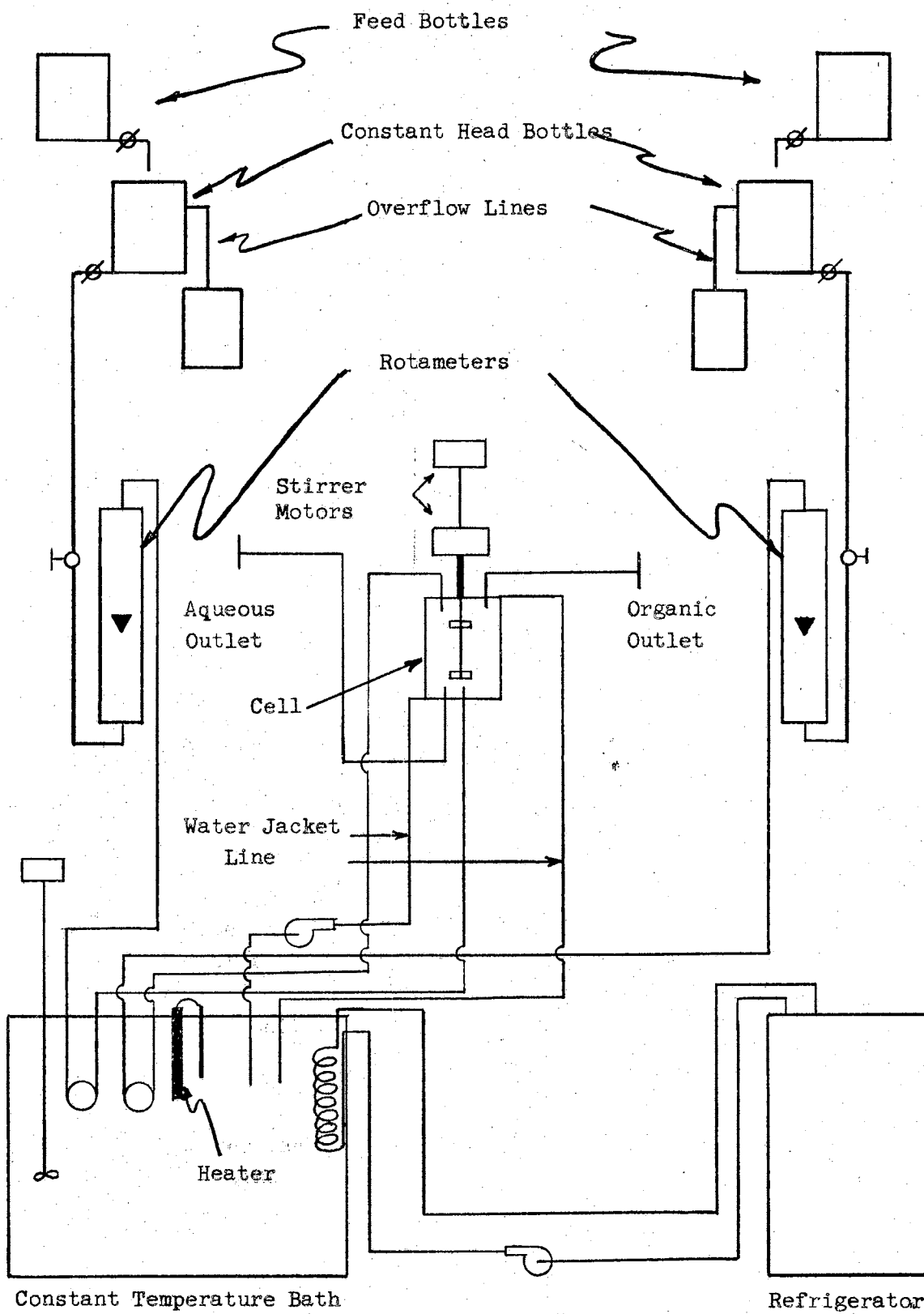had a length of one and one-eighth inches and a height of five-sixteenths

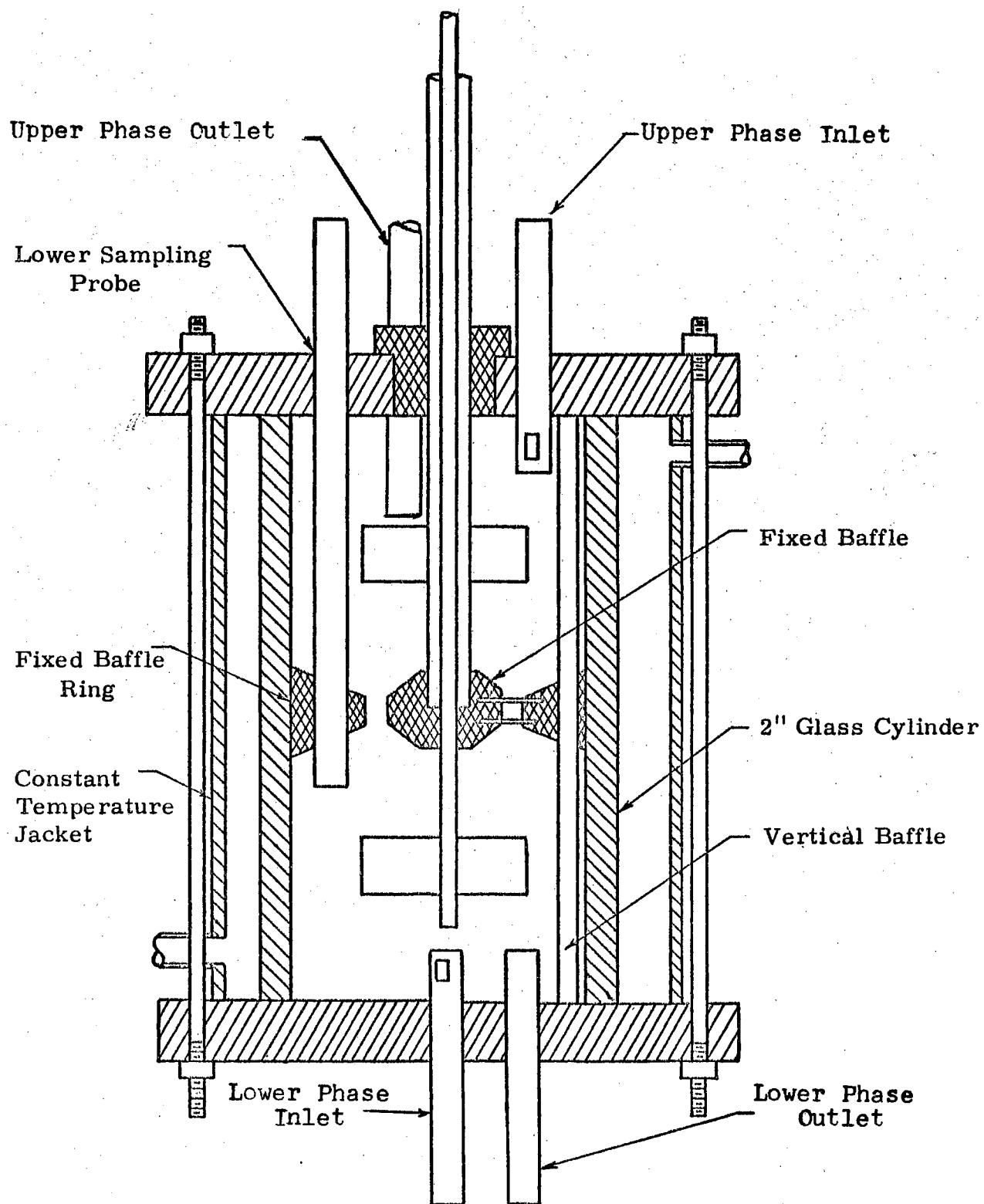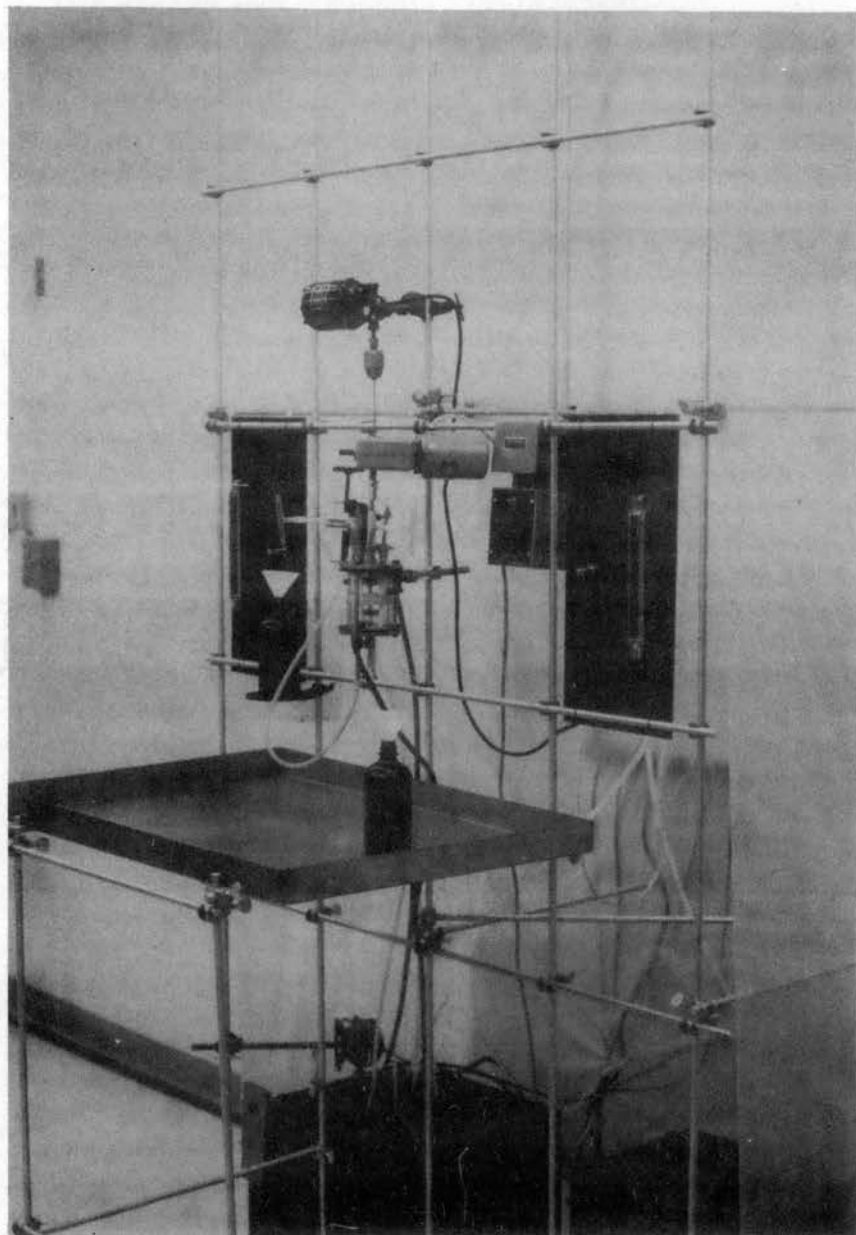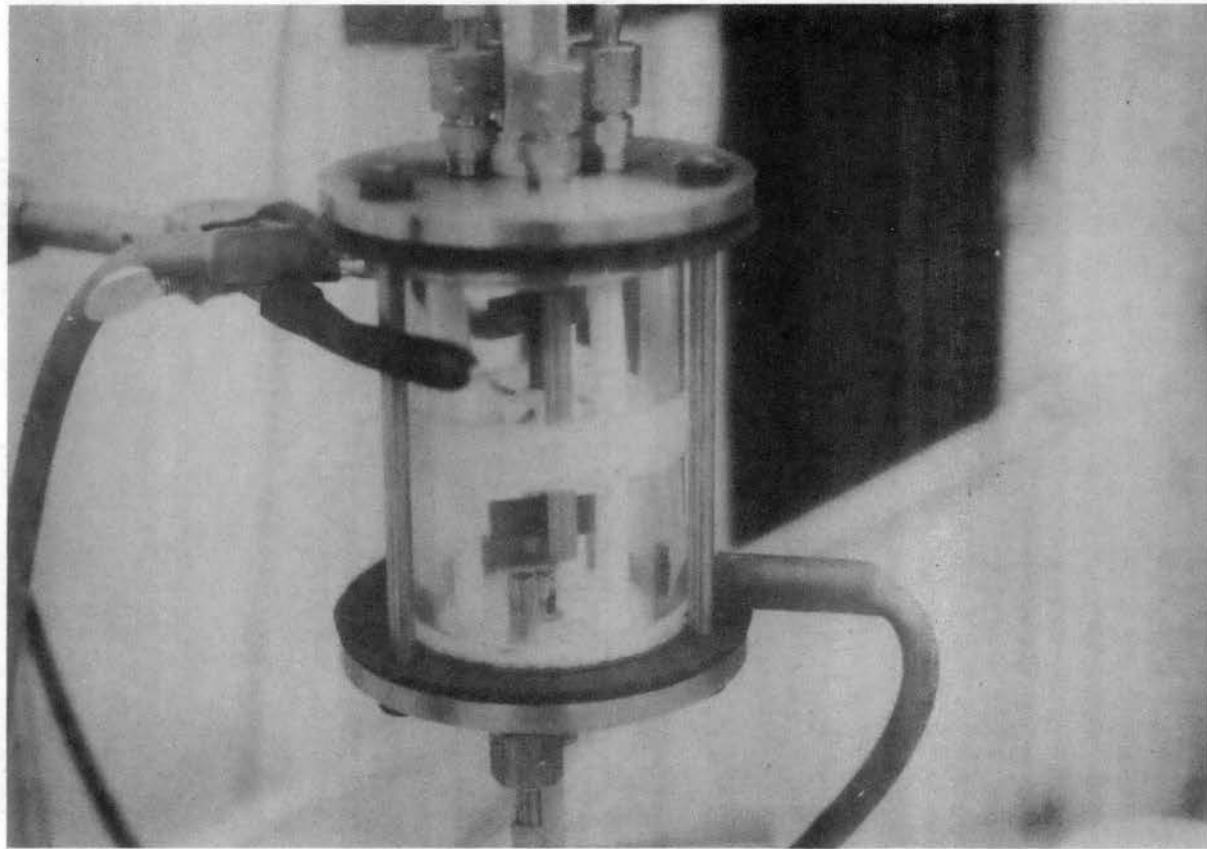Figure 3. Schematic Design of Extraction Cell and Auxiliaries.

Figure 4. Stirred Extraction Cell Schematic.

PLATE I

Extraction Equipment

PLATE II

Stirred Extraction Cell

inches. The upper stirrer was driven by a LaPine variable speed hollow shaft cone drive while the lower stirrer was driven by a G. K. Heller electronic controlled motor. The cell was surrounded by a water jacket for temperature control.

All flow lines were constructed of polyethylene tubing. One-fourth inch Ideal needle valves were used to control the flow rates. Matheson rotameters were used to indicate flow rates.

The temperature control equipment consisted basically of a constant temperature water bath and a refrigeration unit. The constant water bath was made by inserting a glass cylinder, twelve inches in diameter, into a wooden box and surrounding the cylinder with cork insulation. The water was cooled by a copper coil through which fifteen degree Centigrade water from the refrigeration unit was pumped by an Eastman, Model 100 centrifugual pump. The refrigeration unit was a Laird Engineering Company refrigeration unit. The water bath was maintained at $25 \pm 0.3^{\circ}$ C. by a Cutler-Hammer five-hundred-watt immersion heater and a Fenwal adjustable controller. The water from the constant temperature bath was circulated through the water jacket of the cell by a small centrifugal pump. Prior to entering the cell the feed solutions were circulated through the water bath through stainless steel coils.

For the analytical work a Beckman DU Spectrophotometer was used. Also, a Beckman Expanded Scale, Model 76, pH meter was utilized.

CHAPTER IV

EXPERIMENTAL PROCEDURES

All of the runs were made under steady state conditions. The following procedure was used. The temperature bath was turned on and allowed to obtain the desired temperature. The feed bottles were filled and their stopcocks opened so that the solutions could flow into the constant head bottles. The aqueous phase valves were opened, and the lower half of the cell was filled. The upper half of the cell was then filled in a similar manner with the organic phase. While the cell was being filled, the height of the interface was controlled by raising or lowering the height of the aqueous phase outlet line. After filling the cell, the stirrers were turned on. The speeds of both stirrers were adjusted to one hundred revolutions per minute by counting the revolutions and timing them with a stop watch. The approximate flow rates were adjusted to the desired rate of one and one-half milliliters per minute by referring to the rotatmeter. The flow rates were then determined accurately by using a stop watch to obtain the time necessary for filling a ten milliliter volumetric flask. The flow rates were checked at regular intervals throughout the duration of the run and readjusted if necessary. After about three hours, samples of the extracting stream were analyzed for uranium concentration every fifteen minutes. When there was no concentration change over a forty-five minute period, it was assumed that steady state had been reached.

Samples were then taken of each stream and the flow rates measured. The

equipment was turned off and the samples analyzed for both uranium and

nitric acid.

Commercial grade tributyl phosphate purchased from Commercial Solvents

Corporation was used. The tributyl phosphate was purified in a manner

similar to that of Alcock (2). One liter of tributyl phosphate was boiled

with one-half liter of five tenths molar sodium hydroxide under total

reflux for a period of ten hours. The mixture was then boiled for one

hour without reflux. The tributyl phosphate and sodium hydroxide were then

separated using a separatory funnel. The tributyl phosphate was then washed

several times with distilled water until the wash solution was neutral

to litmus paper.

Amsco Odorless Mineral Spirits (W-7), purchased from Missouri Solvents

and Chemical Company, was used as a diluent. When the thirty-volume-percent

tributyl phosphate solution in Amsco was prepared an emulsion resulted.

The emulsion was broken by filtering or by allowing the mixture to stand

overnight.

Uranyl nitrate solutions were prepared from A.C.S. reagent grade

uranyl nitrate purchased from General Chemical Division of Allied Chemical

Company.

In searching for a method for determining the uranium concentration,

two criteria had to be met. The method had to work in the presence of

nitric acid and be relatively rapid in order that periodic analyses might

be made during the duration of a run so that the steady state condition

might be determined. The method chosen was a modification of the colori-

metric method described by Dizdar and Obrennovic (9). This method utilizes

the fact that uranyl and ferrocyanide ions form a colored complex in the
pH range of three to six. P-nitrophenol was used as an internal indicator
in adjusting the pH. With very careful work it was found that this method
was reproducible to within less than one percent. The complete analytical
procedure is presented in Appendix C.

For analyzing nitric acid in the presence of uranium, the method
reported by Rodden (21) was utilized. This method utilizes the following
reaction.

$$UO_2(NO_3)_2 + H_2O_2 = UO_2 + 2HNO_3$$
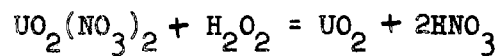
In the pH range of two to five, the above reaction is quantitative.
The sample was reacted with hydrogen peroxide and the resulting mixture
titrated to a pH of 4.5 with sodium hydroxide. The sample was then ana-
lyzed for uranyl nitrate using the previously described method. Since
the amount of uranyl nitrate in the sample was then known, the amount of
free nitric acid was then calculated from the stoichiometry of the reaction
of hydrogen peroxide and uranyl nitrate and the amount of sodium hydroxide
used in the titration. The complete analytical procedure is presented
in Appendix D.

CHAPTER V

PRESENTATION AND DISCUSSION OF RESULTS

In order to become familiar with the cell characteristics and compare results with those of Olander and Reddy (19), the first run was made transferring only nitric acid. The transfer was from thirty-volume-percent tributyl phosphate in Amsco into water. A mass transfer coefficient of 2.92 centimeters per hour was obtained. For a similar concentration driving force, Olander obtained a value of approximately 3.0 centimeters per hour for nitric acid transferring from eighty-five percent tributyl phosphate in hexane into water. No interfacial turbulence was noticed in this experiment.

In choosing the concentration ranges to be studied, it was attempted to choose those concentrations that would be of interest in the Purex Process.

The first series of runs was made by simultaneously transferring uranyl nitrate and nitric acid from thirty-volume-percent-tributyl phosphate in Amsco into water. The runs were made at two uranyl nitrate concentrations (approximately 0.1 and 0.25 molar) and four nitric acid concentrations (approximately 0.1, 0.2, 0.3, and 0.4 molar).

The equilibrium data of Codding, Haas, and Heumann (6) were used for calculating the overall mass transfer coefficients.

When the mass transfer coefficients were calculated and plotted as a function of driving force and compared to those obtained by Bush (5) in the nitric acid free system (See Figure 5), it was seen that the presence of nitric acid significantly reduced the mass transfer coefficients of uranyl nitrate.

Burger (3) reported that transfer from the organic phase to the aqueous phase was diffusion-controlled, where diffusion refers to both molecular and eddy diffusion. Bush concluded that the mass transfer coefficient was dependent only on convective diffusion rather than simple molecular diffusion for the nitric-acid-free system. The reduction in the mass transfer coefficient, caused by the presence of nitric acid, could be explained by either a significant change in the hydrodynamics of the cell, i.e., a change in the viscosity and density so as to produce a smaller Reynolds Number, or a significant reduction in the diffusion coefficient of the uranyl nitrate-tributyl phosphate complex in the presence of nitric acid.

In order for the Reynolds Number to decrease, it would be necessary for the density to decrease or the viscosity to increase, or both. Burger (4) studied the effect of nitric acid on the viscosity of a similar system. In his study, Deobase rather than Amsco was used as the diluent. Deobase and Amsco have viscosities at 25 degrees Centigrade of 17.3 and 14.3 millipoises respectively. Burger found that the effect of nitric acid on the density and especially on the viscosity much smaller than the effect of uranyl nitrate. Saturating the tributyl phosphate-Deobase mixture with nitric acid only raised the viscosity from 18.3 to 18.7 millipoises. It was therefore concluded that the Reynolds Number changed very little with
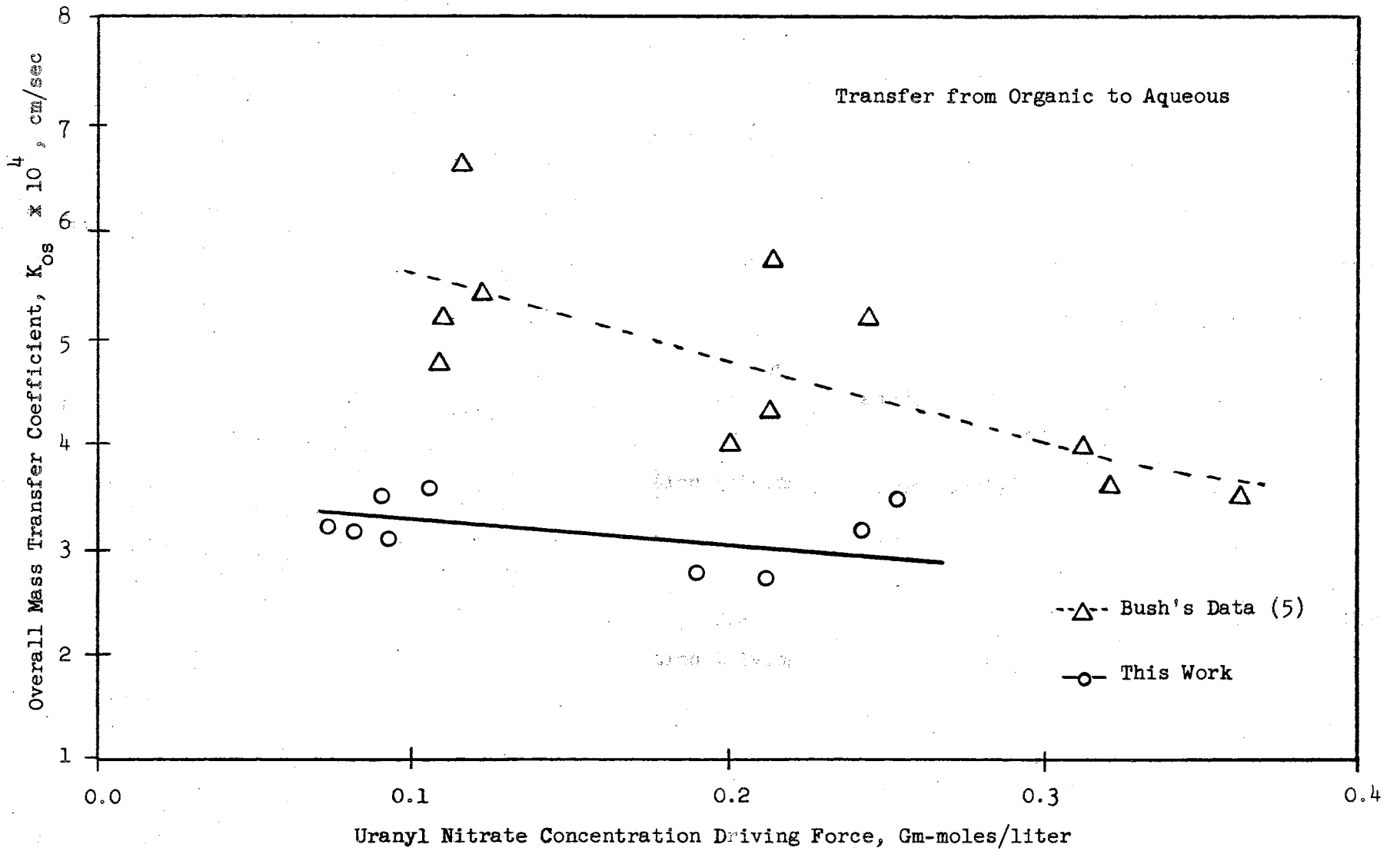
Figure 5. Mass Transfer Coefficients as a Function of Driving Force.

the addition of nitric acid to the system. If the Reynolds Number changed, it would become larger since the density effect is apparently larger than the viscosity effect.

The reduced mass transfer coefficients could be explained by a large reduction of the diffusion coefficient of the tributyl phosphate-uranyl nitrate complex when it diffuses in the presence of nitric acid. If the molecular diffusion coefficient were sufficiently lowered, molecular diffusion could become significant when compared with convective diffusion, which was found to be the controlling factor in Bush's work. Insufficient diffusion data were available to fully evaluate this possibility. Finley (10) noted that the presence of nitric acid significantly lowered the diffusion coefficient of uranyl nitrate diffusing into water. The diffusion coefficient was lowered by as much as fifty percent when uranyl nitrate diffused into two molar nitric acid. If nitric acid also lowers the diffusion coefficient of the uranyl nitrate-tributyl phosphate complex, it would adequately account for the decrease of the mass transfer coefficients. Perhaps the presence of nitric acid promotes polymerization or the formation of a larger complex and the diffusion coefficient decreases according to the Riecke-Grahm Law.

As can be seen by Figure 6, the effect of nitric acid concentration was rather insignificant. Apparently the reduction of the mass transfer coefficients was due simply to the presence of nitric acid and not dependent on the nitric acid concentration.

Although the data were not as scattered as much as Bush's, there was still considerable scattering of the data. Since tributyl phosphate is subject to decomposition, part of the scattering was attributed to
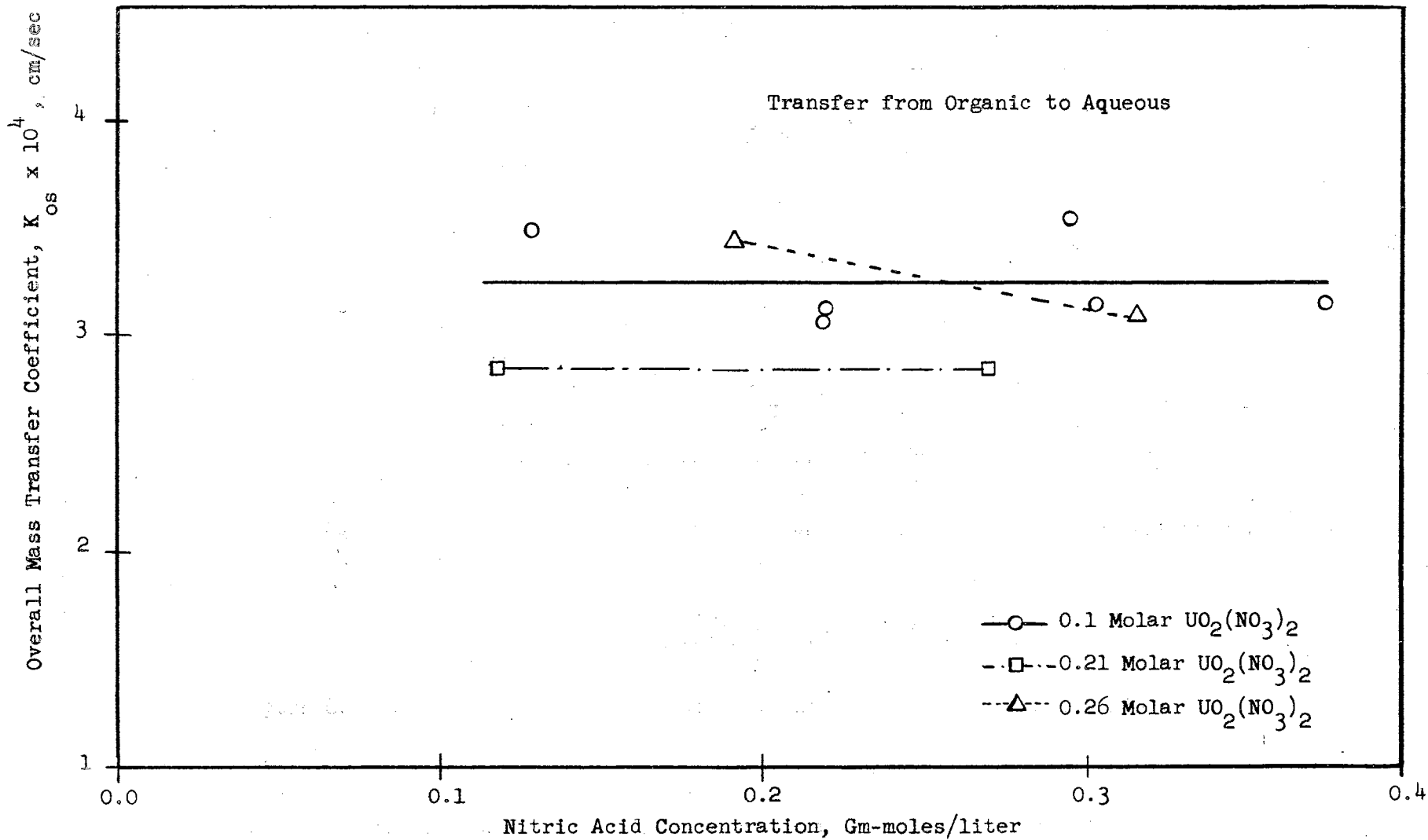
Figure 6. Mass Transfer Coefficients as a Function of Nitric Acid Concentration.

differences in the tributyl phosphate solutions. Sufficient tributyl phosphate for three runs was usually prepared at one time. By the time the last two runs were completed, sometimes several days had elapsed and some decomposition of the tributyl phosphate could have occurred. Undoubtedly, there were small differences between solutions prepared at different times.

It was attempted to keep the overall mass balances within one percent agreement. This goal was achieved in most runs. In runs where it was not, the mass transfer coefficient was based on the extracting stream, since calculating molar fluxes did not involve taking differences between the concentrations of the feed stream and the raffinate stream.

The final series of runs involved transfer from the aqueous phase to the organic phase. The runs were made at two uranyl nitrate concentrations (approximately 1.0 and 1.5 molar) and two nitric acid concentrations (approximately 1.0 and 3.0 molar). Apparently, the nitric acid did not cause a decrease in the mass transfer coefficients as was the case for transfer in the opposite direction. As can be seen in Figure 7, the data from this work correlates quite well with that of Bush's.

The chemical reactions involved in the process are

$$H^+_{aq} + NO^-_{3aq} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP$$

and

$$UO^{++}_{2aq} + 2NO^-_{3aq} + 2TBP_{org} \rightleftharpoons UO_2(NO_3)_2 \cdot TBP$$
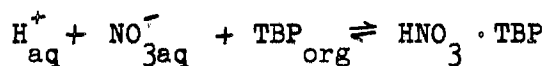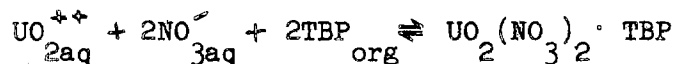
Figure 7.   Mass Transfer Coefficients as a Function of Driving Force.

In the case of transfer from the organic phase to the aqueous
phase, the nitric acid and uranyl nitrate simply free the tributyl phos-
phate at the interface and then dissociate in the aqueous phase. Al-
though the possibility must be considered that this reaction might be
rate controlling, Burger's (3) work indicated otherwise. He found that
transfer from the organic phase to the aqueous phase was probably controlled
by molecular and eddy diffusion of the complexed uranyl nitrate.

When transfer is in the opposite direction, aqueous phase to organic
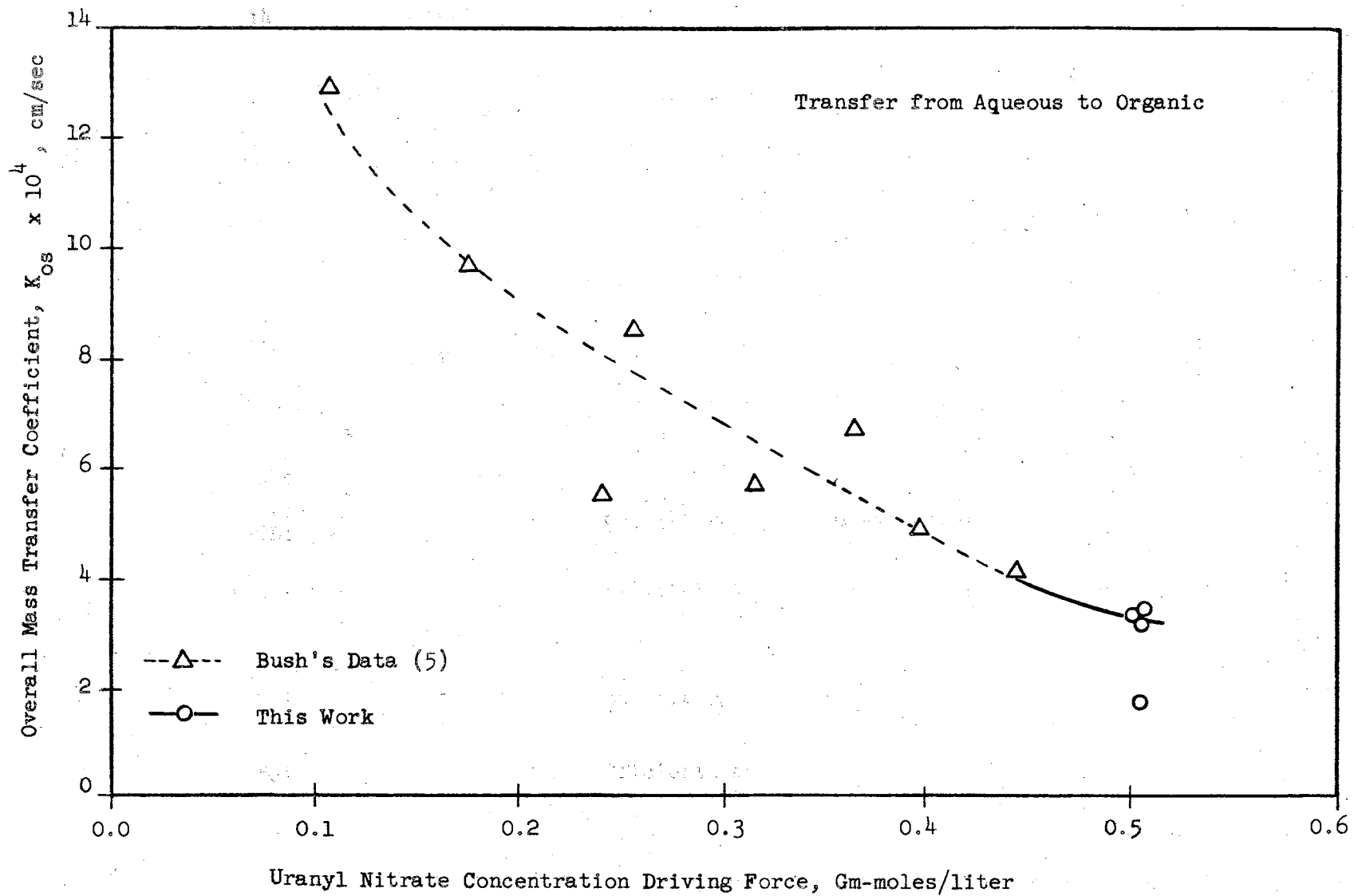phase, the mechanism is more involved. Both nitric acid and uranyl nitrate
form complexes with tributyl phosphate. It would be expected that the
nitric acid and the uranyl nitrate would compete for the available tributyl
phosphate and thus slow down the transfer process. However, as can be
seen by Figure 7, the process was apparently not slowed down by the
presence of nitric acid. This indicated that the chemical reaction was
probably not the rate controlling step. Burger (3) suggested that the
rate controlling reaction was a physical reaction such as orientation
of the molecules at the interface rather than a chemical reaction. The
results of this work seem to support the idea of a physical reaction or
convective diffusion being rate controlling.

Olander and Reddy (19) found that when the overall mass transfer
coefficients were plotted as a function of concentration driving force,
that they increased up to a maximum at a driving force of about 0.1,
decreased to a driving force of about 0.2, and then became relatively
stable. It is of interest to note that the overall mass transfer coef-
ficients in this present work also decreased between driving force of 0.1
and 0.2. However, the mass transfer coefficients did not seem as strong

a function of driving force as they were when nitric acid was not present.

It would have been of interest to extend the work to higher driving forces. However, the organic phase becomes saturated at 0.52 moles of uranyl nitrate per liter of solution so that driving forces much above 0.5 cannot be obtained. As can be seen from Figure 7, initial aqueous concentrations of 1.5 and 1.0 moles of uranyl nitrate per liter produced essentially the same driving force.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The simultaneous transfer of uranyl nitrate and nitric acid across the tributyl phosphate-water interface has been studied.

The presence of nitric acid reduced the mass transfer coefficient for uranyl nitrate transferring from the organic to the aqueous phase. The decreased mass transfer coefficient was possibly due to a reduction in the diffusion coefficient of the uranyl nitrate-tributyl phosphate complex. Nitric acid apparently had no effect on the transfer from the aqueous phase to the organic phase.

The mass transfer coefficients did not seem as strong a function of driving force as they were when nitric acid was not present.

For further study, as diffusion data becomes available, it would be of interest to correlate the mass transfer coefficients for transfer from the organic phase to the aqueous phase with diffusion coefficients. It would also be of interest to correlate the mass transfer coefficients with activity driving forces rather than concentration driving forces.

Burger (3) has reported that since the concentration of acid is greater than the concentration of uranyl nitrate, the acid initially transfers more rapidly. However, due to the low equilibrium concentration of nitric acid in the organic phase, he stated that the nitric acid is driven back into

the aqueous phase as the uranyl nitrate is extracted. It would be of interest to study this phenomenon further by periodically analyzing each stream throughout the course of a run until equilibrium is reached.

The experimental apparatus could be improved by designing a micrometer adjustment for adjusting the height of the stirrers. It is felt that the height of the stirrers with regard to the interface is quite critical. In future work it might be well to use teflon flow lines rather than polyethylene. Over a period of time, the polyethylene sometimes cracked indicating possible extraction of some of its components.

Great care should be taken in future studies to insure that all tributyl phosphate solutions are identical. They should be carefully mixed and used promptly to avoid possible decomposition.

It is recommended that a direct method of analyzing for free nitric acid be used in the future. Burger (3) used ammonium oxalate to complex the uranyl nitrate prior to titrating with sodium hydroxide.

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APPENDIX A

TABLE I

EXPERIMENTAL DATA FOR TRANSFER FROM ORGANIC PHASE TO AQUEOUS PHASE

Run #	Concentrations (moles/liter)						Flow Rates (cm^3/min)	
	Organic Feed		Organic Product		Aqueous Product			
	$UO_2(NO_3)_2$	HNO_3	$UO_2(NO_3)$	HNO_3	$UO_2(NO_3)_2$	HNO_3	Organic	Aqueous
1.	0.000	0.64	0.000	0.5547	0.000	0.689	1.45	1.41
2.	0.0310	0.382	0.02975	0.3780	0.0014	0.04	1.455	1.438
3.	0.0966	0.1302	0.0915	0.087	0.00477	0.045	1.40	1.49
4.	0.110	0.297	0.105	0.277	0.0052	0.025	1.525	1.508
5.	0.0909	0.306	0.087	0.264	0.004075		1.55	1.45
6.	0.0852	0.2160	0.0785	0.1936	0.00358	0.0054	1.59	1.494
7.	0.0908	0.3864	0.0864	0.3461	0.00427	0.023	1.50	1.365
8.	0.115	0.306	0.0921		0.00408		2.66	1.485
9.	0.205	0.115	0.186	0.102	0.00823	0.006	1.12	1.51
10.	0.225	0.275	0.215	0.208	0.00842	0.0180	1.22	1.53
11.	0.253	0.314	0.241	0.286	0.00987	0.0277	1.305	1.662
12.	0.269	0.190	0.2565	0.142	0.01135	0.0190	1.22	1.66

TABLE II

EXPERIMENTAL DATA FOR TRANSFER FROM AQUEOUS PHASE TO ORGANIC PHASE

Run #	Concentrations (moles/liter)						Flow Rates (cm^3/min)	
	Aqueous Feed		Aqueous Product		Organic Product			
	$UO_2(NO_3)_2$	HNO_3	$UO_2(NO_3)_2$	HNO_3	$UO_2(NO_3)_2$	HNO_3	Organic	Aqueous
13.	1.424	2.90	1.398	2.90	0.0164	0.0079	2.2	1.47
14.	1.47	0.78	1.434	0.75	0.0173	0.0052	2.12	1.00
15.	1.014	3.32	1.005	3.27	0.00849	0.00922	2.36	1.91
16.	1.075	0.89	1.025	0.96	0.0293	0.0309	1.33	1.44

TABLE III

CALCULATED DATA

Run #	Driving Force (moles/liter)	Mass Transfer Coefficient K x 10⁴ (cm/sec)	Material Balance (%)
1.	0.4147	9.75	0.28
2.	0.02961	3.18	0.44
3.	0.09061	3.49	0.48
4.	0.1035	3.52	2.5
5.	0.086	3.17	2.3
6.	0.0775	3.21	19
7.	0.0854	3.15	7.6
8.	0.091	3.09	18.2
9.	0.186	2.84	4.2
10.	0.215	2.81	0.368
11.	0.241	3.11	0.0
12.	0.256	3.45	1.1
13.	0.504	3.34	0.05
14.	0.503	3.42	0.0
15.	0.511	1.845	0.0
16.	0.497	3.58	1.0

APPENDIX B

APPENDIX B

SAMPLE CALCULATION

Basic Data

Run # 11 (Transfer from Organic Phase to Aqueous Phase)

Organic Feed:	0.253 Molar $UO_2(NO_3)_2$
	0.314 Molar HNO_3
Organic Product:	0.241 Molar $UO_2(NO_3)_2$
	0.286 Molar HNO_3
Aqueous Product:	0.00987 Molar $UO_2(NO_3)_2$
	0.0277 Molar HNO_3
Equilibrium Concentration (C_o^*):	0.0045 Molar $UO_2(NO_3)_2$
Aqueous Flow Rate:	1.662 cm^3/min
Organic Flow Rate:	1.305 cm^3/min
Interfacial Area:	3.56 cm^2

Calculations

Material Balance:

$$(1.305)(0.253) = (1.305)(0.241) + (1.662)(0.00987)$$

$$0.331 = 0.315 + 0.016$$

$$0.331 = 0.331$$

0.0% Difference

Molar Flux:

$$\frac{(1.662)(0.00987)}{(3.56)(60)} = 7.5 \times 10^{-5} \text{ moles/ sec-cm}^2$$

Driving Force:

$$(0.241-0.0045) = 0.236 \text{ moles/liter}$$

Overall Mass Transfer Coefficient:

$$K_{os} = \frac{(\text{Molar Flux})}{(\text{Driving Force})}$$

$$K_{os} = \frac{7.5 \times 10^{-5}}{(0.236)}$$

$$K_{os} = 3.18 \times 10^{-4} \text{ cm/sec}$$

APPENDIX C

APPENDIX C

ANALYTICAL PROCEDURE FOR URANYL NITRATE

1. The solution to be analyzed was carefully diluted to a concentration
   of greater than 0.002 and less than 0.01 molar uranyl nitrate.

2. A one millilter sample was then pipetted into a twenty five
   milliliter volumetric flask using a one milliliter calibrated
   pipette. Five to ten milliliters of distilled water were added
   and the flask was vigorously shaken. Vigorous shaking was
   especially essential when analyzing organic solutions in order
   to insure extraction of uranium into the water phase.

3. Two drops of one percent p-nitrophenol solution were added.

4. Ammonium hydroxide was added until a permanent yellow color
   resulted.

5. Approximately five molar nitric acid was added dropwise until the
   solution became clear.

6. Three milliliters of ten percent potassium ferrocyanide were
   added and aqueous solution diluted to twenty five milliliters
   with distilled water.

7. After fifteen minutes the absorbance was read on a Beckman DU
   Spectrophotometer at a wave length of 480 mμ and a slit width
   of 0.02 millimeters.

A calibration curve was determined which was found to be linear and could be described by the following equation

$$C = F \left(\frac{A-0.02}{162} \right)$$

where

C = Concentration

F = Dilution factor

A = Absorbance

With very careful work it was found that this method was reproducible to within less than one percent.

APPENDIX D

APPENDIX D

ANALYTICAL PROCEDURE FOR NITRIC ACID

IN THE PRESENCE OF URANIUM

1. A one to ten milliliter sample was pipetted into a
    250 milliliter beaker.

2. The sample was diluted to 100 millilters with
    distilled water.

3. Fifteen milliliters of three percent hydrogen
    peroxide were added.

4. The mixture was titrated to an end point of 4.5
    with 0.1 molar sodium hydroxide using a Beckman,
    Expanded Scale, pH meter.

The sample was then analyzed for uranyl nitrate using the pre-
viously described method. Since the amount of uranyl nitrate in the
sample was then known, the amount of free nitric acid was then calcu-
lated from the stoichiometry of the reaction of hydrogen peroxide and
uranyl nitrate and the amount of sodium hydroxide used in the titration.

APPENDIX E

APPENDIX E

NOMENCLATURE

C   molar concentration (moles/liter)

D   diffusion coefficient (cm^2/sec)

K   overall mass transfer coefficient (cm/sec)

k   individual mass transfer coefficient (cm/sec)

N   molar flux (moles/sec-cm^2)

s   average fractional rate of production of new surface (sec^{-1})

Greek

Δ used to denote a difference

δ film thickness (cm)

θ time (sec)

π constant: 3.1416

Subscripts

A   denotes aqueous phase

i   denotes the interface

o   denotes organic phase

Superscript

*   denotes equilibrium condition

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