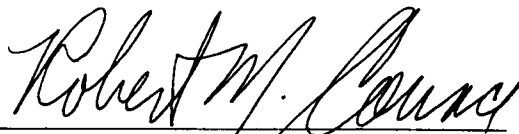


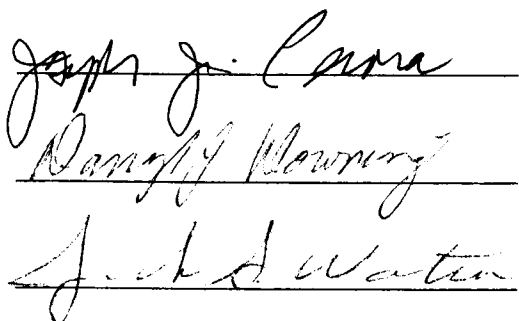
To the Graduate Council:

I am submitting herewith a dissertation written by Joseph Franklin Birdwell entitled "Extraction of Uranium by Dibutyl Carbitol in the System $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.



Robert M. Counce, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor and
Dean of The Graduate School

**EXTRACTION OF URANIUM BY DIBUTYL CARBITOL
IN THE SYSTEM $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$**

A Dissertation
Presented for the Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Joseph Franklin Birdwell
December 1995

DEDICATION

To Marianne, Joey, Katie, and Dexter, with much love.

ACKNOWLEDGMENTS

Listing all individuals who have provide assistance and or encouragement throughout my academic lists is not possible as the lists is long, and the risk of slight by inadvertent omission too great. Of necessity, specific mentions are contributors to this most recent effort, described in this dissertation. Failure to include those whose influences came earlier in no way diminishes their contribution nor my memories of them.

I am greatly appreciative of the efforts of my doctoral committee, particularly my major advisor, Dr. R. M. Counce, whose guidance and motivation were invaluable. My gratitude also goes to Dianne Hovis and Patricia Szczygiel, who performed much of the laboratory work involved in this study, and who did so willingly and with seemingly endless attention to detail. Thanks also to Michael McClung and John Bush, who performed a multitude of chemical analyses efficiently and expeditiously.

Thanks to the Development Division of the Oak Ridge Y-12 Plant, and to its representatives Robert Davis and W. K. Duerksen for their support.

Finally, debts of gratitude are owed my wife Marianne, and children, Joey and Katie for their encouragement, understanding and patience, and to my parents for the many years of support and sacrifice.

ABSTRACT

Multiple experiments have been performed to evaluate aspects of uranium extraction by dibutyl carbitol (DBC) in the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$. Equilibrium distribution of the uranium solute between the aqueous and organic phases has been evaluated. Transfer rate tests have been performed to determine the effect of physical parameters on the rate of transfer. Evaluation of physical parameter correlations with transfer rate has been used to determine the controlling resistance to transfer: reaction kinetics, diffusion, or a combination of the two. Transfer tests have also been performed in which reactant concentrations have been varied. The results of these tests have been used to establish a reaction rate expression applicable to transfer test conditions.

The results of the study indicate that calcium nitrate is effective in increasing the efficiency of uranium extraction by dibutyl carbitol. Results of transfer rate experiments indicate that the rate of transfer is controlled by reaction kinetics, and that the controlling reaction occurs at the interface. Additional transfer rate test results indicate that the rate of transfer is a linear function of the uranium concentration in the aqueous phase, and is not affected by the nitrate concentration under the conditions applied.

Based on the results of transfer tests, a psuedo first-order reaction rate expression is proposed as a transient model for extraction in the subject system. Comparison of predicted transfer rates and observed values shows good agreement. A reaction mechanism for the system which is based on one proposed by Danesi (1980) for basic extractants, and which yields a first order rate expression is proposed.

TABLE OF CONTENTS

SECTION	PAGE
1. INTRODUCTION	1
2. LITERATURE REVIEW	
2.1 Extraction of Uranium by Dibutyl Carbitol	5
2.2 Speciation of Uranium in the System $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-DBC}$	8
2.3 Uranium Solvation Reaction Stoichiometry	8
2.3.1 Determination of Solvation Number	8
2.3.2 Hydration of Solvate	13
2.4 Effect of Salting on Uranium Distribution	17
2.5 Effect of Nitric Acid on Uranium Extraction	23
2.6 Marangoni Effect	24
2.7 Previous Transfer Mechanism Studies -- Uranium into Dibutyl Carbitol	25
2.8 Two-phase Mass Transfer Models	31
2.8.1 Diffusion Mass Transfer Models	33
2.8.1.1 The Stagnant Film Model	33
2.8.1.2 Penetration Model	35
2.8.1.3 Surface Renewal Theory	37
2.8.1.4 Film-penetration model	38
2.8.1.5 Mass transfer in turbulent flow systems	39
2.8.2 Kinetic Regime Models	43
2.8.3 Two-phase Mass Transfer with Chemical Reaction	47
2.8.3.1 Mass transfer with simultaneous first order irreversible reaction	48
2.8.3.2 Mass transfer with simultaneous first order reversible reaction	54
3. EXPERIMENTAL PROGRAM	64
3.1 Equilibrium Distribution Determinations	64
3.2 Mass Transfer Test Program	66
3.3 Mass Transfer Test Apparatus	
3.3.1 Apparatus Selection	66
3.3.1.1 Single Drop Method	67
3.3.1.2 Wetted wall column	68
3.3.1.3 Lewis cell device	68
3.3.2 Development of the Lewis Cell	69
3.3.3 Description of Mass Transfer Apparatus Used	71
3.4 Testing Program	
3.4.1 Acetic Acid Transfer Experiment	73
3.4.2 Uranium Transfer Tests	74
3.4.3 Determination of Reaction Rate Expression	75

SECTION	PAGE
3.5 Experiment Design	75
3.5.1 Distribution Coefficient Determinations	75
3.5.2 Acetic acid and Uranium Transfer Tests	77
3.5.3 Reaction Rate Expression Determination	77
3.6 Statistical Analysis—Significance of Main and Interaction Effects	77
3.6.1 Half Normal Plot Technique	78
3.6.2 Analysis of Variance	79
3.7 Analysis of Significance Results	79
3.7.1 Criteria for Extraction Regime Determination	82
3.7.2 Methods Used for Determination of Extraction Regime	82
3.8 Reagents Used	
3.9 Chemical Analysis Methods	83
3.9.1 Organic Phase Uranium Concentration Determination	84
3.9.2 Free H^+ Determination by Standard Base Titration	84
3.9.3 Determination of Uranium at Low Concentrations in Aqueous Solutions	84
4. THEORETICAL	85
4.1 Relationship Between Overall and Film Coefficients	86
4.2 Calculation of Overall Mass Transfer Coefficients	90
4.3 Model of Bulicka and Prochazka — Extrapolation of Film Coefficients	96
4.4 Kinetic Regime Mass Transfer Modeling —Reaction Rate Expression	101
4.5 Determination of Transfer Rate	107
5. RESULTS AND DISCUSSION	109
5.1 Equilibrium Determinations — Uranium Extraction	110
5.2 Acetic Acid Mass Transfer Tests	111
5.3 Determination of Coefficient for Correlation of Bulicka and Prochazka	118
5.4 Results of Uranium Mass Transfer Tests	120
5.5 Analysis of Uranium Transfer Rate Data	129
5.6 Reaction Rate Expression	134
5.7 Reaction Rate Constant Determination	136
5.8 Transfer Modeling	140
6. CONCLUSIONS	158
7. RECOMMENDATIONS	164
REFERENCES	165

LIST OF SYMBOLS

a	activity
a_s°	activity of pure solvent
B	denotes solvent without functional group
C	solute concentration, moles/L in bulk phase, unless denoted otherwise in text
$C_{i(0)}$	molar concentration of solute in phase i at time $t = 0$
d	diameter of impeller used in mass transfer apparatus
D	diffusion coefficient
h	hydration number for uranyl nitrate per equation (2-2), also used in superscript form
K_d	equilibrium or distribution coefficient for uranium, defined in equation (2-12)
K_D	dissociation constant for uranyl nitrate, defined in equation (2-43)
K_e	reaction equilibrium constant, defined in equation (2-109)
K_h	equilibrium constant for hydration of uranyl nitrate as described in equation (2-2)
K_o	organic-phase based overall transfer coefficient
K_r	chemical reaction rate constant
K_s	equilibrium constant for solvation of uranyl nitrate, defined in equation (2-10)
k_a	film mass transfer coefficient for forward reaction
k_f	reaction rate constant for forward reaction
k_o	film mass transfer coefficient, organic phase
k_r	reaction rate constant for reverse reaction
m	molality
m_{fw}	molality of uncomplexed water, as it appears in equation (2-14)

$m_{w,o}^o$	molal solubility of water in the pure solvent
M	metal cation
M_s	molecular weight of solvent
N	flux of transferring species
N_{Fr}	Froude number
N_{Re}	Reynolds number
N_{Sc}	Schmidt number
N_{We}	Weber number
n	solvation (co-ordination) number as defined in equation (2-3), also rotational speed in rpm, as designated in text
p	proportionality constant from Bulicka model (eq. 2-62) describing apparatus geometry
s	fractional rate of surface renewal in diffusion model of Danckwerts as defined in equation (2-53)
S	interfacial area, also used to designate solvent where indicated in text
t	time
u	macroflow velocity in model of Bulicka (eq. 4-52)
v	velocity, $\bar{v}_o$ 'mean square fluctuation velocity in viscous layer
V	volume of bulk phase
x	distance in direction normal to phase boundary
X	anion associated with metal cation M
y	distance in direction parallel to phase boundary
Y	functional group associated with solvent branch B

Greek symbols

δ	thickness of stagnant layer (film) at interface
δ_1	thickness of viscous sublayer, per model of Levitch
δ_2	thickness of diffusion sublayer, as defined by Levitch
ε	energy dissipation in turbulent mass transfer model of Bulicka and Prochazka
γ	activity coefficient
λ	thickness of viscous sublayer in diffusion model of Levitch
λ_0	scale of turbulence in the viscous layer in Bulicka model
ψ_{ij}	interaction factor describing effect of turbulence in phase j on mass transfer in phase i
μ	absolute viscosity
ν	kinematic viscosity
χ	Langmuir adsorption constant
θ	time scale of turbulence in Bulicka model
ρ	density
σ	surface tension

Subscripts

a	aqueous phase
A	species "A"
ab	species absorbed at interface
B	species "B"
f	denotes transfer of reaction in the forward (left - to - right) direction
n	non-extracting nitrate species used for salting
o	organic phase

- r* denotes transfer or reaction in the reverse (right - to - left) direction
- s* solvent
- u* uranium or uranyl species
- w* water
- x* denotes direction normal to phase boundary
- y* denotes direction parallel to phase boundary

Superscripts

- b* bulk phase
- i* at interface

1. INTRODUCTION

The principal objective of the study performed and reported in this document was the development of a transient model for the extractive transfer of uranium from aqueous nitric acid to dibutyl carbitol (DBC) in the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$. As the transfer is known to include a reaction step, development of a non-empirical model necessarily requires determination of the relative contributions of diffusive and kinetic resistances to the overall transfer resistance, the location(s) of the controlling resistance(s), and a knowledge of the reaction rate expression. It follows that these determinations become secondary objectives of the study performed.

Extraction of uranium into DBC is a principal operation in the recovery of uranium from spent nuclear reactor fuel as applied in the BUTEX process (Benedict et al., 1981). In addition to this application, uranium extraction by DBC is employed in the recovery and purification of uranium from forming operations performed in the manufacture of nuclear weapons components.

The composition of the aqueous system used in this study was established based on a desire to evaluate a system of practical interest. Specifically, it was desired to study a system possessing sufficiently high extraction efficiencies that minimal solute losses to the raffinate stream can be obtained in a minimal number of stages. The presence of nitric acid in the aqueous phase reflects its common use as a dissolvent in uranium processing operations.

Calcium nitrate has been added to the aqueous solution as a non-extracting salting agent to obtain a favorable shift in the extraction equilibrium. The presence of excess nitrate in the aqueous phase is required to achieve efficient extraction, as the dissociated uranyl ion is

essentially inextractable. Use of high concentrations of nitric acid for salting is undesirable as the acid is co-extracted by the organic solvent. The selection of calcium nitrate as a salting agent was based on a review of the literature which indicated a considerable favorable shift in the extraction equilibrium by its addition.

Dibutyl carbitol (also known as diethylene glycol dibutyl ether) is commonly used as a solvent for the purification of heavy metals, particularly uranium and rare earth elements. Specific to the study described in this report, dibutyl carbitol (DBC) is used in the selective extraction of uranium from aqueous nitric acid solutions containing fractions of other soluble metal elements. The solution from which uranium is recovered may be generated by the leaching of ash from the incineration of uranium-contaminated combustible waste. In other applications, the solution may be generated by the dissolution of either spent nuclear reactor fuel elements or of metal scraps produced in the forming of fuel or weapons elements. Among the attributes of DBC which make it desirable for the subject application are its relatively high stability when contacted with HNO_3 solutions of low to moderate concentration ($<10\text{ M}$), its low solubility in aqueous solutions, and its low vapor pressure and high flash point.

For the reader familiar with liquid uranium separation processes, it may be useful to consider the BUTEX process as it relates to the similar (and more widely documented) PUREX (Plutonium URanium EXtraction) process. Whereas the PUREX process utilizes tributyl phosphate (TBP) in a diluent (usually a mixture of paraffinic hydrocarbons similar to kerosene), the BUTEX process utilizes undiluted DBC for two reasons. First, TBP in the pure form has a specific gravity (approximately 0.95) approaching that of the aqueous solutions with which it comes into contact, while the specific gravity of DBC is considerably lower (0.83). As a result, good aqueous organic phase separations can be achieved using DBC without the

addition of a lower specific gravity diluent. Second, uranium extraction coefficients between aqueous nitric acid solutions and DBC are low relative to those between the acid and TBP-diluent mixtures. As diluents generally do not extract uranium it is undesirable to reduce the extraction efficiency of DBC by its dilution with a second organic compound. In the case of extraction by TBP, limitation of uranium uptake by dilution of the extractant facilitates the eventual stripping of the purified uranium from the extract into a dilute nitric acid solution for further processing.

While DBC has been found to be fairly selective for uranium, the purity of the final uranium product may be enhanced by the performance of two extraction processes in series using different extractants. For instance, BUTEX-type extraction may be performed in tandem with a PUREX-type process, thereby taking advantage of the differing element selectivities of DBC and TBP to obtain greater rejection of contaminant species.

In the course of meeting the stated objectives, equilibrium uranium distribution data between the aqueous and organic phases in the subject system have been obtained. In addition, a fairly comprehensive description of key activities in the development of early DBC extraction systems has been compiled, frequently from previously classified documents.

Despite the widespread use of HNO_3 in uranium processing, the literature reviewed in preparation for this study pertaining to kinetic studies was found to be generally limited to aqueous solutions of uranium (as uranyl nitrate) without an excess of nitrate ions.

A review of the literature indicates that DBC extraction of uranium has been studied since the mid 1940's, and has been practiced on a large scale since at least the early 1950's. However, most of the research performed on this subject pertains to determination of equilibrium extraction coefficients, determination of solvation reaction stoichiometry, or

describes problems observed during process operation. Detailed kinetic studies are seldom found in the literature and are limited to aqueous systems which are not applied in practice due to poor extraction efficiency.

While the study performed was limited to a single chemical system having a specific composition, it is expected that the general conclusions as to kinetics, location of the reaction in the system, and general form of the transient model are applicable to uranium extraction by DBC in the presence of other salting agents at concentrations sufficient to obtain high extraction coefficients.

Throughout this document frequent reference is made to distribution and extraction coefficients. In this report these terms are used interchangeably, and refer to the ratio of the solvent (organic) phase solute concentration to the aqueous phase solute concentration. More specifically, these terms refer to the ratio of the total uranium concentration in the organic phase to the total uranium in the aqueous phase, determined at the equilibrium condition.

Frequent use of the terms kinetic, diffusive, and diffusive-kinetic mass transfer regimes is also made. These terms refer to the mechanism(s) which exert control over the rate of solute transfer, and are defined in Section 2.7 of this report.

2. LITERATURE REVIEW

2.1 Extraction of Uranium by Dibutyl Carbitol

The use of solvent extraction processes for the recovery and separation of actinides was first developed as an alternative to actinide precipitation processes for the recovery of plutonium from irradiated uranium (Nicholls, 1957). In a process developed by Seaborg (1963), tetravalent plutonium was co-precipitated with insoluble bismuth phosphate by the addition of bismuth nitrate and sodium phosphate to solutions of plutonium nitrate. In the process (which was developed as part of the Manhattan project), irradiated fuel elements were dissolved in nitric acid, and plutonium in solution was reduced to the tetravalent state by addition of sodium nitrite. Co-precipitation of plutonium and bismuth phosphates was accomplished by addition of bismuth nitrate and sodium phosphate to the dissolver solution. The precipitation process was performed in the presence of sulfate ion to prevent the co-precipitation of uranium. The precipitate was re-dissolved in nitric acid and the plutonium was purified through decontamination cycles in which the plutonium was first oxidized to the hexavalent state by addition of an oxidant to prevent its precipitation, followed by re-precipitation of the bismuth phosphate. After removal of the bismuth precipitate, hexavalent plutonium in solution was again reduced to the tetravalent state, precipitated, recovered and re-dissolved. While plutonium recovery efficiencies from the process were reported to exceed 95%, the process had the significant disadvantages of batch processing, inability to recover uranium, significant chemical usage, and generation of a large volume of waste.

In light of these considerations, when the decision was made by the governments of Canada and the United Kingdom to build a plutonium separation plant in Canada in 1945 a

simple solvent extraction process was recommended for actinide recovery. Two solvents were found to provide exceptional extraction performance -- butex (also referred to as dibutyl carbitol) and hexone (or methyl isobutyl ketone). Dibutyl carbitol was eventually selected because it is less flammable than hexone and was found to have greater chemical stability when contacted with nitric acid. Also significant is the low solubility of DBC in aqueous solutions, reported as 0.0105 moles DBC per liter of water (McKay, 1952). The solubility was found by McKay to change insignificantly with variations in the aqueous phase nitrate concentration in the range 0 - to - 2 M.

Because of its resistance to acid attack, dibutyl carbitol can be used as a solvent with addition of only nitric acid as a salting agent. In extractions using dibutyl carbitol, uranium and plutonium are selectively co-extracted from fission products. Reductants are then added to reduce the plutonium to the +3 state, causing Pu to be rejected by the solvent into an aqueous acid solution. The partitioned uranium and plutonium are then purified separately in additional liquid-liquid extraction processes.

Demonstrations of continuous DBC extraction processes were performed at the Chalk River Laboratory (Canada) until the development team was disbanded in the late 1940's. Subsequent development of the so-called BUTEX process was performed by the Chemical Engineering Division, Atomic Energy Research Establishment (AERE), at Harwell in the United Kingdom. This work consisted of additional extraction tests in pulse column systems to demonstrate satisfactory separations of uranium, plutonium, and fission products. The primary focus of these tests was to demonstrate that no adverse kinetic limitations existed in continuous, counter-current systems (Nicholls, 1958). An additional objective of the testing was to study the effects of mechanical aspects of pulsed columns, particularly distributor design, on the

BUTEX process. Evaluations of temperature effects on the efficiency of uranium extraction were also performed.

Sprague (1954) studied the selectivity of dibutyl carbitol by determining the extraction coefficients of thirty elements between aqueous nitric acid solutions and DBC in the presence of uranium. In these tests, uranium to be used in the equilibrium determinations was first purified by extraction into DBC followed by back-extraction into dilute nitric acid. Magnesium and ammonium nitrates were used as salting agents to enhance extraction. Aqueous solutions were mixed with equal amounts of DBC, then were allowed to separate. The two resulting phases were analyzed for nitric acid and uranium, and the organic phase was analyzed spectrographically to determine the concentration of the second element being extracted.

The results of Sprague's work indicated that DBC is very selective for uranium relative to most of the other elements studied. In particular, extraction of the elements Al, Ba, Ca, Co, Cr, Mg, Ni, and Sr was found to be negligible. Slightly higher extraction coefficients for Be, Cd, Ga, Mn, Pb, and Zn were indicated. Extraction coefficients were higher still for the elements Cu, Fe, In, K, Li, Na, Sb, Si, Sn, and Zr, but these elements were found to be easily washed from the DBC phase using a saturated ammonium nitrate solution. Significant extraction coefficients for Ag, B, Bi, Mo, Ti, Tl, and V were observed, prompting Sprague to recommend that significant concentrations of these elements be avoided in extraction systems utilizing DBC.

Sprague's results indicate that DBC selectivity for uranium is greatest at higher salting agent concentrations and lower nitric acid concentrations. Sprague reports that uranium selectivity suffers at high acid concentrations, as the distribution coefficient for uranium decreases while coefficients for the other elements studied tends to remain unchanged. The

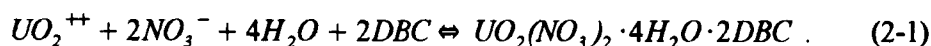
HNO₃ concentration at which this phenomena was observed was not specified. Total nitrate concentrations in the studies performed by Sprague ranged from approximately 7 to 10.5 *M*.

2.2 Speciation of Uranium in the System UO₂(NO₃)₂-HNO₃-H₂O-DBC

In aqueous acids, uranium in the hexavalent state exists as the uranyl ion, UO₂⁺⁺, which has a linear O-U-O configuration and complexes with other ligands equatorially (Baes and Mesmer, 1976). In the hexavalent state, UO₂⁺⁺ is the least hydrolyzed form, which undergoes further hydrolysis at pH > 3.

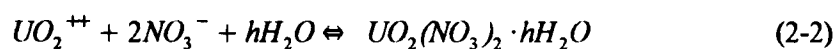
2.3 Uranium Solvation Reaction Stoichiometry

Transfer of uranium from aqueous solutions (generally water) to DBC has been the subject of the efforts of several researchers. The solvation reaction which facilitates uranium extraction by DBC has generally been accepted to be described by the expression



2.3.1 Determination of Solvation Number

To determine the solvation numbers for the extraction of uranyl nitrate (as a hydrate) by a number of organic solvents including DBC, Glueckauf et al. (1951) determined activity coefficients for hydrated uranyl nitrate in the organic phase, based on hydration and solvation equilibria described by the expressions



where h and n are the hydration and solvation numbers, respectively, and S represents a solvent molecule. The equilibrium constant K_h derived for the hydration equilibria is then defined by Glueckauf according to the expression

$$K_h = \frac{[UO_2^{++}][NO_3^-]^2[H_2O]^h}{[UO_2(NO_3)_2 \cdot hH_2O]} \quad (2-4)$$

All terms in brackets are activities. Terms in the numerator refer to components in the aqueous phase, while those in the denominator are in the organic phase. Then the activity of the uranyl nitrate in the aqueous phase is described by the expression

$$[UO_2^{++}][NO_3^-]^2 = 4m_{u,a}^3 \gamma_{u,a}^3 \quad (2-5)$$

where $\gamma_{u,a}$ is the mean molal activity coefficient of the aqueous-phase uranyl nitrate and $m_{u,a}$ is the aqueous phase molality of uranyl nitrate. Similarly, Glueckauf defines the organic phase uranyl nitrate activity coefficient by the expression

$$[UO_2(NO_3)_2 \cdot hH_2O] = m_{u,o} \gamma_{u,o} \quad (2-6)$$

Then at equilibrium

$$4m_{u,a}^3 \gamma_{u,a}^3 a_w^h = K_h m_{u,o} \gamma_{u,o}, \quad (2-7)$$

$$3\log(m_{u,a}\gamma_{u,a}a_w^{h/3}) = \log K_h + \log m_{u,o}\gamma_{u,o} , \quad (2-8)$$

where $a_w = [H_2O]$.

Glueckauf determined values of $\gamma_{u,o}$ for a number of organic solvents based on the assumption that values of $\gamma_{u,a}$ and a_w can be taken ignoring the presence of solvent in the aqueous phase. The organic phase activity coefficients obtained were found to increase significantly with increasing organic phase uranyl nitrate molality $m_{u,o}$, following the expression

$$\log \gamma_{u,o} = km_{u,o} \quad (2-9)$$

where k is a constant dependent on the organic compound. The Gibbs-Duhem equation then suggests that the solvent activity must decrease as $m_{u,o}$ increases. This implies the existence of a strong attraction between solvent and solute. Based on the strength of the attraction, Glueckauf assumed that uranyl nitrate in the organic phase exists only in the solvated form, $UO_2(NO_3)_2 \cdot hH_2O \cdot nS$. The equilibrium constant of solvation is then defined by Glueckauf as

$$K_s = \frac{[UO_2^{++}][NO_3^-]^2[H_2O]^h[S]^n}{[UO_2(NO_3)_2 \cdot hH_2O \cdot nS]} \quad (2-10)$$

Substituting equation (2-5),

$$K_s = \frac{4m_{u,a}^3 \gamma_{u,a}^3 a_w^h [S]^n}{m_{u,o} \gamma_{u,o}} \quad (2-11)$$

The extraction or distribution coefficient is defined as the ratio of the activity of an element in the extract to its equilibrium activity in the raffinate. Generally, the expression is used with activities replaced by concentrations. For uranium extraction according to equation (2-3), the uranium extraction coefficient may be defined as

$$K_d = \frac{[UO_2(NO_3)_2 \cdot hH_2O \cdot nS]}{[UO_2^{++}]} \quad (2-12)$$

and in terms of activity coefficients

$$K_d = \frac{m_{u,o} \gamma_{u,o}}{m_{u,a} \gamma_{u,a}} \quad (2-13)$$

Assuming ideal behavior in the organic phase, Glueckauf applies Raoult's law to obtain

$$[S] = \frac{m_s - nm_{u,o}}{m_s - (n-1)m_{u,o} + m_{fw}} \quad (2-14)$$

where $[S]$ is the true mole fraction of solvent in the organic phase. Glueckauf defines

$m_s = 1000 / M_s$, where M_s is the molecular weight of the solvent. The term m_{fw} is the molal concentration of water which is not combined with either uranyl nitrate or with the solvent (i.e., "free water"). The activity of the uranium complex in the organic phase is proportional to the true molal fraction of the solute species,

$$\frac{m_{u,o}}{m_s - (n-1)m_{u,o} + m_{fw}} \quad (2-15)$$

Equation (2-11) can then be rearranged to yield

$$m_{u,a}^3 \gamma_{u,a}^3 a_w^h = C \times \frac{m_{u,o} [m_s - (n-1)m_{u,o} + m_{fw}]^{n-1}}{(m_s - nm_{u,o})^n}, \quad (2-16)$$

where C is a proportionality constant, and $C \neq K_s / 4$.

As $m_{u,o} \rightarrow 0$, $\gamma_{u,o} \rightarrow 1$ and $m_{u,a}^3 \gamma_{u,a}^3 a_w^h \rightarrow K_s m_{u,o}$. The constant C may then be simplified to yield

$$C = \frac{K_s m_s^n}{4(m_s + m_{fw})^{n-1}} \quad (2-17)$$

Finally, the organic uranyl nitrate activity coefficient is

$$\gamma_{u,o} = \frac{[1 - (n-1)m_{u,o} / (m_s + m_{fw})]^{n-1}}{(1 - nm_{u,o} / m_s)^n} \quad (2-18)$$

Of this derivation, Glueckauf states that the solvation numbers (n values) obtained are approximations, due in part to the existence of a series of hydrate-solvates. Though an approximation, the values calculated do provide a useful idea of the actual solvation stoichiometry. From partition data collected using DBC as the solvent under conditions $0.5 \leq m_{u,o} \leq 1.0$ and $m_{fw} = 0.0, 0.76$, solvation numbers in the 1.6 - 2.3 range were determined. These results support the solvation number of 2 proposed in Equation (2-1).

2.3.2 Hydration of Solvate

McKay and Mathieson (1951) determined the degree of hydration of uranyl nitrate in the solvent complex through equilibrium tests in which the dry solvent was contacted with an aqueous (HNO_3 -free) uranyl nitrate solution. The resultant organic phase was then analyzed for water content. Comparison of the data with laboratory determinations of water solubility in DBC indicated solvent-phase water concentrations significantly exceeding the solubility limit. McKay found the water extraction data to be well represented by the expression

$$m_{w,o} = m_{w,o}^o + hm_{u,o} \quad , \quad (2-19)$$

where $m_{w,o}$ and $m_{u,o}$ are the solvent-phase water and uranyl nitrate molalities (expressed in moles per kilogram of dry solvent), $m_{w,o}^o$ is the molal solubility of water in the pure solvent, and

h is the hydration number, which was found to equal 4 in the case of DBC. McKay determined that equation (2-19) was obeyed by all the ethers, esters, and ketones used in his tests, except at values of $m_{u,o}$ exceeding 3 molal. McKay and other researchers labeled these solvents "linear." Dissociation constants calculated by McKay using experimentally determined conductivity and viscosity values indicate that the degree of uranyl nitrate dissociation in DBC and the other organics tested is negligible.

Subsequent experiments were performed to determine how the water content of organic solutions was affected by changes in the organic phase uranyl nitrate concentration and the external water vapor pressure (Gardner et al., 1952). This work was an extension of that performed earlier by McKay and Mathieson, and resulted in the determination that uranyl nitrate is extracted not only as a tetrahydrate, but as a series of hydrates. The results obtained indicate a nearly linear relationship between the amount of water in the organic phase and the organic-phase uranium concentration at a fixed value of a_w (water activity), which is approximately described by the expression

$$m_{w,o} = m_{w,o}^{\circ} + A m_{u,o} - 1 / 2 B m_{u,o}^2 \quad (2-20)$$

In equation (2-20) the superscript $^{\circ}$ denotes molality in the absence of uranyl nitrate, A (along with $m_{w,o}^{\circ}$) is a function of $a_{w,o}$, and B is a constant determined by Gardner to be equal to 0.5 for the two solvents studied, dibutyl carbitol and penta-ether.

Henry's law was found to apply to the solubility of water in dibutyl carbitol, which was found to be described by the expression

$$a_{w,o}^o = km_{w,o}^o / (1 + .001M_s m_{w,o}^o) \quad (2-21)$$

within experimental error, where M_s is the solvent molecular weight, and k is a constant equal to 1.6. It then follows that the solvent activity will obey Raoult's law, giving

$$a_s^o = 1 / (1 + 0.001M_s m_{u,o}^o) \quad (2-22)$$

As $m_{w,o} \rightarrow 0$, equation (2-20) becomes

$$A = (m_{w,o} - m_{w,o}^o) / m_{u,o} \quad (2-23)$$

with A being the average number of water molecules attached to each uranyl nitrate molecule.

For dibutyl carbitol, Gardner determined $A = 2$ at low values of a_w . As a_w increased, the value of A was found to increase above 4 without any indication of stopping at that value.

Based on these findings, Gardner concluded that hydrates between the di-hydrate up to at least the hexa-hydrate are likely to exist.

Application of equation (2-20) permits development of a more accurate form of the partition law proposed by McKay,

$$a_{u,a} = 4(m_{u,a} \gamma_{u,a})^3 = 4K_s a_{u,o} = 4K_s m_{u,o} \gamma_{u,o} \quad (2-24)$$

In the partition law developed by Gardner et al., $a_{u,o}$ and $\gamma_{u,o}$ are functions of both the organic phase uranyl nitrate content, $m_{u,o}$, and the organic phase water content (considered as either $m_{w,o}$ or $a_{w,o}$). The variation of $m_{w,o}$ and $a_{w,o}$ at constant $m_{u,o}$ is given by McKay as

$$\begin{aligned}
 \ln(a_{u,o} / a_{u,o(1)}) &= \ln(\gamma_{u,o} / \gamma_{u,o(1)}) \\
 &= \int_{m_{w,o(1)}}^{m_{w,o}} (\partial \ln a_{w,o} / \partial m_{u,o})_{m_w} dm_{w,o} \\
 &= - \int_0^{\ln a_{w,o}} (\partial m_{w,o} / \partial m_{u,o})_{a_w} d \ln a_{w,o} \\
 &= I
 \end{aligned} \tag{2-25}$$

where the subscript (1) refers to the condition $a_{w,o} = 1$. Equation (2-24) then becomes

$$a_{u,a} = 4K_s a_{u,o(1)} \exp I = 4K_s m_{u,o} \gamma_{u,o(1)} \exp I, \tag{2-26}$$

where $a_{u,o(1)}$ and $\gamma_{u,o(1)}$ are functions of $m_{u,o}$ only.

For solvents obeying (2-20),

$$\begin{aligned}
 I &= - \int_0^{\ln a_{w,o}} (A - Bm_{u,o}) d \ln a_{w,o} \\
 &= - (f - Bm_{u,o}) \ln a_{w,o}
 \end{aligned} \tag{2-27}$$

(since the integration is at constant $m_{u,o}$),

where f is a function defined by the expression

$$f \ln a_{w,o} = \int A d \ln a_{w,o} \quad (2-28)$$

This yields a partition law of the form

$$a_{u,a} a_{w,o}^{(f - B m_{u,o})} = 4 K_s m_{u,o} \gamma_{u,\alpha(1)} \quad (2-29)$$

2.4 Effect of Salting on Uranium Distribution

Uranyl nitrate cannot effectively be extracted from water as the solubility of uranium is much greater in water than in organic solutions. This solubility is due to the essentially complete dissociation of the compound in aqueous solutions into uranyl and nitrate ions. Undissociated uranyl nitrate is soluble in a number of organic solvents, including ketones, ethers, and alcohols (Weaver and Larson, 1946; Patton et al., 1963). Addition of nitric acid or some non-extracting nitrate is then essential in shifting the phase equilibrium toward the undissociated uranium form, thereby increasing uranium extraction by organic solvents.

The earliest located documentation detailing studies of the extraction of uranium by dibutyl carbitol in the United States is the previously classified report of work performed by Farber, et al. (1945). The objective of this study was to determine the extraction coefficients for uranium into DBC when non-extracting nitrates were added to the aqueous feed to the point of saturation. It is apparent from the scope of this work that previous unreported tests must have indicated either insufficient uptake of uranium by DBC using HNO_3 alone for salting, or

the undesirable co-extraction of the acid by DBC had been observed. (*Note to the reader: Due to classification considerations in effect at the time the work by Farber was performed, uranium is referred to in the report as tuballoy.*)

In the work by Farber, aqueous solutions containing 2.45 g uranium per 50 ml solution were prepared. In tests in which more than one salting agent was used, a predetermined amount of nitrate salt "A" was added to the standard uranium solution. The second salt "B" was then added in weighed portions until saturation was reached. The pH of the solution was then determined by removing a small sample, diluting by a factor of fifty, measuring the pH, and back-calculating the pH of the original saturated solution. Nitric acid was then added in an amount calculated to produce a solution with a pH of 0.3. In each case, the aqueous solution was contacted with a pre-determined volume of DBC. The first extract was discarded, and the uranium remaining in the aqueous solution was extracted by several sequential contacts with clean DBC. The uranium extracted in the first contact was then determined by washing the uranium from the subsequent extractions from the organic phase, and precipitating it by addition of ammonia to form uranium oxide, U_3O_8 . The extraction (or distribution) coefficient was calculated based on the amount of uranium initially present in the aqueous phase and the amount calculated to have been removed in the first extraction.

The results of the work indicated that in two-salt systems, the presence of sodium nitrate in the aqueous phase in concentrations up to 20% enhanced the extraction. At $NaNO_3$ concentrations exceeding 20% the extraction coefficients decreased nearly linearly until a concentration of 40% was reached, at which point the extraction coefficients for the two-salt systems reached the value obtained when only sodium nitrate was present. An ammonium nitrate-aluminum nitrate salt mixture was found to yield maximum extraction coefficients when

the ammonium nitrate concentration was in the 20% to 30% range. In addition to tests with aluminum, ammonium, and sodium nitrates, tests were performed in which quantities of the nitrates of copper, calcium, or aluminum required to achieve predetermined densities were added to the standard solution.

Of the salt formulations studied, the highest extraction coefficients were achieved when calcium nitrate only was present as a salting agent. When sufficient calcium nitrate was present to obtain a solution density of 1.67 g/ml, an extraction coefficient of 925 was observed.

Additional subsequent extraction studies of the effects of magnesium nitrate and sodium nitrate on the extraction of uranium were performed at the Oak Ridge Y-12 Plant (Googin and Sprague, 1949a and 1949b). In all tests, the aqueous phase contained nitric acid in addition to the non-extracting salt. Googin reported that nitric acid concentration was observed to have a significant effect on the equilibrium distribution of uranium (as uranyl nitrate). Googin observed that, in addition to enhancing uranium extraction, the extraction of nitric acid by DBC was also increased by the addition of non-extracting nitrate salts.

At higher salt concentrations, the addition of nitric acid was found to adversely affect the extraction of uranium, probably due to a competition between the acid and uranyl nitrate for solvation sites. This trend was reversed at lower salt concentrations.

Typically, aluminum nitrate has been used for extraction enhancement as it has the advantage of complexing fluoride ions which may be present in the aqueous uranium feed stream from upstream dissolution processes using hydrofluoric acid (Patton et al., 1963). While $\text{Al}(\text{NO}_3)_3$ is a more effective salting agent on an equal concentration basis than nitrates of either copper or calcium, the latter two are more soluble in aqueous solutions. As a result,

extraction enhancement realized from saturated aqueous feed solutions of $\text{Ca}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ is greater than from a saturated aluminum nitrate solution.

Jenkins and McKay (1953) extended the partition laws used by Glueckauf and Gardner to uranium extractions in which a non-extracting salting agent is added to the aqueous phase for extraction enhancement. The form of the partition law remains unchanged as a result of the presence of a second nitrate. However, the aqueous phase uranyl nitrate activity is no longer described by the simple expression of equation (2-5), but by the expression

$$a_{u,a} = m_{u,a} (2m_{u,a} + xm_{n,a})^2 \gamma_{u,a}^3, \quad (2-30)$$

where the subscript n refers to the second, non-extracting nitrate.

Jenkins found that different nitrate salts had varying effects on the efficiency of uranium extraction by the solvents studied (which included dibutyl carbitol). This variation is reflected primarily in differences in the mean molal activity coefficient of the aqueous phase uranyl nitrate, $\gamma_{u,a}$. Expressions proposed by Harned (1943) were used by Jenkins in the determination of activity coefficients:

$$1/2(\log \gamma_{u,a} - \log \gamma_{u,a}^o) = -\frac{1}{2} I_n, \quad (2-31)$$

$$(1/x)(\log \gamma_{n,a} - \log \gamma_{n,a}^o) = -\alpha_n I_u. \quad (2-32)$$

In these expressions, the superscript o refers to the single nitrate solution only, at an ionic strength I corrected to be the same as the mixed nitrate solution. I_u and I_n are the ionic

contributions from uranyl nitrate and the second (supplemental) nitrate $M(NO_3)_x$, respectively, and are defined as:

$$I_u = 3m_{u,a}, \quad I_n = 0.5x(x+1)m_{n,a},$$

$$\text{and } I = I_n + I_u \quad (2-33)$$

Harned determined that for many systems, α 's defined similarly to those in equations (2-31) and (2-32) are constant at constant total ionic strength, that is they are not functions of I_u and I_n independently. Jenkins tested this "Harned rule" and found it to be applicable to the systems in his study. Application of this rule permits extrapolation of results to trace concentrations of uranium (denoted by the superscript t):

$$0.5(\log \gamma_{u,a}^t - \log \gamma_{u,a}^o) = -\alpha_u I \quad (2-34)$$

Having no direct measurements of $\gamma_{n,a}$ Jenkins calculated values using one of the cross differentiation relationships proposed by McKay (1952, 1953):

$$(1/x)(\partial \log \gamma_{n,a} / \partial I)_{I_n} = 1/2(\partial \log \gamma_{u,a} / \partial I)_{I_u} \quad (2-35)$$

$$= 1/2 d \log \gamma_{u,a}^o - \alpha_u - I_n d\alpha_u / dI \quad (2-36)$$

Integrating at constant I_n ,

$$(1/x) \log(\gamma_{n,a} / \gamma_{n,a}^*) = 1/2 \log(\gamma_{u,a}^o / \gamma_{u,a}^{o*}) - \int_{I^*}^I \alpha_u dI - (\alpha_u - \alpha_u^*) I_n, \quad (2-37)$$

where * denotes the lower limit of integration. According to Jenkins this general equation yields $\gamma_{n,a}$ absolutely, provided the lower limit is chosen such that $I_u = 0$, because $\gamma_{n,a}^*$ will then refer to a pure solution of the non-extracting salt, for which a value is generally known.

Combining equations

$$\alpha_n = \bar{\alpha}_u + [(1/x) \log \gamma_{n,a}^o - 1/2 \Delta \log \gamma_{u,a}^o] / I_u + I_n \Delta \alpha_u / I_u \quad (2-38)$$

where Δ denotes differences between values at $I = I_u + I_n$ and $I = I_n$, and $\bar{\alpha}_u$ is the mean value of α_u over this range of ionic strengths. When $I_n = 0$, equation (2-27) becomes

$$\alpha_n = \bar{\alpha}_u + [(1/x) \log \gamma_{n,a}^o - 1/2 \log \gamma_{u,a}^o] / I \quad (2-39)$$

In this case, $\gamma_{n,a}$ becomes $\gamma_{n,a}^t$ and

$$-\bar{\alpha}_u I = (1/x) \log \gamma_{n,a}^t - 1/2 \log \gamma_{u,a}^o \quad (2-40)$$

Equations (2-39) and (2-40) are valid regardless of whether the Harned rule holds for $\gamma_{n,a}$:

Further when the Harned rule is indicated to apply over the range $I = 0$ to $I = I_u$, then

$\bar{\alpha}_u = \alpha_u$, and

$$(1/x) \log \gamma_{n,a}^t = 1/2 \log \gamma_{u,a}^t \quad (2-41)$$

Comparison of partition data with activity coefficients calculated by the procedure described indicates that the salting effect afforded by non-extracting nitrates is directly related to the activity coefficient of the nitrate specie. Of direct interest to the study which is the subject of the present paper, differences between nitric acid and calcium nitrate activities indicate a potential for significant extraction performance by addition of the latter.

2.5 Effect of Nitric Acid on Uranium Extraction

The presence in the aqueous phase of nitric acid at high concentrations without the addition of other salting agents does not elevate extraction coefficient values sufficiently to obtain efficient uranium extractions in a reasonable number of contact stages without severe acid co-extraction (Weaver and Larson, 1946). Desirable extraction coefficients are obtained only when significant concentrations of non-extracting salts are present in the aqueous (feed) solution. Nitric acid in solution in the presence of a non-extracting metal salt may decrease the extent to which uranium is extracted by DBC, as the dissociation of the uranyl nitrate is increased by the hydrogen ion concentration. Results of studies by Clewett et al. (1946), and by Wilcox and Moore (1946) indicated that optimal extraction results were obtained using low nitric acid concentrations in the presence of non-extracting metal salts (nitrates). However, the

feed solution should be kept sufficiently acidic to prevent precipitation of hydroxides of any metals present.

Weaver concluded that nitric acid has two undesirable effects in the purification of uranium by DBC extraction. First, HNO_3 is co-extracted, and can therefore interfere with the extraction of uranium by competing for chelating sites. Secondly, extracted nitric acid interferes with recovery of extracted uranium from the solvent, which is accomplished by washing the solvate with water. Specifically, co-extracted nitric acid is stripped from the solvent into the aqueous wash solution into which uranium is to be stripped from the solvent complex. This co-stripping of nitric acid results in an undesirable increase in the nitrate concentration of the wash solution, causing a shift in the uranium extraction equilibrium away from the aqueous phase.

In extractions from dilute nitric acid solutions, it is possible that sufficient acid will be extracted that the pH of the aqueous solution will increase to the extent that hydroxides of metals present in the aqueous phase will precipitate. To avoid this situation, Weaver recommended that the organic phase acid concentration be adjusted prior to extraction of uranium by pre-equilibrating the organic by contact with a dilute HNO_3 solution.

2.6 Marangoni Effect

A potential contributing factor to mass transfer across a liquid-liquid interface is spontaneous agitation at the interface between unequilibrated solutions. This turbulence, known as the Marangoni effect, results from longitudinal variations in interfacial tension which are generated by the transfer of material in the vicinity of the interface (Sterling and Scriven,

1959). The effect produces higher rates of transfer across the phase boundary than would otherwise be expected or predicted by film, penetration, or surface renewal models.

The Marangoni effect does not occur at the interface between immiscible solutions when no solute transfer occurs (Wei, 1955). Surface activity was found to be common in systems in which both phases contained reacting solutes. The effect has been observed as localized stirring accompanied by rippling of the interface, as slow moving transparent liquid streams leaving the interface, as still slower moving opaque streams from which droplets are observed to emerge, and as mist-like emulsions forming adjacent to the interface.

The effect has been found to be more pronounced when solute transfer is in the organic-to-aqueous direction than vice versa, and when rapid and highly exothermic extraction reactions occur near the interface. Marangoni disturbances have been found to subside as solutions in contact reach equilibrium, and are absent when solutions containing reacting solutes are brought into contact at the equilibrium condition.

2.7 Previous Transfer Mechanism Studies -- Uranium into Dibutyl Carbitol

Murdoch and Pratt (1953) examined the extraction of uranyl nitrate from water into the solvents dibutyl carbitol and methyl isobutyl ketone to determine the uranium transfer rates and to interpret the overall transfer coefficients in terms of interfacial resistances and reaction rate. Testing was performed using a wetted wall column in which the aqueous solution was passed downward along the inner diameter of the column, while the organic solution was allowed to fill the core of the column inside the aqueous film. Samples were collected from the two exiting streams and were analyzed for uranium concentration by a colorimetric procedure.

From the uranium concentration results, overall mass transfer coefficients based on each of the two phases were calculated. Tests were performed for both "forward" (aqueous-to-organic) and "reverse" (organic-to-aqueous) transfer. A total of 169 runs (tests) were performed in 26 sets. In 14 of the 26 sets, the forward transfer of uranium into DBC was studied. In another 4 sets, transfer in the reverse direction was examined. The remaining sets dealt with uranium transfer in the forward direction into MIK.

The data from the tests were interpreted using a model based on the two-film theory as proposed by Lewis and Whitman (1924). In addition, it was assumed that equilibrium existed between the two phases at the interface.

Based on the work of McKay (1951) in which a solvation reaction was indicated, Murdock recognized the potential significance of transfer by chemical reaction in addition to physical (diffusion) transfer. Accordingly, three transfer mechanisms were proposed: (1), separate diffusion of uranyl and nitrate ions into the solvent phase where solvation occurs, (2), solvation at the interface resulting from molecular collisions between uranyl and nitrate ions and the solvent followed by diffusion into the bulk solvent phase, and (3), interfacial reaction between unionized uranyl nitrate and solvent molecules followed by diffusion into the bulk solvent. The authors discounted mechanism (1) based on the essential electrical neutrality of the phase, and rejected mechanism (2) due to the low probability of occurrence of quaternary collisions with solvent molecules.

The rate expressions developed by Murdoch are based on the only source of nitrate being the ionized uranyl nitrate in the aqueous phase. Therefore, the rate is effectively third order, owing to the 2-to-1 stoichiometry between the nitrate and uranyl ions.

Since the solvent is generally present in great excess, Murdoch expressed the reaction between uranyl nitrate and the solvent in terms of pseudo first-order reaction constants, according to the expressions

$$\begin{aligned}\frac{dN}{dS} &= k_f [UO_2(NO_3)_2]_a^i - k_r [UO_2(NO_3)_2]_o^i \\ &= k_f ([UO_2(NO_3)_2]_a^i - [UO_2(NO_3)_2]^*)\end{aligned}\quad (2-42)$$

The latter expression results because, according to Murdoch, the ratio of reverse to forward reaction rate constants, k_r/k_f is equal to the local value of the distribution coefficient, and $[UO_2(NO_3)_2]^*$ is the concentration of undissociated uranyl nitrate at the aqueous interface in equilibrium with the uranyl nitrate concentration in the organic film.

Defining the dissociation constant, K_D as

$$K_D = \frac{[UO_2^{++}]_a [NO_3^-]_a^2}{[UO_2(NO_3)_2]_a} \quad (2-43)$$

$$K_D [UO_2(NO_3)_2]_a = 4[UO_2^{++}]_a^3 \quad (2-44)$$

$$dN = \frac{4k_f}{K_D} dS \left([UO_2^{++}]_a^3 - [UO_2^{++}]^* \right) \quad (2-45)$$

Under the condition in which the uranyl and nitrate ions are present in stoichiometric proportions, the reaction is third order.

In an approach similar to that of Lewis (1958), Murdoch described the overall resistance to transfer ($1/K$) as the sum of individual film resistances and the resistance due to chemical reaction. Values for the aqueous phase-based overall transfer coefficient determined by Murdoch were observed to increase rapidly with increasing reactant concentrations, while the organic phase-based coefficient was found to be unchanged with increases in concentration.

Murdoch determined that the rate of transfer of uranyl nitrate in his tests was controlled by both diffusion and chemical reaction, and that aqueous and organic phase resistances were of the same order of magnitude while the interfacial (reaction) resistance was approximately one order of magnitude less. In the wetted wall system, the transfer results indicated that the relative significance of the chemical reaction resistance increased with increasing flowrate in the column. Aqueous-based overall coefficients calculated by Murdoch were found to vary as the square of the uranium concentration, therefore the transfer rate varied as the cube of the aqueous phase solute concentration. This relationship suggests that the reaction rate is described by a third order expression.

Lewis (1958) determined overall transfer coefficients for the transfer of uranyl nitrate between water and three organic solvents -- dibutyl carbitol, methyl isobutyl ketone, and a 20% solution of tri n-butyl phosphate in a hydrocarbon diluent (primarily C_{12} compounds). In some tests involving DBC, the aqueous and organic phases initially contained nitric acid at concentrations of 3 N and 1.5 N , respectively. The overall coefficients calculated from the data obtained were compared against overall coefficients calculated from film coefficients determined using the correlation developed previously by Lewis (1954) for non-reacting transfer systems.. (The use of the individual coefficients alone to calculate values for the overall

transfer coefficient assumes that the transfer rate is diffusion controlled.) The transfer of nitric acid alone between water and DBC was also investigated.

According to Lewis, the transfer of uranyl nitrate across the aqueous/organic interface must be accompanied by chemical reaction as the uranyl nitrate is essentially completely dissociated in the aqueous solution but is unionized in the solvent phase. Lewis hypothesized that if the unionized uranyl nitrate molecule is the specie crossing the interface, the equilibrium at the interface will be upset, as uranyl and nitrate ions must constantly become associated while transfer takes place from the aqueous to the organic phase. In this case, the rate of transfer should be proportional to the rate of association. This association process could occur either by a three body collision (two nitrate ions and one uranyl ion), or via the formation of an intermediate specie such as $\text{UO}_2(\text{NO}_3)^+$. The formation of the intermediate specie would then be followed by a second association step, after which the solvation of the uranyl nitrate molecule takes place.

Based on the results of the first Lewis cell work (1951), transfer calculations were based on eddy diffusion. There is therefore no quantitative difference between transfer rates in the bulk phase and near the interface in that phase. Lewis suggested that the actual transfer of uranium across the interface can be regarded as being due to a heterogeneous reaction between the uranyl nitrate-solvent complex and water. According to Lewis, the practical approach to analyzing this reaction is to represent it as a homogeneous reaction occurring in one or the other phase. Lewis also states that while it is common to consider the reaction to be pseudo-first order due to the large excesses of all reactants present excepting the solute, a third order reaction model may be more appropriate for the extraction of uranyl nitrate due to the dissociation/association mechanism involved.

Based on the assumption that the solute concentrations in the two phases at the interface are in equilibrium, Lewis calculated the overall transfer coefficients which he related to the individual coefficients according to the expression

$$\frac{1}{K_o} = \frac{K_d}{k_a} + \frac{1}{k_o} + \frac{1}{K_r} \quad (2-46)$$

where the k 's are individual transfer coefficients, K_o is the organic-phase based overall transfer coefficient, K_r is the chemical reaction rate constant, the subscripts a and o indicate aqueous and organic phases, and K_d is the distribution coefficient. The terms in the expression then appear as resistances. Using his correlation for film transfer coefficients, Lewis calculated these quantities and was then able to calculate the reaction resistance term and the reaction rate constant for the systems studied.

In several of the tests performed, Lewis reported observing interfacial turbulence. In these experiments the rates of transfer were always found to be greater than those calculated assuming diffusion resistance only, except for the transfer of uranyl nitrate from water to DBC. Lewis attributed the high rates of transfer to the increase in interfacial area due to the instability at the phase boundary. Lewis also observed that the transfer coefficients decreased as the transfer progressed. Lewis hypothesized that this was due to an increasingly significant chemical reaction resistance at the interface.

In the case of uranyl nitrate transfer from water to DBC Lewis concluded that the interfacial resistance is so large that it overwhelms the effect of increased surface area due to interfacial instability. For this system, an increase in the resistance due to chemical reaction as

the transfer progressed was reported. By contrast, transfer coefficients for uranyl nitrate transfer from DBC to water were found to be slightly greater than those predicted for diffusion resistance only.

2.8 Two-phase Mass Transfer Models

In extraction and absorption processes the transfer of a solute between two phases (including pairs of immiscible liquids) may, in the general case, be a function both of the kinetics of chemical reactions which occur in the system and of diffusion processes within the phases. To accurately describe the transfer of species between phases it is necessary to know which process(es) -- chemical reaction and/or diffusion -- present the greater resistance to transfer, and therefore control the overall transfer rate. Determination of the location of the controlling resistance(s) is also necessary for development of an accurate process model.

Particularly in the extraction of metals, transfer of the metal species nearly always involves chemical reaction(s), as the chemical states of the transferring species in the two phases generally differ. If one or more chemical reaction steps are slow and the accompanying diffusion processes are essentially instantaneous, the extraction process falls into the kinetic regime and its rate may be described in terms of reaction rate expressions only. Chemical reactions which control the rate of species transfer may occur in either of the bulk phases or may be isolated at the interface (Chiarizia and Danesi, 1980). Conversely, if the reaction rate(s) are instantaneous relative the rate of diffusion of the extracting species, the process falls into the diffusion regime. In such cases the rate expression need only address physicochemical processes to accurately represent the transfer. The most complex transfer situation exists when

the rates of chemical reaction and diffusion processes are of the same order of magnitude, and both play significant roles in determining the overall rate of transfer.

Classifications of transfer processes as kinetic (chemical reaction), diffusion, or diffusion-kinetic controlled are generally referred to as regimes. Models developed for the diffusion-kinetic regime are the most general, with kinetic (only) and diffusion (only) regime models representing limiting conditions of the general case. Typically, extraction processes are further subdivided according to the chemical behavior (acid/base/neutral) of the extractant (Danesi and Chiarizia, 1980). Acidic extractants are organic compounds which have a donor group with a dissociating proton. Examples are compounds containing hydroxyl groups. The dissociation of the donor group results in the formation of a conjugate base due to the release of a proton, which can then be replaced by a positively charged metal ion initially present in the aqueous phase. Danesi defines organic bases as those compounds that can easily form salts when contacted by aqueous acid solutions. Examples of organic bases of interest in extraction are the high molecular weight amines. Neutral extractants are organic compounds which possess donor groups having no dissociating protons. Metals extracted by neutral solvents are extracted as neutral complexes. Examples of neutral extractants are trioctyl phosphine oxide, tributyl phosphate, and the crown ethers. The extractant in the subject study, dibutyl carbitol is a neutral extractant.

In the following subsections models applicable to the three transfer regimes will be reviewed, beginning with the less complex kinetic regime and diffusion regime models, and progressing to the diffusion-kinetic general case.

2.8.1 Diffusion Mass Transfer Models

Several models have been proposed to describe the mechanism of mass transfer between two distinct phases. Generally these models have been proposed to describe movement of a specie between a gas and a liquid phase. The models most commonly appearing in the literature are the two-film model of Lewis and Whitman (1924), the penetration model of Higbie (1935), and the surface renewal model of Danckwerts (1951).

2.8.1.1 The Stagnant Film Model. The stagnant film model is based on the concept that the local velocity of a fluid flowing across a phase boundary approaches zero at the boundary. Therefore, the fluid immediately adjacent to the interface is stagnant (Sherwood, 1975). As the resistance to transfer is in the region of the interface, it is appropriate to consider the existence of a stagnant film which separates the interface from the bulk phase. Since the film is stagnant, any transport across the film (in the absence of reaction) must be due to molecular diffusion. The flux across the interface may be described in terms of simple molecular diffusion,

$$N = -D \left. \frac{dC}{dx} \right|_{x=0} \quad (2-47)$$

The film model was first proposed by Nernst (1904), and served as the basis for the two-film model for gas absorption as presented by Lewis and Whitman (1924). The film model has long been recognized as an oversimplification of real transfer systems, in particular because no sharp demarcation exists to separate the hypothetical stagnant film layer from a turbulent bulk phase (Sherwood, 1975). The two-film theory of Lewis and Whitman, though based on

the oversimplified film model, provides reliable predictions of the effect of chemical reaction on mass transfer, when both occur simultaneously.

A major shortcoming of the film model is that it predicts a first order relationship between the flux of the transferring component and the molecular diffusion coefficient. In reality, both turbulence and eddy diffusion die out as the interface is approached ($\delta \rightarrow 0$). Therefore, transport at the interface is solely by molecular diffusion, while transfer in the bulk phase is predominantly due to eddy diffusion (Sherwood, 1975). Mathematically then, as the distance from the interface approaches the film thickness δ , $N \propto D^0$, whereas in the region of the phase boundary ($\delta \rightarrow 0$), $N \propto D^{1.0}$. If a power function of the molecular diffusion coefficient D^n is used to model the overall transfer across the film, it is expected that the value of n should fall between 0 and 1.

Due to the difficulty in quantifying a film layer thickness, the film coefficient is used to account for diffusion and film thickness parameters. This coefficient is defined as the ratio of the molal flux of a transferring specie to the transfer potential as described by concentration gradient

$$N = \frac{D}{\delta}(C^i - C) = k(C^i - C), \quad (2-48)$$

therefore the film mass transfer coefficient is defined as

$$k = \frac{D}{\delta}. \quad (2-49)$$

Like the film thickness, the film coefficient k is dependent on the flow characteristics of the system, and is used in a dimensionless group form (the Sherwood number) to replace the thickness term in the film model.

$$N_{sh} = \frac{kd}{D} \quad (2-50)$$

In the preceding expression, d is defined by Sherwood as a length appropriate to the geometry of the system.

2.8.1.2 Penetration Model. Unlike the film model, the penetration model does not include the accumulation of the transferring specie in a layer near the interface (Higbie, 1935). Rather, the flux is assumed to be approximately constant across small increments of the phase boundary area. The theory was developed based on observations from typical gas-liquid contacting devices in which elements of the two phases come into repeated contact for brief periods of time. As an example, Higbie cites the passage of gas bubbles through a liquid in which elements of liquid at the phase boundary are constantly replaced as the gas bubble rises through the solution. In the penetration concept, small fluid elements of uniform solute concentration are constantly brought to the phase boundary where they remain for some time period t . According to the penetration model the concentration of the transferring specie at the phase boundary remains constant, due to the transient diffusion of the solute away from the interface into the bulk of the second phase at a gradually decreasing rate.

The expression proposed by Higbie for describing the interfacial flux is

$$N = 2(C^i - C) \sqrt{\frac{D}{\pi t}} \quad (2-51)$$

A film mass transfer coefficient based on an time-averaged flux is

$$k = \frac{N}{(C^i - C)} = 2 \sqrt{\frac{D}{\pi t}} \quad (2-52)$$

As the contact time t is usually unknown, the penetration model is useful in the prediction of mass transfer rates only in special cases. However, this model may be used to calculate changes in flux in response to changes in conditions (e.g., changes in transfer rate due to simultaneous diffusion and chemical reaction).

As equation (2-51) indicates, the penetration model predicts that the flux is a function of the one-half power of the molecular diffusivity. This is in contrast to the film theory which predicts a linear relationship between flux and diffusivity. Results reported by a number of researchers for gas-liquid systems seem to support the penetration model one-half power relationship (Gilliland, 1934; Vivian, 1964), while others indicate that the actual power factor falls in the 0.5 to 0.75 range.

Kishinevskii and Pamfilov (1949) developed a model for gas absorption similar to Higbie's penetration theory in which the interface is constantly being renewed. Unlike Higbie's model, the model of Kishinevskii assumes that molecular diffusion plays almost no role in determining the rate of transfer. Instead it is assumed that liquid elements moving to the phase

boundary become instantaneously saturated with the solute gas, and that the saturated element is then transferred back into the bulk liquid. In the case of absorption with reaction, the liquid element is saturated with unreacted solute gas during the time of interfacial exposure, and the rate of increase of reaction product concentration in the element is determined by the kinetics of the reaction.

2.8.1.3 Surface Renewal Theory. In developing the surface renewal theory, Danckwerts (1951) extended the penetration model to include a range of contact times and degrees of penetration, whereas the penetration concept is based on equal duration for each repeated contact between elements of the two phases. To include a range of interfacial contact times, Danckwerts defines a surface-age distribution function

$$\phi = se^{-st}, \quad (2-53)$$

where s is the fractional rate of surface renewal and t is the duration of the interphase contact. The distribution function describes the probability that any element of fluid will be exposed for a given time t before being replaced by a fresh fluid element from the bulk phase. In the surface renewal model the mean steady state of flux normal to the phase boundary is given by the expression

$$N = (C^i - C) \sqrt{D} \int_0^{\infty} \frac{se^{-st}}{\sqrt{\pi t}} dt = (C^i - C) \sqrt{Ds}, \quad (2-54)$$

and the relationship between the transfer coefficient and the fractional rate of surface renewal is described by the expression,

$$k = \sqrt{Ds} . \quad (2-55)$$

Using concentration data, equation (2-55) can be used to calculate the fractional surface renewal rate. Just as the inability to quantify film thickness and contact time limit the application of the film and penetration models respectively, the lack of availability of values for s limit the usefulness of the surface renewal model.

According to Sherwood, the surface renewal model is most applicable to two-phase systems in which one or both phases is stirred or agitated in some manner.

2.8.1.4 Film-penetration model. A general model for mass and heat transfer which incorporates both the film and penetration theories as limiting cases has been developed by Toor and Marchello (1958). The authors cite observations by other researchers indicating that neither of the two previously established models accurately describe transfer phenomena under all sets of conditions. A model which incorporates aspects of both previously accepted theories is proposed. The alternative theory retains the concept of surface renewal, but divides elements of fluid at the interface into "old" and "new." Old elements are those which remain at the surface for a period of time sufficient to reach steady state transfer, such that molecular diffusion as through a stagnant film controls the rate of transfer. Penetration theory applies to new elements, which do not remain at the interface long enough for steady state to be attained. In most cases a mixture of new and old fluid elements are located at the interface, giving rise to

transfer which cannot be accurately described solely by either the film or penetration theories.

The film-penetration model applies the general diffusion equation with the boundary conditions

$$\begin{aligned}t &= 0, C = C^b \\x &= 0, C = C^a \\x &= \delta, C = C^b\end{aligned}\tag{2-56}$$

Assumptions on which the model is based include the penetration of fluid elements from the bulk phase to the interface when the phase is well-stirred; the bulk phase concentration remains unchanged as in the case of a continuous-flow stirred tank; the bulk phase below an imagined layer of thickness δ is homogeneous; and elements penetrating to the phase boundary have the solute concentration of the bulk phase.

2.8.1.5 Mass transfer in turbulent flow systems. A number of theories for mass transfer in fluid-fluid systems in which one or both of the phases are in turbulent motion have been developed. These models range from those based on the film theory to those based on surface renewal.

The model of Levitch (1962) is based on the concept of damped turbulence at the phase boundary in fluid-fluid systems, such that boundary layers are formed in otherwise turbulent phases as the interface is approached. According to Levitch, eddies in each phase are restrained at the phase boundary due a combination of surface tension, gravity, and viscosity effects, as evidenced by the existence of a stable phase boundary. As a result of the interfacial stability, the eddy velocity normal to the phase boundary at the interface is zero in both phases.

However, in accordance with the penetration and surface renewal theories, flow velocity fluctuations in the direction parallel to the interface (y-direction) exist up to the interface.

Levitch describes a zone of thickness λ adjacent to the interface, in which turbulence (velocity in the x-direction) is damped, such that

$$\begin{aligned} v_x &= v_x^b \text{ at } x = \lambda \\ v_x &= 0 \text{ at } x = 0. \end{aligned} \tag{2-57}$$

In this layer (referred to by Levitch as the zone of damped turbulence), the x-direction velocity is described by the expression

$$v_x = v_x^b / \lambda. \tag{2-58}$$

Within the zone of damped turbulence is a thinner layer of thickness δ_l , which is referred to as the viscous sublayer. In this layer the x-direction velocity is so severely damped that flow is essentially laminar. δ_l is defined as the distance from the interface within which the laminar kinematic viscosity exceeds the turbulent (eddy) kinematic viscosity (Davies, 1972). The kinematic viscosity represents the incremental increase in viscosity due to momentum exchange between turbulent fluid elements over that present in laminar flow (Carberry, 1976). Davies describes l as the mean distance an element fluid travels before being mixed into another fluid element. Therefore, l is an indication of the scale of the turbulence eddies.

Within this viscous sublayer is a still thinner diffusion sublayer of thickness δ_2 , in which eddy diffusion is insignificant relative to molecular diffusion. In this layer the turbulence

is reduced to such an extent that the effective diffusion rate may be described by the molecular diffusion coefficient.

Based on turbulence theory the expression

$$k = 0.32D^{1/2} (v^b)^{3/2} \rho^{1/2} \sigma_{equiv}^{-1/2} \quad (2-59)$$

was developed by Levitch for diffusion film coefficients in turbulent liquid-liquid systems.

In equation (2-59), σ_{equiv} is the equivalent surface tension and incorporates both the phase surface tension and gravitational effects at the interface.

Additional conditions arise when two phases in contact are both in turbulent flow.

In this case, the y-direction velocity at the interface is increased at those instants when the turbulent fluctuations (eddies) are synchronized. This synchronization results in greatly increased mass transfer rates, so much so that most mass transfer in turbulent systems may take place under the condition of synchronized turbulence (Davies, 1972). At the interface itself the effects of turbulent fluctuations in the two phases are additive. However, as the distance from the interface increases in each phase, the y-direction velocity component in one bulk phase has a diminishing effect on mass transfer in the other phase. Applying Levitch's turbulence approach, Davies developed the expression

$$k_i = \frac{0.32D^{1/2} (v_i)^{3/2} \rho^{1/2}}{\sigma_{equiv}^{1/2}} \left[1 + \frac{\rho_2 (v_j)^2}{\rho_1 (v_i)^2} \right]^{1/2} \left[1 + \frac{v_j}{v_i} \right]^{1/2} \quad (2-60)$$

to account for the turbulence interaction effect on film mass transfer coefficients. For the special case of stirred cells of similar geometries, the bulk phase velocities may be related to the speed of agitation n and length of stirring apparatus l , yielding the expression

$$k_i \propto \frac{D_i^{1/2} l^{1/2} n_i^{3/2}}{g^{1/2}} \left[1 + \frac{\rho_j n_j^2}{\rho_i n_i^2} \right]^{1/2} \left[1 + \frac{n_j}{n_i} \right]^{1/2} \left[\frac{\rho_i}{\Delta \rho} \right]^{1/2} \quad (2-61)$$

Bulicka and Prochazka (1972) developed an enhanced model for systems in which both phases are in turbulent motion, based on the physicochemical approaches of Levitch and Davies. The Bulicka model represents an extension of the model of Davies in that turbulence interaction between the phases at the interface is accounted for. Unlike the models of Levitch and Davies, the model of Bulicka is based on the assumption (from Kolar, 1961) that the rate of transfer is controlled by unsteady molecular diffusion of the solute into the vortices of the viscous sublayer, rather than by steady diffusion across a laminar boundary layer. For the general case, Bulicka and Prochazka developed the expression

$$N_{Sh,i} = p N_{Sc,i}^{1/2} N_{Re,i}^{3/4} \psi_{ij}, \quad (2-62)$$

where the interaction factor ψ_{ij} describes the effect of turbulence in phase j on mass transfer in phase i , and is defined by the expression

$$\psi_{ij} = \left[\frac{1 + \left(\frac{n_j}{n_i} \right)^3 \frac{l_i \rho_j}{l_j \rho_i} \left(\frac{v_j}{v_i} \right)^{1/2}}{1 + \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{3/2}} \right]^{1/4} \quad (2-63)$$

In equation (2-62) p is a proportionality constant describing the geometry of the specific contacting device.

2.8.2 Kinetic Regime Models

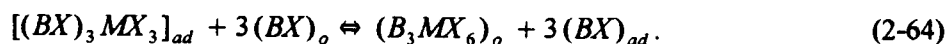
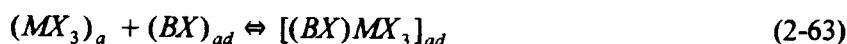
Reaction kinetics are considered to control the overall rate of transfer when the rate of diffusion of the reagents is instantaneous relative to the rate at which one or more chemical reaction steps occur. In liquid-liquid systems the lack of diffusion resistance may be due either to thorough agitation of the bulk phases resulting in very thin diffusion films on either side of the phase boundary, or to very high rates of surface renewal. While kinetic control can be the result of slow chemical reactions occurring in one or both bulk phases, the resistance to transfer in extraction systems is more commonly confined to the liquid-liquid interface. Restriction of reaction resistance to the interface can generally be attributed to the mutual insolubilities of the reactants in the two phases. In the case of diluted extractants (i.e. extracting reagents diluted by non-extracting organic compounds), interfacial reaction may also be favored due to an increased extractant concentration (exceeding the bulk phase value) in the region near the interface. According to Cox and Flett (1977), this phenomena is due the hydrophobic/hydrophilic nature of many extractants. Hydrophilic properties are exhibited by the functional group on the extractant molecule which interacts with the metal at the interface, while hydrophobic behavior is exhibited by the lack of organic reagent solubility in the aqueous

phase. As a result of these properties, the region of the interface may be the most favored location for the solvation reaction.

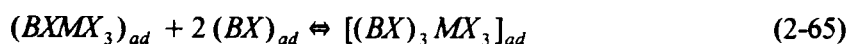
A rate expression found to accurately describe the rate of transfer of a species in the kinetic regime (i.e. a reaction rate expression) does not necessarily provide an indication of the reaction mechanism, as multiple reaction paths can give rise to identical reaction rate expressions (Danesi and Chiarizia, 1980). Steps in the reaction mechanism commonly found to be rate-limiting are chelation and water substitution reactions in the aqueous phase, and complexation reactions, absorption, and desorption processes at the interface.

Aqueous bulk phase kinetic control is limited to systems in which the extractant is at least partially soluble in the aqueous phase, and is most common when the extractant is weakly acidic (Danesi and Chiarizia, 1980). Basic and neutral extractants are more surface active than acidic reagents, particularly basic solvents possessing long alkyl chains. Both basic and neutral reagents extract species only when they are present in the aqueous phase as complexes (i.e. the transferring species are undissociated).

Danesi presents a proposed mechanism for kinetic-regime extraction of a trivalent metal by a basic solvent in which the controlling steps occur at the interface. For the simplified case in which the functional group on the extractant and the aqueous phase anionic species are the same, the interface is saturated with solvent, and the concentration of the anionic species in the aqueous phase is considered constant,

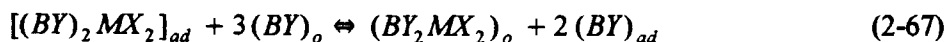


The first step represents the interfacial complexation of the undissociated metal species and the absorbed extractant. The second expression represents desorption of the organometallic complex from the interface and its replacement with extractant molecules. The reaction steps described in equations (2-63) and (2-64) are both slow and rate controlling. An additional and intermediate step, described by the expression



is assumed to occur instantaneously relative to the other two processes.

When the extractant is neutral (e.g. dibutyl carbitol, tributyl phosphate), the mechanism and resultant rate expression are similar to those for basic extractants. However, the donor group of the extractant may differ from the complexed aqueous phase metal species anion, and the value of the exponent assigned to the extractant concentration will reflect the number of donor groups required to saturate the coordinate bonds of the metal cation (Danesi, 1980). For a divalent metal cation (such as the uranyl ion) extracted by a neutral solvent, expressions (2-63) through (2-65) become



where X and Y are the aqueous phase complexing anion and the extractant functional group, respectively.

On the basis that the rate-limiting steps occur at the interface, Danesi assumes that absorption of the extractant can be described by a Langmuir form

$$[S]_{ad} = \frac{\chi_o [S]_a / \chi_i}{1 + [S]_o / \chi_i}, \quad (2-69)$$

where the χ 's are Langmuir adsorption constants with characteristic values for each specific chemical system, and $[S]$ is the solvent concentration. For the ideal case, $1 \gg [S]_a / \chi_i$ (the aqueous phase solvent concentration is negligible), and

$$[S]_{ad} = \frac{\chi_o}{\chi_i} [S]_o = \chi^* [S]_o. \quad (2-70)$$

For saturation at the interface $1 \ll [S]_a / \chi_i$, and

$$[S]_{ad} = \chi_o. \quad (2-71)$$

The second expression is valid for strong surfactants over the entire range of concentrations of practical interest in rate studies (Danesi, 1980). In general, the aqueous/organic phase boundary becomes saturated with the extractant at bulk solvent concentrations on the order of 10^{-4} to $10^{-5} M$.

2.8.3 Two-phase Mass Transfer with Chemical Reaction

The area of mass transfer accompanied by simultaneous chemical reaction has been widely studied, particularly in the case of gas/liquid absorption due to the wide application of such processes. A review of the literature verified the existence of a number of models based on the film, penetration, or the general film-penetration theories for mass transfer. Models for mass transfer with simultaneous chemical reaction are also classified by the order and type of reaction (reversible or irreversible) taking place.

General diffusion-kinetic models are based on the film-penetration theory of Toor and Marchello (1958), as this theory represents a general case which yields the expressions for film and penetration models as limiting conditions. The general model is similar to the surface renewal model in that the interface is assumed to consist of infinitesimally small liquid elements which are periodically replaced with fresh liquid elements from the bulk solution. Overall transfer is accomplished by the combination of two processes: renewal of elements at the interface, and molecular diffusion and chemical reaction within the liquid elements. As the time individual elements reside at the interface approaches infinity, the model describes the behavior of mass transfer as if through a stagnant film. However, as the bulk solution turbulence increases and the duration of interfacial exposure becomes short, the general model may be simplified, yielding a surface renewal model identical to that proposed by Danckwerts (1951).

The general model as derived by Huang and Kuo (1963) differs from that of Danckwerts in that an average, finite fluid element thickness δ is assumed as proposed by Toor and Marchello (1958). Fresh elements at the interface are of the same chemical composition as the bulk liquid. During the residence time of a fluid element at the interface, unsteady mass

transfer and chemical reaction occur simultaneously across the thickness of the element.

Depending on the duration of interfacial contact and the speed of the chemical reaction, the reaction may either be confined to a reaction zone beginning at the surface of the element (instantaneous reaction), or may extend throughout the liquid element (slow reaction relative to the diffusion rate).

Development of models incorporating reaction effects begins with the general transfer equation to which are added terms taking into account the effects of irreversible or reversible reaction

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - k_f C \quad (2-72)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - k_f C + k_r C \quad (2-73)$$

respectively, for first order irreversible and first order reversible chemical reactions.

2.8.3.1 Mass transfer with simultaneous first order irreversible reaction. Huang and Kuo (1963) develop the general solution for the initial and boundary conditions:

$$\begin{aligned} x = 0, \quad t > 0, \quad C &= C^a \\ x = \delta, \quad t > 0, \quad C &= C^b \\ x > 0, \quad t = 0, \quad C &= C^b \end{aligned} \quad (2-74)$$

For the case in which the exposure time of elements at the interface is long, Huang expressed the concentration gradient within the fluid element in terms of a trigonometric function series

$$C = C^i \frac{C^i - C^b}{\delta} \left[x + \frac{2\delta}{\pi} \sum_{n=1}^{\infty} \frac{1 + n^2 \pi^2 \alpha e^{-(1+n^2 \pi^2 \alpha) k_f t}}{n(1 + n^2 \pi^2 \alpha)} \sin \left[\frac{n \pi x}{\delta} \right] \right] \quad (2-75)$$

where α is defined as

$$\alpha = \frac{D}{k_f \delta^2} \quad (2-76)$$

Substituting (2-75) into the expression for the point mass flux to a single element

$$N = -D \left[\frac{\partial C}{\partial x} \right]_{x=0} \quad (2-77)$$

yields

$$N = \frac{D}{\delta} (C^i - C^b) \left[1 + 2 \sum_{n=1}^{\infty} \frac{1 + n^2 \pi^2 \alpha e^{-(1+n^2 \pi^2 \alpha) k_f t}}{1 + n^2 \pi^2 \alpha} \right] \quad (2-78)$$

For the case in which the exposure time $t \rightarrow \infty$, mass transfer occurs according to the film theory and (2-78) reduces to

$$N = \frac{D}{\delta} (C^i - C^b) \left[1 + 2 \sum_{n=1}^{\infty} \frac{1}{1 + n^2 \pi^2 \alpha} \right]. \quad (2-79)$$

Expressed in terms of hyperbolic functions

$$N = \frac{D}{\delta} (C^i - C^b) \frac{1}{\sqrt{\alpha}} \coth \frac{1}{\sqrt{\alpha}}. \quad (2-80)$$

Expression (2-80) is identical to that derived by Hatta (1928) for transfer across a film when the bulk phase concentration of the transferring component is low relative to the interfacial concentration. In very reactive systems the hyperbolic cotangent approaches unity, and the point transfer rate may be expressed as

$$N = (Dk_f)^{1/2} (C^i - C^b). \quad (2-81)$$

The film theory is then a limiting case of the film-penetration concept of Toor. The corresponding effective transfer coefficient (with reaction) is

$$k_i^e = (Dk_f)^{1/2}. \quad (2-82)$$

For relatively shorter contact times, Huang solves the transfer equation (2-77) in terms of error function series by means of Laplace transformation.

Recall the Laplace transform of a function $f(x)$ is defined as

$$L\{f(x)\} = F(s) = \int_0^{\infty} e^{-st} f(x) dt, \quad (2-83)$$

so

$$L\{f'(x)\} = \int_0^{\infty} e^{-st} f'(x) dt. \quad (2-84)$$

Integrating by parts

$$L\{f'(x)\} = \int_0^{\infty} e^{-st} f'(x) dt = \left[e^{-st} f(x) \right]_0^{\infty} + s \int_0^{\infty} f(x) dt = sL(f) - f(0). \quad (2-85)$$

Then

$$L \frac{\partial C}{\partial t} = sL\{C(x,t)\} - C(x,0) = s\bar{C} - C^b \quad (2-86)$$

in which the Laplace form of $C(x,t)$ with respect to t is designated by $C(x,s)$ or simply as $\bar{C}$.

Assuming that the order of integration and differentiation can be reversed to transform the second term in equation (2-72)

$$L\left\{D \frac{\partial^2 C}{\partial x^2}\right\} = DL\left\{\frac{\partial^2 C}{\partial x^2}\right\} = D \frac{\partial^2}{\partial x^2} L\{c(x,t)\} = D \frac{\partial^2 \bar{C}}{\partial x^2}, \quad (2-87)$$

and the transform of (2-72) is

$$s\bar{C} - C^b = D \frac{\partial^2 \bar{C}}{\partial x^2} - k_f \bar{C}. \quad (2-88)$$

The solution of the transform and the inversion are presented in the reference by Huang and Kuo (1963). Insertion of their solution into the expression for the point mass flux yields

$$\begin{aligned}
 N = & \sqrt{\frac{D}{\pi t}} \left[C^i e^{-k_f t} + C^b \left(e^{-1/4\alpha} + 2e^{-(1/4\alpha + k_f t)} - 1 \right) \right] + C^i \sqrt{k_f D} \operatorname{erf} \sqrt{k_f t} + \\
 & C^i \sum \left[2 \sqrt{\frac{D}{\pi t}} e^{-(n^2/\alpha k_f t + k_f t)} + \sqrt{k_f D} \left\{ e^{-2n/\sqrt{\alpha}} \operatorname{erfc} \left(\frac{n}{\sqrt{\alpha k_f t}} - \sqrt{k_f t} \right) - \right. \right. \\
 & \left. \left. e^{-2n/\sqrt{\alpha}} \operatorname{erfc} \left(\frac{n}{\sqrt{\alpha k_f t}} + \sqrt{k_f t} \right) \right\} \right] + \\
 & C^b \sum \left[\sqrt{\frac{D}{\pi t}} \left\{ (-1)^n e^{-\frac{(n+1)^2}{4\alpha}} + 2e^{-\left[\frac{(2n+1)^2}{4\alpha} + k_f t\right]} - (-1)^n e^{-\frac{n^2}{4\alpha}} \right\} + \right. \\
 & \left. \sqrt{k_f D} \left\{ e^{\frac{2n+1}{\sqrt{\alpha}}} \operatorname{erfc} \left(\frac{2n+1}{2\sqrt{\alpha k_f t}} + \sqrt{k_f t} \right) - e^{-\frac{2n+1}{\sqrt{\alpha}}} \operatorname{erfc} \left(\frac{2n+1}{2\sqrt{\alpha k_f t}} - \sqrt{k_f t} \right) \right\} \right]. \quad (2-88)
 \end{aligned}$$

If the thickness of a surface element approaches infinity and $C^b = 0$, the preceding equation can be reduced to

$$N = C^i \left[\sqrt{\frac{D}{\pi t}} e^{-k_f t} + \sqrt{k_f D} \operatorname{erf} \sqrt{k_f t} \right], \quad (2-89)$$

which is the expression derived by Danckwerts based on the penetration theory. For small values of $k_f t$ (less reactive systems)

$$N = C^i \sqrt{\frac{D}{\pi t}} (1 + k_f t + \dots), \quad (2-90)$$

and for large values of $k_f t$ (more reactive systems)

$$N \approx C^i \sqrt{\frac{D}{\pi t}} \left[1 + \frac{e^{-k_f t}}{2\sqrt{\pi(k_f t)^3}} + \dots \right]. \quad (2-91)$$

The rate of transfer in accordance with the surface renewal concept is found by averaging the rate of transfer into elements having a range of interface exposure times. The expression for mass transfer with first order irreversible reaction as presented by Sherwood (1975) is

$$\begin{aligned} N_{avg} &= s \int_0^{\infty} e^{-st} N(t) dt = -D s \int_0^{\infty} e^{-st} \frac{\partial C}{\partial x}(0, t) dt \\ &= -D \left[\frac{d}{dx} \right]_{x=0} \left[s \int_0^{\infty} e^{-st} C(x, t) dt \right]. \end{aligned} \quad (2-92)$$

The corresponding Laplace transform of equation (2-72) applicable to the surface renewal theory is

$$s\bar{C} = D \frac{\partial^2 \bar{C}}{\partial x^2} - k_f \bar{C}. \quad (2-93)$$

For the boundary conditions

$$\begin{aligned}\bar{C}(0) &= C^i = C(0, t) \\ \bar{C}(\infty) &= 0 = C(\infty, t)\end{aligned}\quad (2-94)$$

the solution given by Sherwood is

$$\bar{C} = C^i e^{\left[-\sqrt{\frac{k_f + s}{D}} x \right]}, \quad (2-95)$$

and evaluating $\frac{\partial C}{\partial x}$ at the interface

$$N = C^i \sqrt{D(k_f + s)}. \quad (2-96)$$

The corresponding expression for the reaction (enhancement) factor is

$$\phi = \left[1 + \frac{k_f}{s} \right]^{1/2} = \left[1 + \frac{Dk_f}{k_L^o{}^2} \right]^{1/2}. \quad (2-97)$$

2.8.3.2 Mass transfer with simultaneous first order reversible reaction. Development of models for mass transfer with simultaneous reversible first-order reaction requires solution of the expressions

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C}{\partial x^2} - k_f C_A + k_r C_B \quad (2-98)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C}{\partial x^2} - k_f C_B + k_r C_A \quad (2-99)$$

for reactions which may be represented by



Based on the film theory assumptions that mass transfer across stagnant layers at the interface is by molecular diffusion only and that there is no accumulation of transferring species in either of the two films,

$$\frac{\partial C_A}{\partial t} = 0 \text{ and } \frac{\partial C_B}{\partial t} = 0 \quad (2-101)$$

and expressions (2-98) and (2-99) may be reduced to

$$D_A \frac{\partial^2 C}{\partial x^2} - k_f C_A + k_r C_B = 0 \quad (2-102)$$

$$D_B \frac{\partial^2 C}{\partial x^2} - k_f C_B + k_r C_A = 0 \quad (2-103)$$

For many chemical systems it may be assumed that the reaction product cannot cross the phase boundary into the aqueous phase due to the very limited solubility of the organic specie. Boundary conditions applicable to the film model with reversible reaction are then

$$x = 0, \quad t > 0, \quad C_A = C_A^i, \quad \frac{dC_B}{dt} = 0 \quad (2-104)$$

and at the boundary between the film and bulk phase

$$x = \delta, \quad C_A = C_A^b, \quad C_B = C_B^b. \quad (2-105)$$

Solutions for the concentrations of the two components derived by Huang and Kuo (1965) are

$$C_A = \left[\left\{ u \frac{K_e}{D_{BA}} (x - \delta) + \sinh ux + u \delta \frac{K_e}{D_{BA}} \cosh ux \right\} \frac{\left\{ C_A^i - C_A^b + \frac{1 - \frac{1}{1 + \frac{K_e}{D_{BA}}}}{\cosh u\delta} (C_A^b - K_e C_B^b) \right\}}{\left\{ \tanh u\delta + u\delta \frac{K_e}{D_{BA}} \right\}} \right] \\ + \left[C_A^i - C_A^b + \frac{C_A^b - K_e C_B^b}{1 + \frac{K_e}{D_{BA}}} \right] \cosh u\delta - \frac{C_A^b - K_e C_B^b}{1 + \frac{K_e}{D_{BA}}} + C_A^b \quad (2-106)$$

and

$$C_B = -\frac{1}{D_{BA}} \left[\left\{ u(x - \delta) - \sinh ux - u\delta \frac{K_e}{D_{BA}} \cosh ux \right\} \frac{\left\{ C_A^i - C_A^b + \frac{(C_A^b - K_e C_B^b) - \operatorname{sech} u\delta}{1 + \frac{K_e}{D_{BA}}} \right\}}{\left\{ \tanh u\delta + u\delta \frac{K_e}{D_{BA}} \right\}} \right]$$

$$-\frac{1}{D_{BA}} \left[C_A^i - C_A^b + \frac{C_A^b - K_e C_B^b}{1 + \frac{K_e}{D_{BA}}} \right] \cosh u\delta - \frac{1}{K_e} \frac{C_A^b - K_e C_B^b}{1 + \frac{K_e}{D_{BA}}} + \frac{C_A^b}{K_e} \quad (2-107)$$

Substituting into the rate expression yields

$$\begin{aligned} \bar{N}_A = N_A &= -D_A \left[\frac{dC_A}{dx} \right]_{x=0} \\ &= \frac{D_A}{\delta} \left[\frac{\left[\left(1 + \frac{D_{BA}}{K_e} \right) (C_A^i - C_A^b) + \frac{D_{BA}}{K_e} (1 - \operatorname{sech} u\delta) (C_A^b - K_e C_B^b) \right]}{1 + \frac{D_{BA}}{K_e} \frac{\tanh u\delta}{u\delta}} \right] \end{aligned} \quad (2-108)$$

$$\text{where } K_e = \frac{k_r}{k_f}, \quad D_{BA} = \frac{D_B}{D_A}, \quad u = \left[\frac{k_f}{D_A} \left(1 + \frac{K_e}{D_{BA}} \right) \right]^{1/2}. \quad (2-109)$$

When equilibrium may be assumed to exist in the bulk phase

$$C_A^b = K_e C_B^b \quad \text{and} \quad K_e = K_r \quad (2-110)$$

and

$$\bar{N}_A = \frac{D_A}{\delta} \left[\frac{\left[1 + \frac{D_{BA}}{K_e} \right] (C_A^i - C_A^b)}{1 + \frac{D_{BA}}{K_e} \frac{\tanh u\delta}{u\delta}} \right] \quad (2-111)$$

substituting into the expression

$$\bar{N}_A = k (C_A^i - C_A^b) \quad (2-112)$$

yields

$$k = \frac{D_A}{\delta} \left[\frac{\left[1 + \frac{D_{BA}}{K_e} \right]}{1 + \frac{D_{BA}}{K_e} \frac{\tanh u\delta}{u\delta}} \right] \quad (2-113)$$

For the conditions of transfer according to the surface renewal theory of Danckwerts it is assumed that overall transfer is by molecular diffusion into eddies of fluid at the interface accompanied by chemical reaction. Concentrations of reactants and products in eddies brought to the interface from the bulk phase are uniform and are the same as those in the bulk. The initial condition is then expressed as

$$x > 0, \quad t = 0, \quad C_A = C_A^b, \quad C_B = C_B^b, \quad (2-114)$$

and the boundary conditions at the interface are the same as those applied in the film theory concept.

Due to the short residence time of fluid elements at the interface, it is likely that the transferring specie does not diffuse to the surface of the element before the element is replaced with another. On this basis it may be assumed that the depth of the penetration is infinite and that there is no mass flux at the edge of the fluid element. Mathematically

$$x = \infty, \quad t > 0, \quad \frac{\partial C_A}{\partial x} = 0, \quad \frac{dC_B}{dt} = 0. \quad (2-115)$$

The concentration gradients have been obtained by Huang and Kuo (1965) by solving the partial differential equations (2-98) and (2-99) applying the sets of boundary and initial conditions (2-104), (2-114), and (2-115). For a single surface element, the rate of transfer as a function of its age (residence time at the interface) is

$$N_A = -D_A \left[\frac{\partial C_A}{\partial x} \right]_{x=0}. \quad (2-116)$$

Applying the surface age distribution of Danckwerts

$$\phi(t) = se^{-st}, \quad (2-117)$$

the average mass flux is expressed by

$$\bar{N}_A = \int_0^\infty N_A \phi(t) dt, \quad (2-118)$$

and by substitution

$$\bar{N}_A = -D_A s \left[\frac{\partial \bar{C}_A}{\partial x} \right]_{x=0} \quad (2-119)$$

Based on their solution for the concentration gradient, Huang and Kuo derive

$$\bar{N}_A = \frac{D_A UV(U+V)}{U^2 + UV + V^2 - W} \left[C_A^i - \frac{(K_e + \beta)C_A^b + K_e C_E^b}{1 + \beta + K_e} \right], \quad (2-120)$$

where

$$U = \left[\frac{k_f}{2D_a} \left\{ 1 + \beta + \frac{K_e + \beta}{D_{BA}} + \sqrt{\left[1 + \beta + \frac{K_e + \beta}{D_{BA}} \right]^2 - \frac{4\beta}{D_{BA}}(1 + \beta + K_e)} \right\} \right]^{1/2} \quad (2-121)$$

$$V = \left[\frac{k_f}{2D_a} \left\{ 1 + \beta + \frac{K_e + \beta}{D_{BA}} - \sqrt{\left[1 + \beta + \frac{K_e + \beta}{D_{BA}} \right]^2 - \frac{4\beta}{D_{BA}}(1 + \beta + K_e)} \right\} \right]^{1/2} \quad (2-122)$$

$$\beta = \frac{s}{k_f} \quad (2-123)$$

$$W = \frac{k_f}{D_A}(1 + \beta). \quad (2-124)$$

For the special case in which the reactant A and product B are present in equilibrium concentrations in the bulk phase, (2-120) may be simplified by the substitution $C_A^b = K_e C_B^b$ to obtain

$$\bar{N}_A = \frac{D_A UV(U + V)}{U^2 + UV + V^2 - W} [C_A^i - C_A^b], \quad (2-125)$$

and the mass transfer coefficient becomes

$$k = \frac{D_A UV(U + V)}{U^2 + UV + V^2 - W} \quad (2-126)$$

For a second special case in which the diffusivities of the reactant and the product are the same, $D_{B,A} = 1$ and

$$k = \frac{\sqrt{D_A s} (1 + K_e) \sqrt{1 + \frac{1 + K_e}{\beta}}}{K_e + \sqrt{1 + \frac{1 + K_e}{\beta}}} \quad (2-127)$$

For the general case based on the film-penetration theory of Toor, it is assumed that fluid elements at the interface have a constant finite thickness through which mass transfer

occurs by molecular diffusion. The partial differential equations (2-98) and (2-99) are still valid, and the boundary conditions are

$$x = \delta, \quad t > 0, \quad C_A = C_A^b, \quad C_B = C_B^b. \quad (2-128)$$

The initial conditions and boundary conditions at the interface applied for the surface renewal model are also applicable to the film-penetration model.

The average transfer rate for the film-penetration model conditions, as obtained by Huang and Kuo (1965) is

$$\bar{N}_A = \frac{\frac{D_A}{\delta} (U^2 - V^2) [C_A^i - f(C_A^b, C_B^b)]}{(W - V^2) \frac{\tanh U\delta}{U\delta} - (W - U^2) \frac{\tanh V\delta}{V\delta}}, \quad (2-129)$$

where

$$f(C_A^b, C_B^b) = \frac{1}{1 + \beta + K_e} \left\{ \frac{C_A^b - K_e C_B^b}{U^2 - V^2} \left[\frac{k_f}{D_A} (1 + \beta + K_e) \left(\frac{1}{\cosh U\delta} - \frac{1}{\cosh V\delta} \right) \right] + \left(\frac{U^2}{\cosh V\delta} - \frac{V^2}{\cosh U\delta} \right) + (K_e + \beta) C_A^b + K_e C_B^b \right\}. \quad (2-130)$$

For the case in which the reactant and product are in equilibrium in the bulk phase,

$$f(C_A^b, C_B^b) = C_A^b, \quad (2-131)$$

and the expression for the rate of transfer simplifies to

$$\bar{N}_A = \frac{\frac{D_A}{\delta} (U^2 - V^2) [C_A^i - C_A^b]}{(W - V^2) \frac{\tanh U\delta}{U\delta} - (W - U^2) \frac{\tanh V\delta}{V\delta}} \quad (2-132)$$

The mass transfer coefficient is described by

$$k = \frac{\frac{D_A}{\delta} (U^2 - V^2)}{(W - V^2) \frac{\tanh U\delta}{U\delta} - (W - U^2) \frac{\tanh V\delta}{V\delta}} \quad (2-133)$$

3. EXPERIMENTAL PROGRAM

A multi-phase experimental program was performed to define the system under study and to obtain the data required to evaluate and model the transfer of the uranium component. Preliminary experiments were performed to establish a chemical system for study which possessed desirable extraction capability. Once a system was defined, a mass transfer test apparatus was selected. An experiment was then performed using a non-reacting chemical system to obtain model parameters required to calculate apparatus-specific film mass transfer coefficients for other chemical systems. Transfer rate determinations were then performed for the chemical system of interest ($\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$), and overall transfer coefficients were calculated from the data obtained. Comparison of predicted film coefficients with observed overall coefficients has been used to determine if the rate of transfer is controlled by diffusion resistance in aqueous- or organic-phase diffusive films.

An analysis of the significance of various system physical parameters on the rate of transfer was performed to determine the transfer regime and its location. In addition, comparison of effective overall transfer coefficients for uranium with film coefficients extrapolated from the non-reacting system has been used as an indication of the relative effect of reaction kinetics on the rate of uranium transfer.

3.1 Equilibrium Distribution Determinations

Initially, it was intended that the rate study be performed for the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-DBC}$. Accordingly, a preliminary set of equilibrium distribution determination tests ("shakeouts") were performed at a variety of nitric acid concentrations. The "shakeout"

terminology reflects the common practice of performing these tests by placing the feed and extractant into a separatory funnel which is manually shaken. The phases are then allowed to separate, and samples from the resulting solutions are withdrawn.

Because of the number of equilibrium tests performed in the subject study, extractions were accomplished by placing equal volumes of feed and extractant solutions into small glass beakers. The contents of the beakers were thoroughly mixed by means of a magnetic stirrer. Stirring bars placed in solutions were Teflon-encapsulated to prevent chemical contamination of the system due to corrosion of the magnets. In each extraction, thorough mixing was maintained for a minimum of 5 minutes. After agitation, the phases were allowed to separate for a minimum of three minutes. Samples were removed directly from the mixing vessel by means of a pipettor. To minimize contamination of aqueous samples with organic solution, air was bubbled through the pipettor after insertion of the pipette tip into the aqueous phase to purge the pipette of any organic collected during the insertion process.

The initial scoping tests on the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-DBC}$ were performed under ambient conditions without temperature control. These tests were performed with initial uranium concentrations of 1g/L over a range of nitric acid concentrations from 0.14 to 6N. The low uranium concentration value used was selected based on the desire to eliminate saturation and effects on uranium distribution. From a practical standpoint, the results of the extraction tests were not satisfactory due to poor uranium extraction at low acid concentrations and considerable co-extraction of HNO_3 .

Consequently, it was decided to include a non-extracting salt in the extraction system to enhance uranium transfer while attempting to minimize co-extraction of the acid. A review of the literature indicated that calcium nitrate addition would significantly enhance extraction

performance. Results from a single extraction test confirmed this fact. Subsequently, a series of extraction tests were performed for the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$. The procedure followed for these tests was the same as for the system without calcium nitrate, except that the dispersions were submerged in a constant temperature bath after mixing so as to achieve equilibrium at 25°C. Sample collection was performed while the solutions remained in the water bath.

3.2 Mass transfer test program

Three separate mass transfer experiments were performed. The first two experiments were performed to achieve one primary goal—determination of the rate-controlling mechanism in the transfer of uranium from the aqueous to the organic phase in the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$. The objective of the third experiment was to obtain data needed to determine the correct rate expression for the solvation reaction that accompanies the transfer process.

3.3 Mass Transfer Test Apparatus

3.3.1 Apparatus Selection

The objective of developing a transient model of mass transfer in the subject system necessitates determining both the mass transfer regime and the location of the controlling mechanism. Therefore, the test apparatus must provide data such that diffusion and kinetic effects can be separated. In addition, the apparatus must provide a stable system in which the physical parameters, particularly interfacial area, can be quantified and controlled. Separation of kinetic and diffusion effects can be achieved either by establishing testing parameters such

that the system falls entirely under kinetic or diffusion control, or can be accomplished mathematically. In the investigations performed in this study, the latter method was used.

The three types of devices most commonly used in mass transfer studies are single drop contactors, wetted wall columns, and Lewis-type cells. The latter category has grown significantly due to improvements made on the original design of J. B. Lewis.

A Lewis cell apparatus was selected for the subject application primarily because the most applicable precursor study in the subject area had been performed using this device (Lewis, 1958). This type of apparatus has a critical advantage over other types of transfer test apparatuses in that it provides an easily quantified and controlled interfacial area. In addition, the turbulent exchange (i.e. surface renewal) of fluids to the interface provided by the Lewis cell more nearly simulates extraction processes than the laminar flow present in wetted wall column and single drop devices. Differences between types of test devices are discussed in the following sections.

3.3.1.1 Single Drop Method. Drop methods generally utilize an injection nozzle of some sort (frequently a hypodermic needle) through which a solution is metered so as to produce discrete droplets. These droplets are then passed vertically (upward or downward) through a second immiscible solution to obtain solute transfer. Transfer may be either into or out of the droplet. Drop devices are relatively simple to configure and control, and can provide a constant, quantifiable interfacial area assuming shear effects during transfer do not cause drop deformation. The primary disadvantage is the difficulty in eliminating end effects, i.e. mass transfer which occurs during drop formation and during pooling of drops prior to removal from the apparatus.

3.3.1.2 Wetted wall column. In wetted wall columns, contact is achieved by passing one solution in an infinitesimally thin layer down the inner surface of a vertical cylinder while the second solution is passed upward through the center of the column. A constant and easily determined interfacial area is achieved if the inner wall of the vessel is smooth and the flows of the two phases are controlled to remain constant and laminar. In practical terms, a stable interface between two liquids may be difficult to achieve due to shear forces between the solutions.

3.3.1.3 Lewis cell device. The transfer device now commonly referred to as the Lewis cell was initially developed by J. B. Lewis (1954a) for use in the determination of individual transfer coefficients in diffusion mass transfer. The device and subsequent variations all consist of a cylindrical vessel into which the two liquid phases are introduced. Baffles located inside the cell prevent vortex formation. The phases are agitated by impellers which are located in each phase, and may be mounted on a common shaft or on separate shafts. The latter arrangement allows independent control of the Reynolds number in each phase. Rings or discs may be placed inside the cell at the phase boundary permitting variation of the interfacial area. Lewis cell devices can provide both turbulent mixing of the bulk phases and a stable, quantifiable interfacial area. A principal disadvantage of the Lewis cell is poor mixing at the interface (Hanna and Noble, 1985). In addition, the mass transfer regime within a Lewis cell may shift in response to changes in the degree of agitation of one or both bulk phases.

3.3.2 Development of the Lewis Cell

The Lewis cell was developed for the purpose of investigating the validity of the two film theory developed by Whitman (1923), based on the boundary layer theory of Nernst (1904). A goal of Lewis was the extension of the findings regarding mass transfer rate resistances from the solid-liquid case investigated by Van Name (1916) to liquid-liquid systems. The work of Van Name and others verified that when a chemical reaction takes place at a solid-liquid interface the process is reaction controlled if the reaction is very slow, diffusion controlled if the reaction is fast, and intermediate if the rate of reaction is of the same order as the rate of diffusion.

The Lewis cell was developed as a test apparatus in which the degree of turbulence at the phase interface could be readily controlled. Lewis measured the rate of mutual saturation of a number of partially miscible binary systems, and applied the method of Colburn and Welsh (1942) to determine the individual transfer coefficients for these systems. Lewis then evaluated the relationships between the individual transfer coefficients and various system parameters such as Reynolds number and diffusion coefficients.

Mass transfer coefficients were calculated on the assumptions that the interface was at chemical equilibrium, and that the rate-controlling step in the saturation of a phase is the rate of transfer of the other component away from the interface and into the bulk of that phase. As part of his testing, Lewis performed experiments in which the impellers in the two phases were contra-rotating and in which the impellers were rotated in the same direction. No significant difference between the transfer coefficients calculated for the two cases was observed.

Lewis attempted to correlate the transfer coefficients calculated by dimensional analysis according to the expression

$$k_i = f(L, n_i, n_j, \rho_i, \rho_j, \mu_i, \mu_j, \gamma, D_{ji}, g) \quad (3-1)$$

where L was the length of the stirrer (with the lengths in the two phases equal), and n_i and n_j were the impeller speeds in the two phases. Based on the pi-theorem, Lewis arranged these ten variables into seven dimensionless groups including N_{Re} , N_{Sc} , N_{We} , and N_{Fr} . Of the dimensionless groups, only the ratio of phase viscosities and the Reynolds numbers in the two phases appeared to have any relevance with respect to the transfer coefficients. Eliminating the inconsequential terms, Lewis arrived at the correlation

$$k_i / \nu_i = f(N_{re,i}, N_{re,j}, \mu_j / \mu_i) \quad (3-2)$$

From his results Lewis concluded that transfer in his cell was by eddy diffusion rather than molecular diffusion, due to the lack of dependence of k_i on the Schmidt number.

Subsequently, Lewis (1954b) performed transfer tests in which overall transfer coefficients were calculated for a number of ternary organic systems. The overall coefficients calculated from the concentration data obtained were then compared against values predicted assuming no chemical reaction resistance, using individual coefficients calculated from the correlation developed in his earlier work. Tests were performed as before, except that a solute spike was added to one of the phases at the start of the test.

Among the systems studied was the system water-isobutanol to which acetic acid was added as a solute. As before, overall transfer coefficients were calculated on the basis that the

interfacial concentrations in the two phases were in equilibrium. Good agreement was found between the calculated and predicted overall transfer coefficients for acetic acid between water and isobutanol, and for transfer of ammonia from water to isobutanol. The results establish these systems as representing diffusion controlled transfer systems.

3.3.3 Description of Mass Transfer Apparatus Used

Transfer experiments were performed in a Lewis-type device (Figure 3-1), similar to the one used by DeMuth (1989). This device differs from the one originally developed by Lewis in that a common shaft is used to drive the impellers in both phases, whereas Lewis' apparatus was equipped with independent drive shafts. The mixing cell in the current study consisted of a 1-liter glass beaker to which 4 longitudinal vanes were welded at 90° intervals. Each vane extended inward from the vessel wall a distance of 0.25 inch. Agitation of the phases was produced by insertion of two impellers, one into each phase, attached to a single shaft. The impellers consisted of 4, evenly-space blades welded to a disc. All impeller components were constructed of 316 stainless steel for corrosion resistance. During all testing, the impellers were attached to the shaft such that the blades extended from impeller disc away from the solution interface. This configuration was used to increase the stability of the phase boundary. Impeller positions were established such that each impeller disc was located approximately one inch from the interface. In all tests, the mixing cell was submerged in a water bath which was constantly maintained at a temperature of 25 ± 0.1 °C.

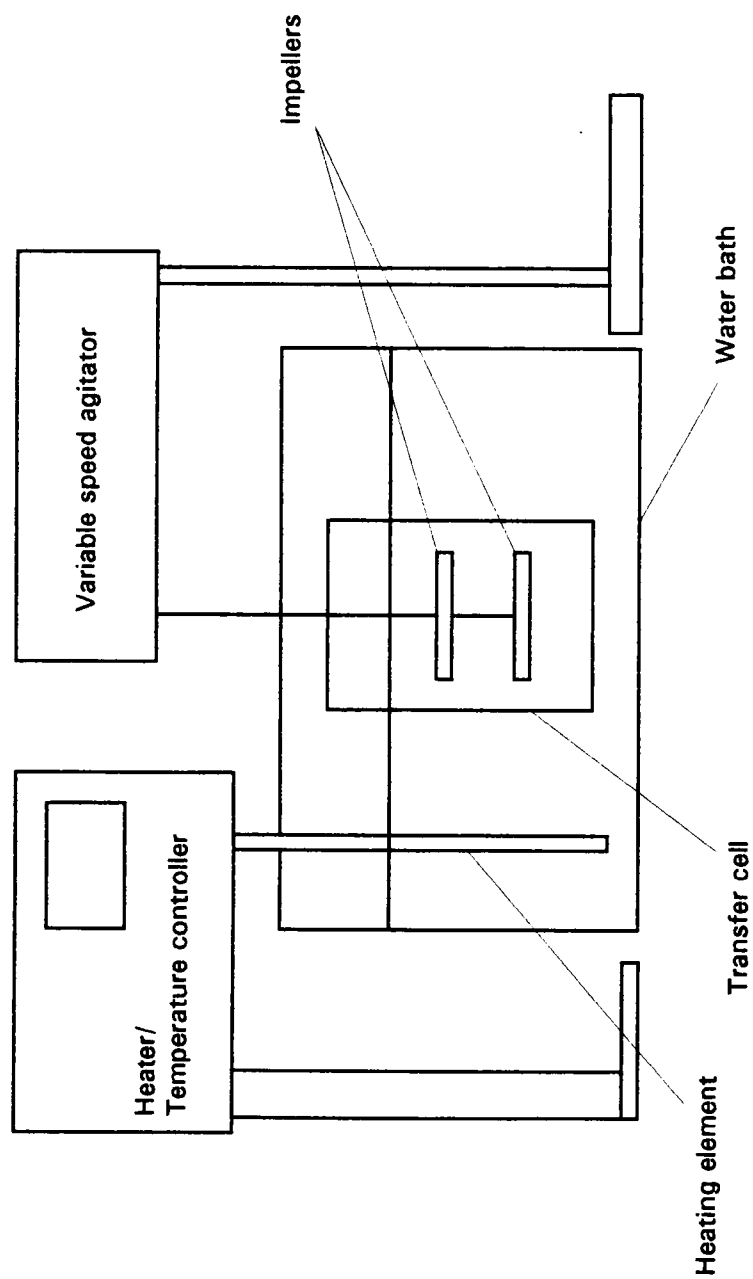


Figure 3.1 Lewis cell schematic.

3.4 Testing Program

3.4.1 Acetic Acid Transfer Experiment

The purpose of the first experiment was the determination of mass transfer coefficients for a non-reacting transfer system. Coefficients obtained could then be used to determine parameters needed to calculate film mass transfer coefficients for other chemical systems using diffusion mass transfer models (e.g. film, penetration, surface renewal models). The system acetic acid-water-isobutanol was selected for use in this experiment as it had been verified to undergo no reaction (Lewis, 1954b) and had been used successfully for the purpose of "calibrating" a Lewis cell previously (DeMuth (1989).

In the experiment performed in this study, transfer of acetic acid was always from the aqueous phase into the organic phase. The procedure for acetic acid transfer tests consisted of first establishing a steady bath temperature of 25°C. A capillary tube was then placed into the cell and suspended from the cell rim such that it extended to the bottom of the vessel near the cell wall. The two bulk phases were measured and placed into the mixing vessel, which was lowered into the temperature bath. The impellers were placed on the motor shaft and the shaft was lowered into the cell such that the impeller discs were equidistant from the interface at approximately one inch. After insertion, agitation of the phases was initiated at a speed of 100 rpm. This speed condition was maintained throughout all experiments, as it was found to provide good bulk phase mixing with a stable interface.

Once agitation was established, a premeasured volume of solute (acetic acid) was injected into the aqueous phase through the capillary tube by means of a syringe. Following insertion of the solute, samples were collected from both the aqueous and organic phase at intervals 30, 45, and 60 minutes. Aqueous phase samples were withdrawn using a syringe.

The needle attached to the syringe was inserted into the bulk aqueous phase through the capillary tubing suspended in the cell. Organic samples were removed directly from the top of the cell using a pipettor. Samples were limited to 3 ml in volume to minimize the change in bulk phase volume during each test.

In the acetic acid experiment the impeller diameters, interfacial area, and bulk phase volumes were varied, according to a half factorial experiment design. Based on the lack of chemical reaction in the acetic acid transfer process, individual phase volumes have no impact on the rate of transfer. However, these variables were included in the experimental design both to provide practice for the subsequent uranium transfer test and to generate error contrasts for use in the analysis of the data.

The procedure used during the experiment is presented in Appendix A.3.4.1.

3.4.2 Uranium Transfer Tests

The procedure for uranium transfer tests in the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$ was similar to that used for the acetic acid tests with only a few deviations. In the uranium transfer tests, bulk solutions were thoroughly mixed for a minimum of 15 minutes to pre-equilibrate the nitric acid in the system prior to introduction of the solute (uranyl nitrate). Pre-equilibration was performed to eliminate interference by HNO_3 co-extraction during the uranium transfer process. In addition, sample volumes collected during the uranium test were 5 ml versus 3 ml in the previous acetic acid test. The increase in volume was necessitated by the requirement to perform both uranium and nitric acid analyses. Finally, samples were withdrawn 20, 40, 80, 160, and 300 minutes after introduction of the uranyl nitrate solution spike. The experimental procedure used is presented in Appendix A.3.4.2.

3.4.3 Determination of the Reaction Rate Expression

Based on the stoichiometry of the solvation reaction described in equation (2-1), and in light of the considerable excesses of all reactants other than uranium in the transfer experiments performed, it seemed likely that the reaction rate should be described by a pseudo-first order expression. To test the validity of this assumption, an experiment was performed in which the effects of reactant concentrations on transfer rate was performed. Unlike the previously described transfer rate experiments, no physical system parameters were varied.

The detailed procedure for this experiment is located in Appendix A3.4.3.

3.5 Experiment Design

3.5.1 Distribution Coefficient Determinations

The preliminary (scoping) shakeout tests in which calcium nitrate was not present were multi-level two factor tests in which the factors were the initial aqueous phase concentrations of nitric acid and uranium. As a rule, two replications were performed for each treatment combination, although three replications were performed in some instances. Distribution coefficient determinations for the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$ were one-factor tests (aqueous phase calcium nitrate concentration) with two replications performed for each test condition.

3.5.2 Acetic acid and Uranium Transfer Tests

By definition, a full factorial experiment is one in which tests are performed for all possible treatment combinations. Two level factorial tests are commonly used to test the significance of specific test parameters (Anderson and McLean, 1974). If properly designed, 2^n

experiments will provide information regarding all main effects and all possible two-factor interactions.

Acetic acid and uranium transfer rate determinations were performed using half factorial experiments. For both the acetic acid and uranium transfer experiments, a total of five factors were investigated, with each factor having two test levels. Therefore, a full factorial experiment having only one experimental unit (result) per treatment combination would include 2^5 tests. Half-factorial experiments reduce the test program effort by 50%, as the number of treatment combinations used is cut in half. The benefit in the subject study is considerable, due to the cost associated with chemical analysis of samples and the time required to perform a test for a single treatment combination. (Test durations were approximately 2 hours for an acetic acid test, 6 hours for a uranium transfer test).

Acetic acid and uranium transfer experiments were randomized designs without blocking. The designs were randomized as the experiments were isolated from external variables (primarily temperature) throughout the testing period. Furthermore, no residual effects from previous treatments existed in subsequent contrasts as all tests were started from identical initial conditions. Hence, contrasts due to variations in these conditions are eliminated and contrasts observed are due only to changes in the treatment combinations. Any potential impact on the uranium transfer results due to the use of two different uranium spike solutions has been eliminated as the effects observed and analyzed (overall transfer coefficient) are derived from changes in concentration, not absolute concentration values. Furthermore, the spike solutions were added in proportions so as to produce equivalent initial aqueous phase concentrations, within experimental error.

3.5.3 Reaction Rate Expression Determination

The experiment performed to determine the order of the solvation reaction with respect to the individual reactant concentrations was of a completely randomized design for the same reasons as the transfer rate experiments. This experiment examined two factors (nitrate and uranium concentration) at three levels.

3.6 Statistical Analysis—Significance of Main and Interaction Effects

Determination of the significance of single and two-factor interaction effects on experimental contrasts was critical to this study, as it provides an indication of the relative importance of reaction and mass transfer in the removal of uranium from the aqueous phase. In addition, the significance of test parameters on experimental yields (transfer rates) allows determination of the location of the controlling mechanism. Factor significance in the transfer rate studies performed has been both by analysis of variance and by use of half normal plots.

3.6.1 Half Normal Plot Technique

The half-normal plotting technique developed by Daniel (1959) is a graphical means for evaluating data from two-level full and fractional factorial experiments. In addition to providing indications of the significance of experiment factors, half normal plots may give indication of bad data points, dependence of error variance on that data mean, and defective randomization. The technique allows the detection of a small number of effects or interactions in the presence of mostly error contrasts. A key capability of this analysis procedure is the ability to provide an error estimate without test replications or assumption that one or more treatment combinations are null.

According to Zahn (1975), the half normal plot technique has been widely accepted for analysis of two-level factorial experiments, and has resulted in an increased interest in graphical statistical methods. A search of the Science Citation Index and Statistics and Probability Citation Index by Tukey (1973) located 66 citations of the article by Daniel in the period from 1959 through 1973.

Based on the work by Daniel, Zahn has developed simplified techniques based on the work of Daniel, and has established corrected confidence interval guard rails. The procedure used in the subject work is described in detail in Appendix A.3.6.1.

3.6.2 Analysis of Variance

The subject of analysis of variance (ANOVA) was developed originally with the work of Fisher (1918, 1925, 1935). In general terms, ANOVA is the process of evaluating the relationships between several factors (or treatments) and a response variable. Like the half normal plot technique, ANOVA uses factor contrasts in the determination of significant effects. Application of ANOVA requires that an error estimate be made, either by replication of one or more treatment combinations or by assumption that one or more treatments are null (insignificant). Contrasts calculated from these null treatments must then represent error. Analysis of variance in the subject study has been performed primarily by application of the general linear model in the SAS statistical analysis software package (SAS Institute, Cary, North Carolina). A more detailed description of a typical ANOVA procedure is presented in Appendix A.3.6.2.

3.7 Analysis of Significance Results

In practice it is hard to make a clear determination that an extraction process falls into either the diffusion or kinetic regime. As a result, it is frequently necessary to model extraction processes in terms of both diffusion and chemical reaction contributions, which requires simultaneous solution of diffusion and reaction kinetic equations.

3.7.1 Criteria for Extraction Regime Determination

Criteria which may be used to distinguish between diffusional and kinetic regimes are 1), dependency of the rate of extraction on degree of mixing of the two phases, 2), comparison of stirring effects on heat transfer and mass transfer coefficients, and 3), evaluation of the activation energy of the extraction process (Danesi, 1980).

Applying criteria 1), increases in the rate of extraction corresponding to increases in agitation are indicative of diffusion control. Conversely, when the rate of transfer is independent of phase mixing, it is in some cases possible to assume that the extraction falls into the kinetic regime. The basis for stirring as a test criteria is the reduction of the diffusion layer thickness due to increased mixing, which shortens the diffusion path. It must be noted that this criteria is not fool-proof and may lead to erroneous conclusions in some cases.

In applications involving constant interfacial area, a correlation between stirring and transfer rate is certainly an indication of diffusion control. Conversely, a lack of correlation between stirring and transfer rate is not necessarily an indication of kinetic control, as increased stirring speed may not necessarily result in a decreased film thickness due to loss of stirrer efficiency at higher speeds. In addition, the existence of any interfacial films produced by the

occurrence of side reactions can result in significant diffusion resistances which are unaffected by the degree of agitation.

In vigorously stirred systems, observed increases in the rate of extraction in response to stirring rate increases may result from enhancing the dispersion (creating more interfacial area), rather than decreasing the diffusion layer thickness. Also, in highly agitated systems the lack of correlation between stirring and extraction rates does not necessarily indicate kinetic control, as at high stirring speeds the number of droplets in the dispersion may become constant. It therefore seems that highly agitated systems are to be avoided when attempting to evaluate extraction mechanisms, due to the high level of ambiguity of the results.

Applying the second criteria, similar linear relationships between the rate of agitation and the mass and heat transfer coefficients is indicative of diffusion-regime extraction. The limitation to applying this criteria lies in the experimental difficulty in measuring the heat transfer coefficient and the problem of separating out the heat effect for the specie of interest in multi-component systems (Danesi, 1980).

Using the third criteria, observation of an activation energy which is higher than is generally observed for diffusion-controlled processes may be indicative of kinetic-regime transfer. Application of this criteria is problematic as activation energies associated with solvation reactions are typically small (on the order of a few kcal/mol), hence activation energies associated with kinetic regime extractions differ little from those exhibited by diffusion-controlled extractions. In addition, activation energies are commonly determined by observing the rate of extraction at various temperatures. Inaccuracies in activation energy determinations due to temperature induced variations in both diffusion rates and chemical

equilibrium make distinction between diffusion and kinetic regimes by this method unrealistic (Danesi, 1980).

Danesi recommends use of a constant interfacial area cell (such as a Lewis cell) in which the bulk phase stirring rates can be varied as the best approach to identifying extraction regimes. Danesi reports that the initial rate of extraction determined in these devices is always found to be a linear function of the aqueous phase stirring speed. This is because the thickness of the diffusion layer at low stirring speeds is such that diffusion processes predominate initially, even in cases in which slow heterogeneous (interfacial) or homogeneous (bulk phase) reactions occur. Therefore, while a diffusion regime process always exhibits a linear relationship between initial flux and stirring speed, such a relationship should not preclude consideration of the kinetic regime.

Chemical reactions which control the extraction kinetics may occur either at the interface or in either of the bulk phases. Distinction between heterogeneous (interfacial) and homogeneous (bulk phase) reactions can be made by evaluating the dependence of the initial extraction rate on both the volume of the bulk phase from which the solute is being extracted and the interfacial area.

Danesi proposes that bulk phase reactions will exhibit no dependence on either the phase volume or the interfacial area. Conversely, the rate of solute disappearance from a phase by interfacial reaction will be directly proportional to the interfacial area and inversely proportional to the volume of the bulk phase. The direct relationship between area and extraction rate $-dC/dt$ is due to the increased number of molecules crossing the interface, while the inverse relationship between $-dC/dt$ and volume results from "dampening" of the concentration change due to the increase in solute molecules available for transfer.

Commonly, the dependence of the rate of transfer on phase volume and interfacial area is evaluated in terms of the specific interfacial area, defined as the ratio of interfacial area to bulk phase volume. Extraction processes occurring in the kinetic regime are indicated by a linear relationship between the initial rate of transfer and the specific interfacial area. Testing performed to evaluate the relationship between extraction rate and specific interfacial area must be designed to provide constant hydrodynamic conditions. As both the volume and interfacial area may affect hydrodynamics, neither can be varied over too wide a range.

3.7.2 Methods Used for Determination of Extraction Regime

For uranium transfer, determination of the extraction regime was made by evaluating the effects of interfacial area, bulk phase volumes, and agitator impeller diameters on the extraction rate after the method suggested by Danesi (1980). As no reaction occurs in the transfer of acetic acid from water to isobutanol, only the impeller diameters, interfacial area, and interaction effects on transfer rate were evaluated. Impeller diameter changes were used to alter phase agitation instead of impeller speed as any significant increase in impeller speed above that needed to obtain well-mixed bulk phases was found to result in interfacial turbulence. In addition, the single shaft configuration of the test apparatus used precluded control of agitation of the individual phases by varying the agitator speed.

3.8 Reagents Used

Dibutyl Carbitol (a.k.a. diethylene glycol dibutyl ether, carbitol) used in testing was of ACS (American Chemical Society) reagent grade as obtained from the Aldrich Chemical Company (Milwaukee, Wisconsin), Aldrich catalog number 20,562-1. DBC was received in

darkened 1-liter bottles sealed under nitrogen, and was stored unopened in sealed, dark storage cabinets to prevent photochemical decomposition to peroxides.

Isobutanol (2-methyl 1-propanol) of ACS reagent grade was used as received from both the Aldrich Chemical Company (Milwaukee, Wisconsin, catalog number 32,004-8) and the Eastman Kodak Company (Rochester, NY, catalog number 116-6339).

Nitric acid (15.8M, ACS grade) and glacial acetic acid (ACS reagent grade, aldehyde free) were purchased from the J. T. Baker Company (Phillipsburg, NJ, catalog numbers 9601-33 and 9508-02, respectively), and were used as received.

All water used in testing was demineralized, then deionized and stripped of organic contaminants by being passed through an ion exchange column (SYBRON/Barnstead "Ultrapore," Barnstead Company Division of SYBRON Corporation, Boston MA).

Calcium nitrate solutions were produced by dissolving ACS reagent grade calcium nitrate tetrahydrate, which was procured from J.T. Baker.

3.9 Chemical Analysis Methods

3.9.1 Organic Phase Uranium Concentration Determination

Uranium determination in organic solutions (i.e. DBC) was by a spectrophotometric method using dibenzoylmethane, which is a sensitive spectrophotometric reagent for uranium. The method used is accurate for total uranium determination over a wide range of concentrations from the ppm level to > 100 g/L.

In the method an aliquot of the uranium solution is taken such that the estimated total uranium mass falls in the range 0.010 to 500 μg uranium. Aliquots of pyridine and

dibenzoylmethane are added to the uranium solution to develop a yellow color. The sample is then read on a spectrophotometer at a wavelength of 416 nM against a reagent blank.

Indications using this method are susceptible to interferences from chromium, iron, and other heavy metals. These interferences are mitigated when uranium has been selectively extracted into the organic phase from aqueous solutions.

3.9.2 Free H^+ Determination by Standard Base Titration

Routine determination of free hydrogen ion concentration in both aqueous and organic solutions was performed by first pipetting an aliquot of the solution to be analyzed into a sodium fluoride/potassium oxalate solution to complex any heavy metals present, thus preventing hydrolysis from occurring. Bromothymol blue is then added as an end-point indicator, and the acid sample is neutralized with a standard sodium hydroxide solution. There are no known interferences to the analysis method.

3.9.3 Determination of Uranium at Low Concentrations in Aqueous Solutions

The Arsenazo III method used is applicable to aqueous solutions containing uranium at concentrations less than 100 μ g/mL. In the procedure, a sample aliquot is treated with a solution of zinc metal in hydrochloric acid. The treated aliquot is then spiked with Arsenazo III, which reacts spectrophotometrically with the sample. The aliquot is then read using a spectrophotometer at a wavelength of 665 nM against a reagent blank.

4. THEORETICAL

Determination of the transfer regime for the chemical system under study was made by evaluation of the effect of variation of test apparatus parameters on the rate of uranium transfer. Indications of controlling regime based on comparison of observed overall transfer rates (calculated from test data) with predicted aqueous and organic film coefficients have also been considered. Development of a model describing transient mass transfer in a system in which chemical reaction takes place also requires determination of the reaction rate expression and reaction rate constant.

The overall experimental program was described in Section 3 of this document. Determination of the applicable extraction regime and of the location of the controlling resistance has been made by evaluating the significance of system parameters on the rate of solute transfer. Transfer rates used for this evaluation have been calculated using expressions presented in Section 4.2.

In addition to analyzing system parameters effects to determine the transfer regime, observed overall uranium transfer coefficients have been compared with film coefficients to determine if the resistance to uranium transfer can be equated to that in a single film layer.

Transfer rate data for the system acetic acid-water- isobutanol has been used to calculate overall transfer coefficients for the non-reacting system using equations presented in Section 4.2. These coefficients have been used to calculate film coefficients for the non-reacting system using the expression derived in Section 4.1. The film coefficients obtained have been used to "calibrate" the transfer device used, by allowing determination of the

proportionality constant p which appears in the turbulent mass transfer model of Bulicka and Prochazka as described in Section 4.3.

Having calibrated the cell using a non-reacting chemical system, the Bulicka model was used to calculate film coefficients for the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$. These coefficients have been compared with observed aqueous- and organic-phase based overall transfer coefficients, which were calculated using expressions derived in Section 4.2.

Finally, modeling a kinetic or diffusion-kinetic transfer process requires the determination of reaction rate constants, in accordance with the rate expression presented in Section 4.4.

4.1 Relationship Between Overall and Film Coefficients

Use of the model of Bulicka (1972) to determine film coefficients in a Lewis cell requires the determination of film coefficients for a mass transfer system in which chemical reaction does not occur. The film coefficients determined are used to calculate an apparatus-specific proportionality constant, which may then be used to calculate diffusion-only film coefficients for systems other than that which was used to "calibrate" the cell.

In the limiting case diffusion transfer regime, it is likely that the rate at which a component transfers between two phases is controlled by the rate of diffusion through a stagnant film layer located on one side of the phase boundary. In the case of extraction controlled by the rate of solute diffusion through an aqueous film, the calculated overall transfer coefficient K_a should be closely approximated by the aqueous film coefficient k_a , as the organic film coefficient is relatively insignificant in this case. For diffusion-regime transfer controlled

by resistance in the organic film, the organic phase-based transfer coefficient K_o should be approximately equal to the organic film coefficient k_o .

In the present study, transfer of acetic acid from water into isobutanol was used for cell calibration. As reported in Section 2, transfer of the solute in this chemical system has been found to be the result of diffusion alone. Overall transfer coefficients for this system have been calculated by the method described in Section 4.2. On the basis that the rate of acetic acid transfer is found to be controlled predominantly by diffusion through one film layer, calculation of film coefficients from the overall coefficients can be performed using the expressions derived below.

In terms of concentration, the steady state flux equation is

$$N_A = k_a (C_{A,a}^b - C_{A,a}^i) = k_o (C_{A,o}^i - C_{A,o}^b) = K_a (C_{A,a}^b - C_{A,a}^*) \quad (4-1)$$

where $C_{A,a}^*$ is the equilibrium aqueous phase concentration of the transferring component corresponding to the concentration of the component in the bulk organic phase,

$$C_{A,o}^b = K_d C_{A,a}^* \quad (4-2)$$

By definition, the concentrations in the two phases at the interface are related to one another using the distribution coefficient, according to the expression

$$C_{A,o}^i = K_d C_{A,a}^i \quad (4-3)$$

Equation (4-1) can be reduced by rearranging to obtain the equality

$$\frac{1}{K_a} = \frac{(C_{A,a}^b - C_{A,a}^*)}{k_a (C_{A,a}^b - C_{A,a}^i)}, \quad (4-4)$$

which is expanded to

$$\frac{1}{K_a} = \frac{(C_{A,a}^b - C_{A,a}^*)}{k_a (C_{A,a}^b - C_{A,a}^i)} = \frac{(C_{A,a}^b - C_{A,a}^i) + (C_{A,a}^i - C_{A,a}^*)}{k_a (C_{A,a}^b - C_{A,a}^i)}. \quad (4-5)$$

Separating terms and substituting,

$$\frac{1}{K_a} = \frac{1}{k_a} + \frac{(C_{A,a}^i - C_{A,a}^*)}{k_a (C_{A,a}^b - C_{A,a}^i)} = \frac{1}{k_a} + \frac{\frac{1}{K_d} (C_{A,o}^i - C_{A,o}^b)}{k_a (C_{A,a}^b - C_{A,a}^i)}. \quad (4-6)$$

From equation (4-1),

$$(C_{A,o}^i - C_{A,o}^b) = \frac{k_a (C_{A,a}^b - C_{A,a}^i)}{k_o}, \quad (4-7)$$

so

$$\frac{1}{K_a} = \frac{1}{k_a} + \frac{\frac{1}{K_d} \frac{k_a (C_{A,a}^b - C_{A,a}^i)}{k_o}}{k_a (C_{A,a}^b - C_{A,a}^i)} = \frac{1}{k_a} + \frac{1}{K_d k_o} \quad (4-8)$$

Similarly, in terms of organic phase accumulation

$$N_A = k_a (C_{A,a}^b - C_{A,a}^i) = k_o (C_{A,o}^i - C_{A,o}^b) = K_o (C_{A,o}^* - C_{A,o}^b). \quad (4-9)$$

From the definition of K_d ,

$$C_{A,o}^* = K_d C_{A,a}^b \quad (4-10)$$

Rearranging (4-9)

$$\frac{1}{K_o} = \frac{(C_{A,o}^* - C_{A,o}^b)}{k_o (C_{A,o}^i - C_{A,o}^b)}, \quad (4-11)$$

and expanding,

$$\frac{1}{K_o} = \frac{(C_{A,o}^* - C_{A,o}^b)}{k_o (C_{A,o}^i - C_{A,o}^b)} = \frac{(C_{A,o}^* - C_{A,o}^i) + (C_{A,o}^i - C_{A,o}^b)}{k_o (C_{A,o}^i - C_{A,o}^b)}. \quad (4-12)$$

Separating terms and substituting,

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{(C_{A,o}^* - C_{A,o}^i)}{k_o (C_{A,o}^i - C_{A,o}^b)} = \frac{1}{k_o} + \frac{K_d (C_{A,a}^b - C_{A,a}^i)}{k_a (C_{A,a}^b - C_{A,a}^i)}, \quad (4-13)$$

which reduces to the expression

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{K_d}{k_a} \quad (4-14)$$

4.2 Calculation of Overall Mass Transfer Coefficients

Determination of overall transfer coefficients for the non-reacting system in this study is necessary to obtain film coefficients from which the proportionality constant for the Bulicka model can be calculated. The model can then be used to calculate film coefficients for other chemical systems, including those in which chemical reaction occurs simultaneously with diffusion mass transfer.

From the expanded definition of overall mass transfer coefficient

$$\frac{-V_a}{S} \frac{dC_a}{dt} = K_a (C_a^b - C_a^*) \quad (4-15)$$

on an aqueous phase basis, and for the organic phase

$$\frac{V_o}{S} \frac{dC_o}{dt} = K_o (C_o^* - C_o^b), \quad (4-16)$$

where the sign conventions indicate that the transferring component is being depleted in the aqueous phase and accumulated in the organic.

Recalling the earlier definition of the distribution coefficient, and with an initial material balance expression (time $t = 0$, no solute transferred to the organic phase)

$$V_a C_{a(0)} = V_a C_a + V_o C_o, \quad (4-17)$$

an expression can be developed that permits calculation of the overall coefficients from the initial solute concentration and transient concentration

$$\frac{dC_a}{dt} = \frac{-S}{V_a} K_a (C_a^b - C_a^*) = \frac{-S}{V_a} K_a (C_a^b - C_o^b / K_d). \quad (4-18)$$

From the material balance

$$\frac{V_a}{V_o} (C_{a(0)} - C_a) = C_o \quad (4-19)$$

$$\frac{dC_a}{dt} = \frac{SK_a}{-V_a} \left(C_a^b - (1/K_d)(V_a/V_o) [C_{a(0)} - C_a] \right). \quad (4-20)$$

Defining a group

$$(1/K_d)(V_a/V_o) = X' \quad (4-21)$$

equation (4-14) becomes

$$\begin{aligned}
\frac{dC_a}{dt} &= \frac{SK_a}{-V_a} [C_a - X'(C_{a(0)} - C_a)] \\
&= \frac{SK_a}{-V_a} [(1 + X')C_a - X'C_{a(0)}] .
\end{aligned} \tag{4-22}$$

Rearranging to solve for C_a by integration

$$\int \frac{dC_a}{[(1 + X')C_a - X'C_{a(0)}]} = \int \frac{SK_a}{-V_a} dt . \tag{4-23}$$

Integration yields

$$\frac{SK_a t}{-V_a} = \left| \frac{1}{1 + X'} \ln[(1 + X')C_a - X'C_{a(0)}] \right|_{C_{a(0)}}^{C_a}$$

$$\frac{SK_a t}{-V_a} = \frac{1}{1 + X'} \ln[(1 + X')C_a - X'C_{a(0)}] - \frac{1}{1 + X'} \ln[(1 + X')C_{a(0)} - X'C_{a(0)}]$$

$$\frac{SK_a t}{-V_a} = \frac{1}{1 + X'} \langle \ln[(C_a + X'C_a) - X'C_{a(0)}] - \ln[C_{a(0)}] \rangle . \tag{4-24}$$

Rearranging

$$\frac{SK_a t}{-V_a} = \frac{1}{1 + X'} \ln \left\langle \frac{[(1 + X')C_a - X'C_{a(0)}]}{[C_{a(0)}]} \right\rangle = \frac{1}{1 + X'} \ln \left\langle \frac{[(1 + X')C_a]}{[C_{a(0)}]} - X' \right\rangle . \tag{4-25}$$

Defining

$$Y' = \frac{(1+X')SK_a t}{-V_a}, \quad (4-26)$$

then

$$Y' = \ln \left\langle \frac{[(1+X')C_a]}{[C_{a(0)}]} - X' \right\rangle \quad (4-27)$$

and

$$\exp(Y') = \frac{(1+X')C_a}{C_{a(0)}} - X', \quad (4-28)$$

$$C_a = \frac{C_{a(0)}[\exp(Y't) + X']}{(1+X')} \quad (4-29)$$

and

$$\begin{aligned} K_a &= \frac{-Y'V_a}{St(1+X')} = \frac{-V_a}{St(1+X')} \ln \left[\frac{(1+X')C_a}{C_{a(0)}} - X' \right] \\ &= \frac{-V_a}{St[1 + (1/K_d)(V_a/V_o)]} \ln \left[\frac{(1 + (1/K_d)(V_a/V_o))C_a}{C_{a(0)}} - (1/K_d)(V_a/V_o) \right]. \end{aligned} \quad (4-30)$$

This solution is consistent with that presented by DeMuth, and has been verified at the limiting conditions $t = 0$, (at which $C_a = C_{a(0)}$), and $t = \infty$.

Solving for K_a on the basis of the organic phase solute concentration,

$$\frac{V_o}{S} \frac{dC_o}{dt} = K_a (C_a^b - C_o^b / K_d), \quad (4-31)$$

and from the material balance equation (4-11)

$$C_a = \frac{V_a C_{a(0)} - V_o C_o}{V_a} = C_{a(0)} - \frac{V_o C_o}{V_a} \quad (4-32)$$

Rearranging

$$\begin{aligned} \frac{dC_o}{dt} &= \frac{SK_a}{V_o} (C_{a(0)} - \frac{V_o}{V_a} C_o^b - C_o^b / K_d) \\ \frac{dC_o}{dt} &= \frac{SK_a}{V_o} \left[C_{a(0)} - C_o^b \left(\frac{V_o}{V_a} + \frac{1}{K_d} \right) \right] \end{aligned} \quad (4-33)$$

Combining terms,

$$X'' = \left(\frac{V_o}{V_a} + \frac{1}{K_d} \right) \quad (4-34)$$

$$\frac{dC_o}{dt} = \frac{SK_a}{V_o} (C_{a(0)} - C_o^b X''). \quad (4-35)$$

Separating terms and integrating

$$\int \frac{dC_o}{(C_{a(0)} - X'' C_o)} = \int \frac{SK_a}{V_o} dt \quad (4-36)$$

$$-\frac{1}{X''} \ln(C_{a(0)} - X''C_o) \Big|_0^{C_o} = \frac{SK_a t}{V_o} \quad (4-37)$$

$$\frac{-X''SK_a t}{V_o} = \ln \left[\frac{C_{a(0)} - X''C_o}{C_{a(0)}} \right] = \ln \left[1 - \frac{X''C_o}{C_{a(0)}} \right], \quad (4-38)$$

then

$$K_a = \frac{V_o}{-X''St} \ln \left[1 - \frac{X''C_o}{C_{a(0)}} \right]. \quad (4-39)$$

Again, the resulting solution is consistent with that of DeMuth, and has been checked at the boundary conditions $t = 0$ and $t = \infty$.

In a similar manner, the overall coefficient based on the organic phase flux is derived.

Solving based on the organic phase solute concentration

$$\frac{V_o}{S} \frac{dC_o}{dt} = K_o(K_d C_a^b - C_o^b). \quad (4-40)$$

Substituting for C_a from equation (4-32) and rearranging

$$\frac{dC_o}{dt} = \frac{SK_o}{V_o} \left[K_d \left[C_{a(0)} - \frac{V_o}{V_a} C_o^b \right] - C_o^b \right] \quad (4-41)$$

$$\frac{dC_o}{dt} = \frac{SK_o K_d}{V_o} \left[C_{a(0)} - C_o^b \left[\frac{V_o}{V_a} + \frac{1}{K_d} \right] \right]. \quad (4-42)$$

Combining terms as before,

$$X'' = \left[\frac{V_o}{V_a} + \frac{1}{K_d} \right] \quad (4-34)$$

$$\frac{dC_o}{dt} = \frac{SK_o K_d}{V_o} (C_{a(0)} - C_o^b X''). \quad (4-43)$$

Separating terms and integrating

$$\int \frac{dC_o}{(C_{a(0)} - X'' C_o)} = \int \frac{SK_o K_d}{V_o} dt \quad (4-44)$$

$$-\frac{1}{X''} \ln(C_{a(0)} - X'' C_o) \Big|_0^{C_o} = \frac{SK_o K_d t}{V_o} \quad (4-45)$$

$$\frac{-X'' SK_o K_d t}{V_o} = \ln \left[\frac{C_{a(0)} - X'' C_o}{C_{a(0)}} \right] = \ln \left[1 - \frac{X'' C_o}{C_{a(0)}} \right], \quad (4-46)$$

then

$$K_o = \frac{V_o}{-X'' K_d S t} \ln \left[1 - \frac{X'' C_o}{C_{a(0)}} \right]. \quad (4-47)$$

Overall mass transfer coefficient results are presented and discussed in Section 5.

4.3 Model of Bulicka and Prochazka – Extrapolation of Film Coefficients

In an extension of the surface renewal theory, Bulicka and Prochazka (1976) investigated the effect of forced turbulence on the rate of mass transfer between two liquid

phases. According to Bulicka, the case of mass transfer across free interfaces (i.e. phase boundaries) is complicated when either or both of the phases are in turbulent motion, due to transfer of fluid momentum across the interface. As a result of their work, Bulicka and Prochazka developed an expression describing diffusion mass transfer in a Lewis-type cell. This correlation can be used to determine film mass transfer coefficients once the value of a proportionality constant " p ," peculiar to the specific transfer apparatus is known. The value of the constant may be determined by performing mass transfer experiments on a non-reacting chemical system.

The work of Bulicka is based on the assumptions of Danckwerts (stated previously) that turbulence in the bulk liquid phases penetrates toward the phase boundary causing periodic exchange (renewal) of fluid elements at the interface. While models based on the penetration theory of Higbie assume the rate-controlling transfer mechanism is the unsteady molecular diffusion of liquid elements to the interface, approaches of Levitch (1962) and Davies (1972) are based on the assumption of steady molecular diffusion into a boundary layer.

Assumptions applied by Bulicka and Prochazka as the basis for their model are:

1. surface renewal takes place by the action of vortices throughout a phase.
2. The overall rate of mass transfer is controlled by unsteady diffusion into vortices of characteristic dimension λ_o and velocity $\bar{v}_o'$.
3. The turbulence in the cores of the phases are homogeneous.
4. The rate of boundary layer renewal is proportional to the characteristic frequency, $\bar{v}_o'/\lambda_o$, and the mass transfer within the boundary layer takes place by unsteady

diffusion with the initial concentration in a semi-infinite layer having an initial concentration equal to that in the bulk phase.

5. The total energy dissipation in the boundary layers in the two phases is equal to the sum of that caused by each phase in the absence of the other (i.e. in the absence of an interface), and the renewal frequency is the same in each phase.

Bulicka and Prochazka then define

$$\lambda_o = (\nu^3 / \varepsilon)^{1/4}; \quad \bar{v}_o' = (\varepsilon \nu)^{1/4}; \quad \theta = \frac{\lambda_o}{\bar{v}_o'} = \left(\frac{\nu}{\varepsilon} \right)^{1/2}. \quad (4-48)$$

Based on the assumption that the renewal rate is proportional to the characteristic frequency

$$k \propto \sqrt{D/\theta} = \sqrt{D(\varepsilon/\nu)^{1/2}}. \quad (4-49)$$

From the last assumption (additivity of the energy dissipations in the two boundary layers)

$$\varepsilon_{ib} \rho_i \lambda_{oi} + \varepsilon_{jb} \rho_j \lambda_{oj} = \varepsilon_i \rho_i \lambda_{oi} + \varepsilon_j \rho_j \lambda_{oj} \quad (4-50)$$

and

$$\theta_i = \theta_j, \quad (4-51)$$

and from the assumption of homogeneous turbulence in the bulk phases

$$\varepsilon \approx u^3 / l. \quad (4-52)$$

Combining the first, third, and fourth expressions

$$\varepsilon_i = v_i \frac{\varepsilon_{ib} \rho_i v_i^{1/2} + \varepsilon_{jb} \rho_j v_j^{1/2}}{\rho_i v_i^{3/2} + \rho_j v_j^{3/2}}, \quad (4-53)$$

and substituting into the second equation

$$k_i \propto \sqrt{D_i (\phi_{ij})} \quad (4-54)$$

$$\phi_{ij} = \frac{\varepsilon_{ib} \rho_i v_i^{1/2} + \varepsilon_{jb} \rho_j v_j^{1/2}}{\rho_i v_i^{3/2} + \rho_j v_j^{3/2}}, \quad (4-55)$$

where ϕ_{ij} represents the rate of surface renewal as a function of the physical properties and energy dissipation in both phases.

Bulicka and Prochazka offer the following form for expressing the mass transfer coefficient in a dimensionless expression

$$N_{Sh_i} \approx N_{Sc_i}^{1/2} N_{Re_i}^{3/4} \psi_{ij}, \quad (4-56)$$

where

$$\psi_{ij} = \left[\frac{1 + \left(\frac{u_j}{u_i} \right)^3 \frac{l_i}{l_j} \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{1/2}}{1 + \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{3/2}} \right]^{1/4} \quad (4-57)$$

The grouping ψ_{ij} describes the effect of turbulence in the j th phase on mass transfer within the i th phase and is referred to by Bulicka as the interaction factor. It then follows that

$$\phi_{ij} = \phi_{ji}, \text{ and } k_i / k_j = \sqrt{(D_i / D_j)}. \quad (4-58)$$

The expression developed indicates that for a given chemical system and apparatus geometry, the interaction factor is a function the ratio of the macrovelocities alone. When the geometry is unchanged, the dependence of the mass transfer coefficient (ergo the Sherwood number) is described by application of the appropriate power to the Reynolds number term.

Describing the macro velocity by the proportionality

$$u_i \propto n_i d_i, \quad (4-59)$$

and equating the impeller diameter to the characteristic cell dimension l

$$N_{Sh_i} = \rho N_{Sc_i}^{1/2} N_{Re_i}^{3/4} \left[\frac{1 + \left(\frac{nd_j}{nd_i} \right)^3 \frac{d_i}{d_j} \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{1/2}}{1 + \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{3/2}} \right]^{1/4} \quad (4-60)$$

Since the rotational speed n was maintained constant in all test conditions and in both phases at 100 rpm, $n/n_j = 1$ and (4-46) becomes

$$N_{Sh_i} = p N_{Sc_i}^{1/2} N_{Re_i}^{3/4} \left[\frac{1 + \left(\frac{d_j}{d_i} \right)^2 \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{1/2}}{1 + \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{3/2}} \right]^{1/4} \quad (4-61)$$

Rearranging,

$$p = N_{Sh_i} / \left\{ N_{Sc_i}^{1/2} N_{Re_i}^{3/4} \left[\frac{1 + \left(\frac{d_j}{d_i} \right)^2 \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{1/2}}{1 + \frac{\rho_j}{\rho_i} \left(\frac{v_j}{v_i} \right)^{3/2}} \right]^{1/4} \right\} \quad (4-62)$$

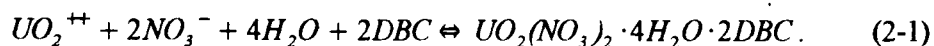
The value of p determined for a non-reacting system using equation (4-62) is substituted in equation (4-61) along with the applicable physicochemical properties to calculate film coefficients for mass transfer in the other chemical systems using the same apparatus.

4.4 Kinetic Regime Mass Transfer Modeling --Reaction Rate Expression

A wide ranging description of fairly complex models for mass transfer in the general diffusion-kinetic regime was presented in Section 2 of this report. However, results presented

and discussed in Section 5 indicate that the extraction of uranium into dibutyl carbitol in the system under study falls into the kinetic transfer regime. In addition, the results obtained indicate that only the concentration of uranium affects the rate of transfer. It is therefore expected that the rate of transfer will be accurately represented by a first-order rate expression.

The stoichiometry of the complexation reaction, as proposed by McKay is



An extensive search of literature located no information concerning the relationships between reactant concentrations and the rate of reaction. For the relatively low initial uranium concentrations applied in this study, negligible quantities of DBC, water, and HNO_3 are consumed in the reaction. It is therefore assumed that the concentrations of these components remain constant at their initial concentrations.

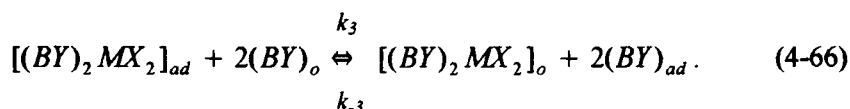
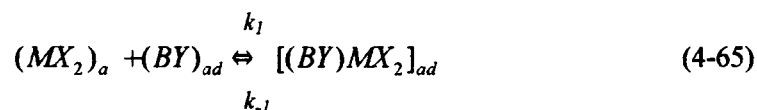
The effects of concentration were evaluated in a supplemental test as part of the experimental program. These tests are described in detail in Section 5. Based on the results of these tests, it is indicated that the rate dependency with $[UO_2^{++}]$ is first order, and the nitrate ion concentration has no significant effect on the rate of transfer. The reaction rate expression becomes

$$\frac{V_a d[UO_2^{++}]}{S dt} = k_f [UO_2^{++}] - k_r [UO_2(NO_3)_2 \cdot 4H_2O \cdot 2DBC]. \quad (4-63)$$

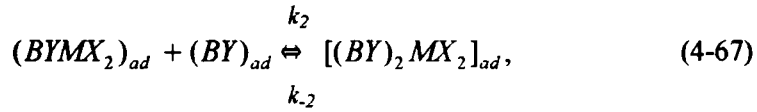
Additionally, due to the high distribution coefficients determined for the system of interest, and the low concentrations of the uranium species in the two phases, (4-63) may be further simplified by eliminating the expression for transfer in the reverse direction

$$\frac{V_a d[UO_2^{++}]_a}{S dt} = k_f [UO_2^{++}]_a \quad (4-64)$$

Based on a mechanism proposed by Danesi (1980) for extraction of a metal cation by a basic reagent, the following extension to transfer of the bivalent uranyl ion complexed with nitrate to the neutral extractant DBC is developed:



The first step represents the interfacial complexation of the undissociated metal species and the adsorbed extractant. The second expression represents desorption of the organometallic complex from the interface and its replacement with extractant molecules. The reaction steps described in equations (4-65) and (4-66) are both slow and rate controlling. An additional and intermediate step, described by the expression



is considered to occur instantaneously at the interface.

Equations (4-65) and (4-66) may be combined give an expression for $[(BY)_2MX_2]_{ad}$.

$$k_1[MX_2]_a[BY]_{ad} - k_{-1}[BYMX_2]_{ad} = k_3[(BY)_2MX_2]_{ad}[BY]_o^2 - k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2$$

$$k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2 = k_3[(BY)_2MX_2]_{ad}[BY]_o^2 + k_{-1}[BYMX_2]_{ad}$$

$$\frac{k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2 - k_{-1}[BYMX_2]_{ad}}{k_3[BY]_o^2} = [(BY)_2MX_2]_{ad}. \quad (4-68)$$

From the assumption that the reaction step described by (4-67) occurs instantaneously, thereby remaining essentially at equilibrium due to control by steps (4-65) and (4-66)

$$\frac{[(BY)_2MX_2]_{ad}}{[BYMX_2]_{ad}[BY]_{ad}} = K_e, \quad (4-69)$$

which is rearranged to give

$$[BYMX_2]_{ad} = \frac{[(BY)_2MX_2]_{ad}}{K_e[BY]_{ad}} \quad (4-70)$$

Substituting (4-70) into (4-68)

$$\frac{k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2 - k_{-1} \frac{[(BY)_2MX_2]_{ad}}{K_e[BY]_{ad}}}{k_3[BY]_o^2} = [(BY)_2MX_2]_{ad}$$

$$k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2 = \left[k_3[BY]_o^2 + \frac{k_{-1}}{K_e[BY]_{ad}} \right] [(BY)_2MX_2]_{ad}$$

$$[(BY)_2MX_2]_{ad} = \frac{k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2}{\left[k_3[BY]_o^2 + \frac{k_{-1}}{K_e[BY]_{ad}} \right]} \quad (4-71)$$

At steady state,

$$\frac{d[MX_2]}{dt} = \frac{d[(BY)_2MX_2]_{ad}}{dt} \quad (4-72)$$

As a result of the slow complexation reaction (4-65) at the interface, the concentration of the complex at the interface is always low, permitting the use of the steady state approximation.

Then

$$\frac{d[MX_2]}{dt} = \frac{S}{V_a} \left[\frac{k_3[BY]_o^2 \frac{k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2}{\left[k_3[BY]_o^2 + \frac{k_{-1}}{K_e[BY]_{ad}} \right]} - k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2 \right], \quad (4-73)$$

and for the transfer when k_1/k_{-1} is large (i.e. k_1 is small)

$$\begin{aligned} \frac{d[MX_2]}{dt} &= \frac{S}{V_a} \left[\frac{k_3[BY]_o^2 \frac{k_1[MX_2]_a[BY]_{ad} + k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2}{(k_3[BY]_o^2)}} - k_{-3}[(BY)_2MX_2]_o[BY]_{ad}^2 \right] \\ &= \frac{S}{V_a} k_1[MX_2]_a[BY]_{ad}. \end{aligned} \quad (4-74)$$

Substituting for the adsorbed solvent according to expression (2-71) with $[BY_2] = [S]$

$$\frac{d[MX_2]}{dt} = \frac{S}{V_a} k_1[MX_2]_a \chi_o, \quad (4-75)$$

which can be simplified by incorporating the Langmuir constant with the reaction constant

$$\frac{d[MX_2]}{dt} = \frac{S}{V_a} k_1 [MX_2]_a \quad (4-76)$$

4.5 Determination of Transfer Rate

As described in Section 2, Danesi (1980) recommends evaluation of system parameters on the transfer rate as a means of determining the extraction regime and the location of the controlling mechanism. The rate of transfer of the uranyl specie can be obtained by plotting concentration of uranium in either phase as a function of time and graphically estimating the slope, by calculating the rate using equation (4-33), or can be obtained by regressing the concentration data and differentiating the expression obtained. In the present study, graphical determination was not attempted as locating lines tangent to the concentration curve is somewhat subjective and therefore prone to error.

The most accurate method for calculating the rate utilizes the concentration data obtained directly from testing. However, this method allows determination of rates only for those points in the transfer process at which samples were collected. A desirable alternative method for rate determination is regression of the test data. The equation determined by the regression can then be differentiated, and the derivative form used to calculate the transfer rate at any point in time over which the regression is valid.

In the subject study transfer rates of both acetic acid and uranium have been determined directly using test data. An attempt to determine the rates by regression of the concentration data was made using the "LOGEST" exponential regression function included in the Excel

software package developed by the Microsoft Corporation. This statistical function generates a regression equation of the form

$$y = bm^x, \quad (4-77)$$

where m and b are regression constants, x is the independent variable, and y is the dependent variable (concentration). Substituting the transfer time t for the independent variable and the concentration C for the dependent variable, and differentiating to obtain the rate dC/dt yields the expression

$$\frac{dy}{dt} = \frac{dC}{dt} = b(m^t \ln m). \quad (4-78)$$

Unfortunately, the particular form of equation (4-77) did not result in model which fit the test data adequately, and the attempt to determine the transfer rate by this method was abandoned.

5.0 RESULTS AND DISCUSSION

Data obtained from the experimental program has confirmed the effectiveness of calcium nitrate salting in raising uranium distribution coefficients in the system $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 - H_2O - $\text{Ca}(\text{NO}_3)_2$ -DBC sufficiently to obtain efficient extraction of the solute (Section 5.1). The data obtained resulted in the selection of initial aqueous phase calcium nitrate and nitric acid concentrations (3.5*M* and 1.0*M*, respectively) suitable for application in the study performed.

Concentration data obtained for the transfer of acetic acid from water into isobutanol (a non-reacting system) have been used to calculate overall transfer and diffusion film coefficients (Section 5.2). Film coefficients obtained were subsequently used to determine the proportionality constant p used in the Bulicka model, which describes mass transfer in the Lewis cell apparatus (Section 5.3). This cell "calibration" is necessary in order to apply the model to systems in which diffusion mass transfer is accompanied by chemical reaction.

Evaluation of the effect of test apparatus parameters on the rate of solute transfer by the half normal plotting technique and by analysis of variance is discussed in Section 5.4. The results presented indicate that the rate of uranium transfer in the system $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 - H_2O - $\text{Ca}(\text{NO}_3)_2$ -DBC, and in the apparatus used, is controlled by chemical reaction kinetics.

In Section 5.5, the results of film coefficient calculations for the system $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 - H_2O - $\text{Ca}(\text{NO}_3)_2$ -DBC are reported and are compared to the "observed" overall uranium transfer coefficients K_a and K_o . Film coefficients for uranium transfer are significantly greater than the observed overall coefficient values, indicating that the rate of the extraction process is

controlled by a resistance other than those posed by diffusion through film layers. This conclusion supports the one reached from the analysis presented in Section 5.4.

Results of tests performed to determine the reaction rate expression are presented in Section 5.6. The rate expression derived was then used to determine a pseudo first-order reaction rate constant, needed to model transient solute transfer. Finally, in Section 5.7, transient concentration values predicted from the model have been compared to concentration data collected during the mass transfer experiment.

5.1 Equilibrium Determinations – Uranium Extraction

In a preliminary step, equilibrium determinations were made for the system $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 - H_2O -DBC in which the initial nitric acid concentration ranged from 1 to 8M. These scoping tests were performed at uncontrolled (ambient) temperature in an effort to obtain high extraction coefficients. A significant improvement in extraction was observed at the higher acid concentrations. However, as discussed in Section 2.0, the solvent used in these extractions may become unstable in the presence of high concentrations of HNO_3 . In addition, results of these experiments indicated significant concentrations of nitric acid in the extract. Co-extraction of HNO_3 is undesirable in practical applications due to the resultant difficulty in stripping the uranium from the solvent back into aqueous solutions.

Subsequently, extraction equilibrium determinations were performed in which calcium nitrate was added to the aqueous solution for salting purposes. Selection of calcium nitrate for use as a non-extracting salting agent was based on data reported by Farber et al. (1946). Distribution coefficient determinations were made under controlled temperature conditions at 25°C. Extraction efficiencies similar to those obtained under the PUREX process conditions

(Benedict et al., 1976) were obtained at aqueous phase calcium nitrate concentrations of approximately 3.5M (in 1M HNO₃). (The PUREX process has been used as a basis for comparison due to demonstrated efficient uranium extraction in a minimal number of equilibrium stages.) Uranium extraction coefficients obtained in the scoping studies and those determined using calcium nitrate for salting are presented in Figure 5-1. Nitric acid concentrations extracted by dibutyl carbitol as a function of nitrate concentration using only HNO₃, and a combination of calcium nitrate and 1M HNO₃ are presented in Figure 5-2. Data from which distribution coefficients were determined is presented in Appendix A5.1. Taken together, the results presented in Figures 5-1 and 5-2 indicate that high extraction efficiencies can be achieved through the addition of either nitric acid (at high concentrations) or calcium nitrate, and that distribution coefficient values for nitric acid are essentially unchanged by the addition of the non-extracting salting agent. As the HNO₃ distribution coefficients are similar in the two cases and the initial aqueous phase acid concentration is lower in the calcium nitrate-salted system, lower acid concentrations in the extract are achieved when the non-extracting salt is used.

5.2 Acetic Acid Mass Transfer Tests

Mass transfer tests in the Lewis cell for the non-reacting system water-acetic acid-isobutanol were performed in which acetic acid was transferred from the aqueous solution into isobutanol. These tests were performed to obtain data needed to characterize or "calibrate" the

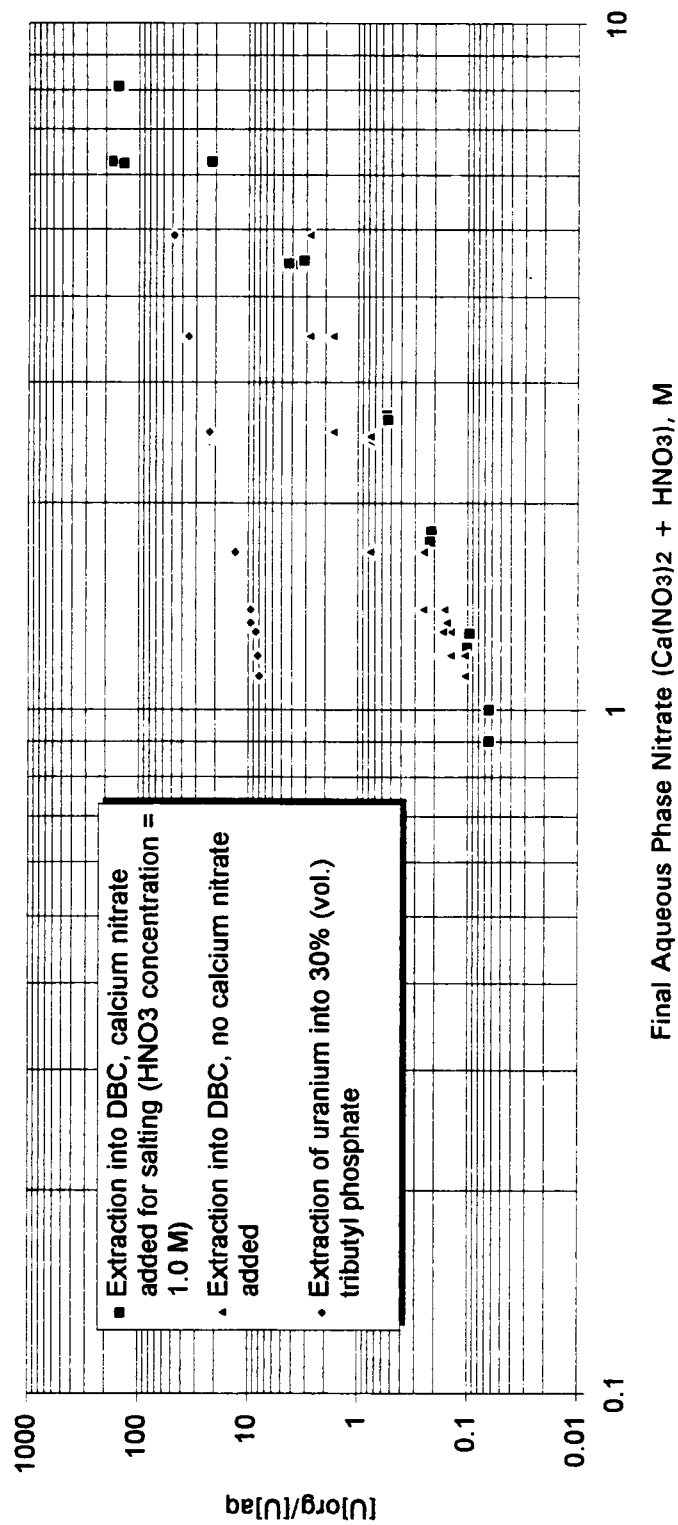


Figure 5-1. Nitrate salting effect on uranium distribution coefficient

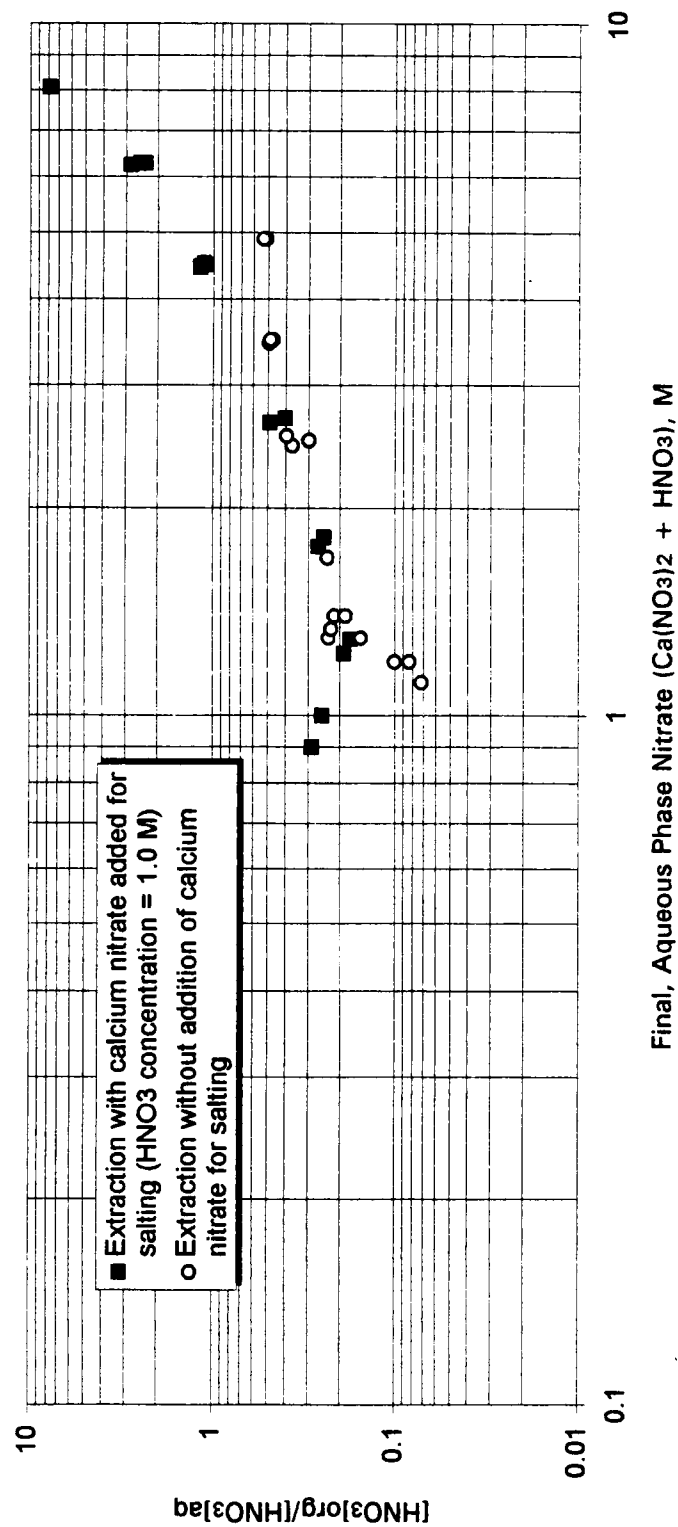


Figure 5-2. Nitrate salting effect on nitric acid distribution coefficient

transfer device, permitting determination of diffusion film coefficients for mass transfer in other chemical systems. Treatment combinations applied during testing are listed in Table 5.2A.

Overall coefficients were calculated based on organic phase acetic acid concentration results, using equation (4-39). The diffusion coefficient value used was taken from the report by DeMuth (1989), and was calculated using the Wilke-Chang correlation. The extraction coefficient used was regressed from literature data by DeMuth. Other properties required for the calculations were obtained from the literature.

Overall coefficients for acetic acid transfer were calculated using the Microsoft Excel spreadsheet software (Version 5.0). Spreadsheet results and the formulas used in the spreadsheet cells are presented in Appendix A5.2a. Results are summarized Table 5.2B.

To determine the location of the controlling diffusion resistance to acetic acid transfer, the significance of the impeller diameters in the two phases (d_a and d_o), the interfacial area (S), and of two-factor interactions on the rate of transfer were evaluated. This methodology is consistent in theory with that proposed by Danesi for determination of extraction regimes and their location (ref. Section 3.5). Transfer rates were calculated from test data using equation (4-33), and are presented in Table 5.2C.

In diffusion regime extractions, variation of the impeller diameters in the bulk phases is expected to result in changes in the thickness of the film layers or the surface renewal rates at the interface. Variation of impeller diameter was selected over variation of impeller speed (the latter being recommended by Danesi), as significant speed increases were found to result in rippling of the interface. A significant change in the rate of transfer in response to a change in the impeller diameter in the i th phase indicates controlling diffusion resistance in that phase. In the non-reacting system, correlation between the interfacial area and the rate of transfer serves

Table 5.2A. Acetic acid mass transfer test conditions.

Test Number	Aqueous Phase Volume, ml	Organic Phase Volume, ml	Aqueous Impeller diameter, cm	Organic Impeller diameter, cm	Interfacial area, cm ²
1	350	350	4.4958	4.4958	59.242
2	350	350	5.85978	5.85978	59.242
3	450	350	5.85978	4.4958	59.242
4	450	350	4.4958	5.85978	59.242
5	350	450	5.85978	4.4958	59.242
6	350	450	4.4958	5.85978	59.242
7	450	450	4.4958	4.4958	59.242
8	450	450	5.85978	5.85978	59.242
9	350	350	5.85978	4.4958	81.352
10	350	350	4.4958	5.85978	81.352
11	450	350	4.4958	4.4958	81.352
12	450	350	5.85978	5.85978	81.352
13	350	450	4.4958	4.4958	81.352
14	350	450	5.85978	5.85978	81.352
15	450	450	5.85978	4.4958	81.352
16	450	450	4.4958	5.85978	81.352

Table 5.2B. Overall transfer coefficients for acetic acid transfer from water to isobutanol.

Test No.	K_a			K_a average
	30 min	45 min	60 min	
1	0.001070093	0.001150671	0.001101545	0.001107436
2	0.001631039	0.001468726	0.001518553	0.001539439
3	0.001264763	0.001342682	0.001125977	0.001244474
4	0.001264763	0.001342682	0.001260122	0.001289189
5	0.001461295	0.001386658	0.001314755	0.001387569
6	0.001461295	0.001386658	0.001314755	0.001387569
7	0.001499929	0.001146043	0.001266446	0.001304139
8	0.001719064	0.001688595	0.001644547	0.001684068
9	0.001604329	0.001663847	0.001428315	0.001565497
10	0.001312772	0.001185278	0.001247885	0.001248645
11	0.00131099	0.001093276	0.001160804	0.001188357
12	0.001639914	0.001547739	0.001518999	0.001568884
13	0.001514685	0.001442835	0.00167227	0.001543263
14	0.001914857	0.001893379	0.002056952	0.001955063
15	0.00142771	0.001398639	0.001197589	0.001341313
16	0.001251853	0.001229665	0.001197589	0.001226369

Table 5.2C. Transfer rates for acetic acid transfer from water to isobutanol.

Test No.	dC_o/dt , mol/s			dC_o/dt average
	30 min	45 min	60 min	
1	4.95e-05	3.55e-05	2.74e-05	3.74e-05
2	5.53e-05	3.65e-05	2.40e-05	3.86e-05
3	4.46e-05	3.32e-05	2.48e-05	3.42e-05
4	4.46e-05	3.32e-05	2.45e-05	3.41e-05
5	4.56e-05	3.20e-05	2.32e-05	3.36e-05
6	4.56e-05	3.20e-05	2.32e-05	3.36e-05
7	3.98e-05	2.77e-05	2.17e-05	2.98e-05
8	4.16e-05	2.90e-05	2.05e-05	3.04e-05
9	5.47e-05	2.92e-05	1.92e-05	3.44e-05
10	5.57e-05	3.55e-05	2.19e-05	3.77e-05
11	4.92e-05	3.31e-05	2.25e-05	3.50e-05
12	4.97e-05	3.00e-05	1.85e-05	3.27e-05
13	4.80e-05	2.95e-05	1.55e-05	3.10e-05
14	4.63e-05	2.46e-05	1.13e-05	2.74e-05
15	4.28e-05	2.85e-05	2.05e-05	3.06e-05
16	4.16e-05	2.90e-05	2.05e-05	3.04e-05

merely as an indication of diffusion control, and does not provide an indication of the location of the resistance. The significance of volume effects has been discounted for the acetic acid transfer tests as no chemical reaction takes place and the bulk phases are thoroughly mixed. Contrasts calculated for volume effects and two-factor interactions which include volume may therefore be used for error estimation in the ANOVA procedure. The results of the ANOVA procedure for acetic acid transfer are presented graphically in Figure 5-3; computer output from which the figure was developed are located in Appendix A5.2b.

The results of the ANOVA presented in Figure 5-3 indicate significance of interfacial area on transfer rate at the first sampling at a probability level of approximately 60%. As the

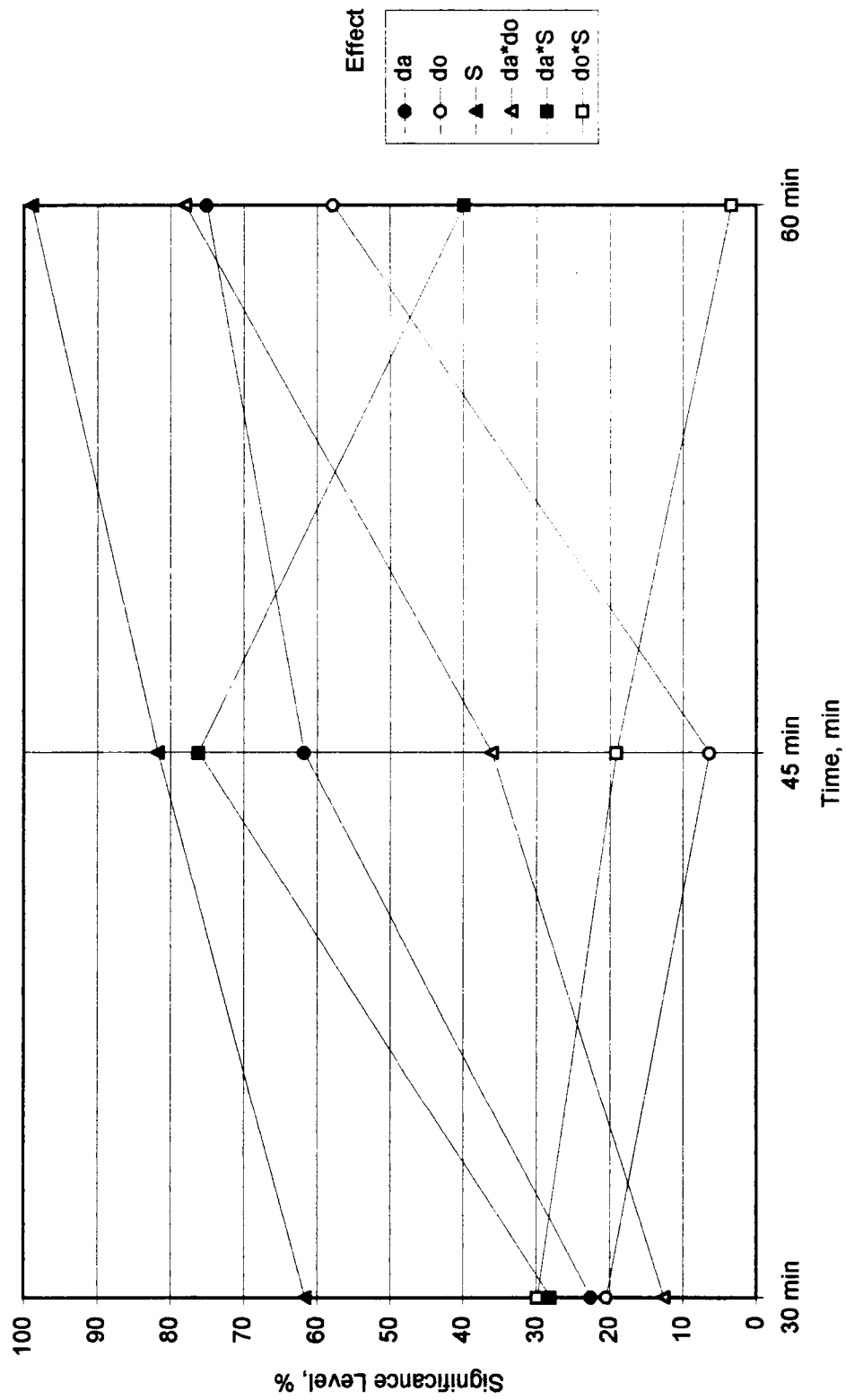


Figure 5-3. Results of ANOVA for acetic acid transfer

transfer continues, the level of significance of interfacial area increases to approximately 99% after one hour of transfer, and the probability that aqueous phase agitation (as controlled by impeller diameter) is significant reaches approximately 76%. The levels of interfacial area significance and the observed increase in significance probability with time indicate diffusion control (as expected in the absence of reaction), and also indicate increasing diffusion resistance as the concentration difference between the bulk phases decreases. The difference between significance probabilities for aqueous and organic phase impeller diameters at 60 minutes (76% versus 58%) provides some indication that aqueous film diffusion may exhibit more control on the rate of transfer than the resistance in the organic film. In addition, the aqueous impeller diameter effect has greater significance on the rate of transfer than the organic impeller diameter after 45 minutes of transfer (37% versus 7%), though neither probability is high enough to suggest any significant correlations with the solute transfer rate.

5.3 Determination of Coefficient for Correlation of Bulicka and Prochazka

Based on the indication of aqueous film diffusion control at 60 minutes, the aqueous film coefficient was determined by simplification of equation (4-8) to

$$\frac{1}{K_a} = \frac{1}{k_a} \text{ or } K_a = k_a. \quad (5-1)$$

Values of k_a obtained for the 16 treatment combinations after 60 minutes of transfer were substituted into the Sherwood number in equation (4-62) to obtain values of p . An average of these p -values (which are presented in Table 5.3) has been used in film coefficient

Table 5.3 Proportionality constants calculated from acetic acid transfer data.

Test No.	Proportionality constant, p
1	0.041123
2	0.049656
3	0.039832
4	0.042806
5	0.04651
6	0.044662
7	0.047279
8	0.053776
9	0.050528
10	0.042391
11	0.043335
12	0.049671
13	0.062429
14	0.067261
15	0.042366
16	0.040682
Mean	0.047769

determinations for the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$, as presented in Section 5.4. Details of the p calculations, which were performed using a spreadsheet, are presented in Appendix A5.3. In general, the calculated values for p derived from individual test results fall closely around the mean value. It is recognized that the use of equation (5-1) equating K_a with k_a is somewhat tenuous as the aqueous impeller diameter correlation is strong only at one observation time. However, the comparison of film coefficients with overall coefficients to determine the transfer mechanism is secondary to the results obtained by evaluation of system physical parameter effects on transfer rate, which provide a stronger basis for the conclusions reached.

5.4 Analysis of Uranium Transfer Rate Data

Uranium transfer testing to determine the extraction regime was performed in a manner similar to the acetic acid transfer experiment. However, the analysis differed as no a priori assumption could be made that bulk phase volumes were insignificant relative to the observed transfer rates. Test conditions applied in the uranium mass transfer tests are presented in Table 5.4A.

Overall transfer coefficients calculated from concentration data were inserted into equation (4-33) to calculate rates of organic phase uranium concentration change (transfer rates) which are presented in Table 5.4B. (The spreadsheet from which the transfer rates have been calculated is presented in Appendix A5.4a.) Organic phase transfer rates were used (as yields) to calculate contrasts used in the construction of half normal plots to test for effect significance, as described in Section 3.6.1 and Appendix A3.6.1. Transfer rates were also used to test for effect significance by analysis of variance.

Half normal plots from the transfer rate values are presented in Figures 5-4 through 5-7; calculation details are presented in spreadsheet form in Appendix A5.4b. The results of the half normal plots indicate the strongest relationship between the rate of transfer, and the main effects S (interfacial area) and V_o (organic bulk volume), and the $d_i S$ (aqueous impeller diameter - interfacial area) interaction effect. Analysis of variance was performed to further evaluate effect significance. The a priori assumption used in the ANOVA of acetic acid transfer data that volume effects are not significant cannot be applied to the $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O- Ca}(\text{NO}_3)_2\text{-DBC}$ system due to the possible significance of kinetic effects on the rate of uranium transfer. Instead, the interaction effects $V_o V_i$, $V_o d_i$, and $V_i d_i$ were assumed to be insignificant, and therefore represent error contrasts. The assumption that $V_i d_i$'s are

Table 5.4A. Treatment combinations for uranium mass transfer tests.

Test No.	Aqueous Phase volume, ml (V _a)	Organic Phase volume, ml (V _o)	Aqueous Impeller diameter, cm (d _a)	Organic Impeller diameter, cm (d _o)	Interfacial area, cm ² (S)	Initial Aqueous Phase U Conc., mg/l
1	350	350	4.4958	4.4958	59.242	1000
2	350	350	5.85978	5.85978	59.242	1000
3	450	350	5.85978	4.4958	59.242	1000
4	450	350	4.4958	5.85978	59.242	1000
5	350	450	5.85978	4.4958	59.242	1000
6	350	450	4.4958	5.85978	59.242	1000
7	450	450	4.4958	4.4958	59.242	1000
8	450	450	5.85978	5.85978	59.242	1000
9	350	350	5.85978	4.4958	81.352	1000
10	350	350	4.4958	5.85978	81.352	1000
11	450	350	4.4958	4.4958	81.352	1000
12	450	350	5.85978	5.85978	81.352	1000
13	350	450	4.4958	4.4958	81.352	1000
14	350	450	5.85978	5.85978	81.352	1000
15	450	450	5.85978	4.4958	81.352	1000
16	450	450	4.4958	5.85978	81.352	1000

Table 5.4B. Transfer rates for uranium extraction into dibutyl carbitol.

Test No.	dC_o/dt (mol/s) at 10 min	dC_o/dt (mol/s) at 20 min	dC_o/dt (mol/s) at 40 min	dC_o/dt (mol/s) at 80 min
1	6.27535E-07	4.94456E-07	3.61416E-07	2.42706E-07
2	2.72305E-07	3.00514E-07	3.02201E-07	2.65925E-07
3	3.07376E-07	3.17438E-07	3.17694E-07	2.76728E-07
4	7.036E-07	5.82664E-07	5.02426E-07	3.6916E-07
5	2.61386E-07	2.5213E-07	2.33652E-07	1.94967E-07
6	4.49947E-07	3.50138E-07	2.96147E-07	2.00044E-07
7	3.71503E-07	3.74997E-07	2.80048E-07	2.29991E-07
8	3.31758E-07	3.59603E-07	2.95338E-07	2.27346E-07
9	1.05797E-06	9.09386E-07	6.23202E-07	2.38843E-07
10	8.47147E-07	7.5035E-07	5.73781E-07	2.99483E-07
11	6.7799E-07	4.40057E-07	3.96229E-07	3.31785E-07
12	1.0032E-06	9.03083E-07	6.98484E-07	4.01417E-07
13	6.52431E-07	4.64558E-07	3.57937E-07	2.16945E-07
14	5.12404E-07	5.07819E-07	4.19855E-07	2.4082E-07
15	9.42192E-07	6.99892E-07	5.30173E-07	3.15696E-07
16	6.08616E-07	5.68488E-07	5.02656E-07	3.15245E-07

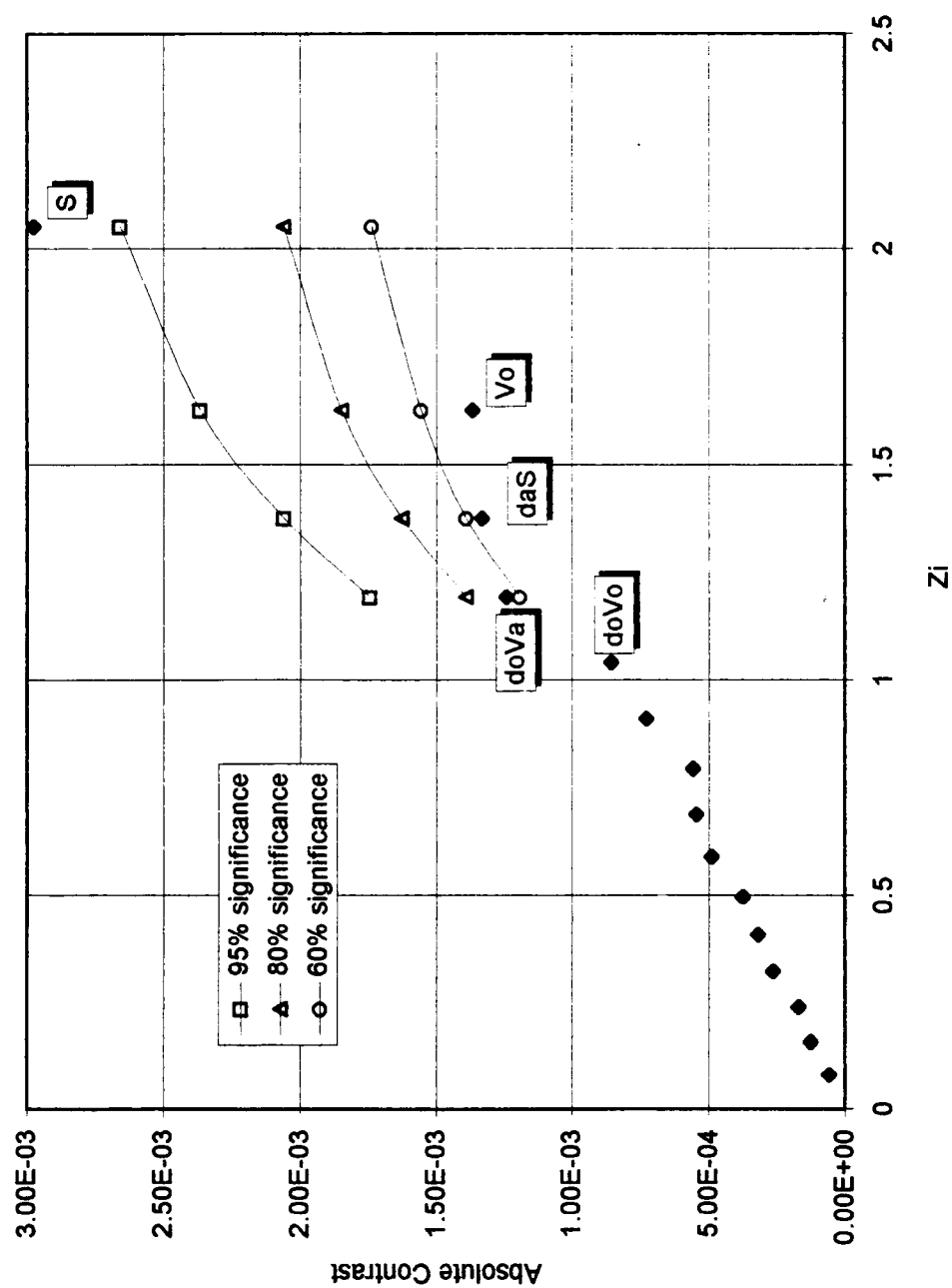


Figure 5-4. Half normal plot of uranium transfer rate after 10 minutes

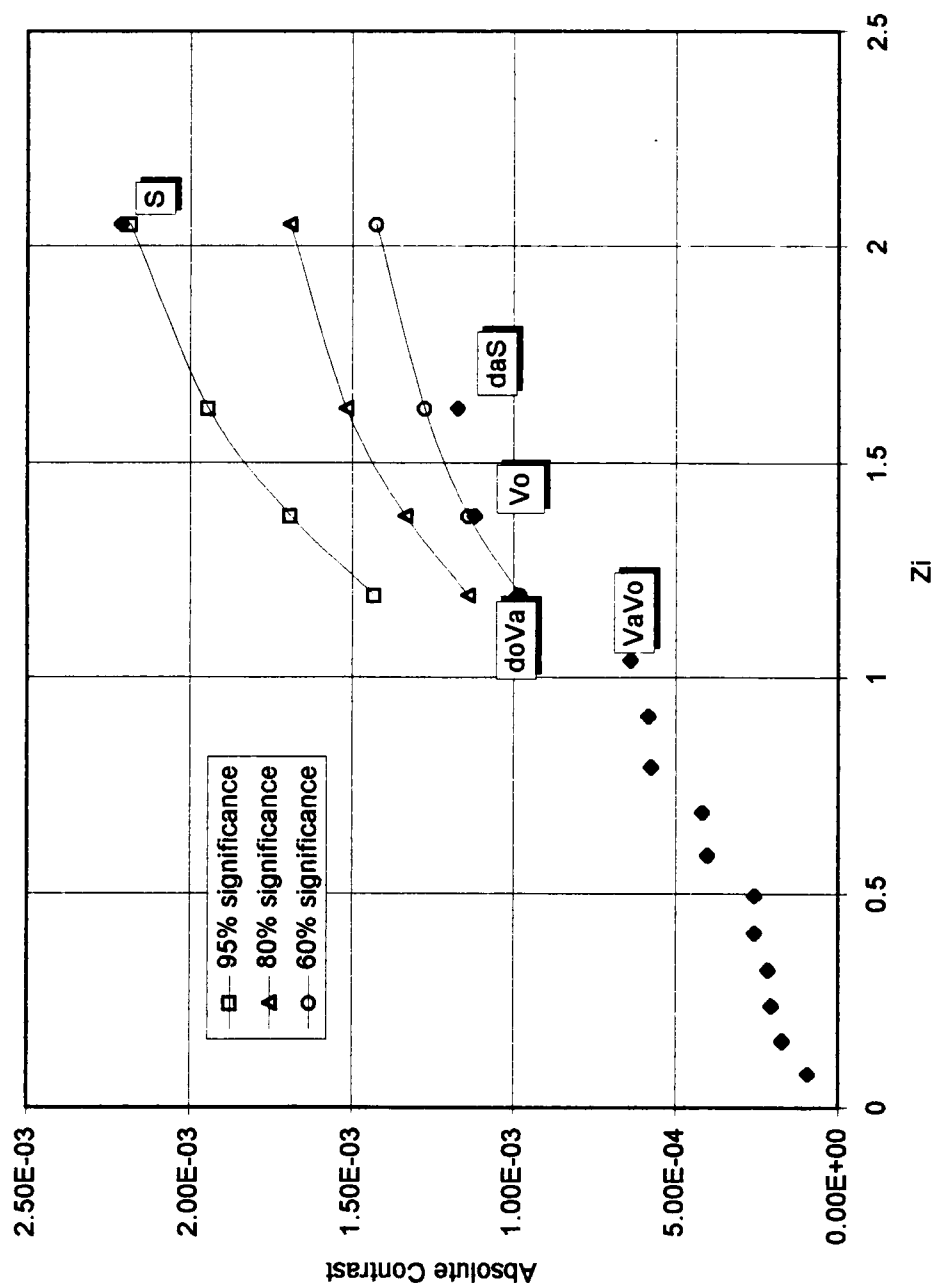


Figure 5-5. Half normal plot of uranium transfer rate after 20 minutes

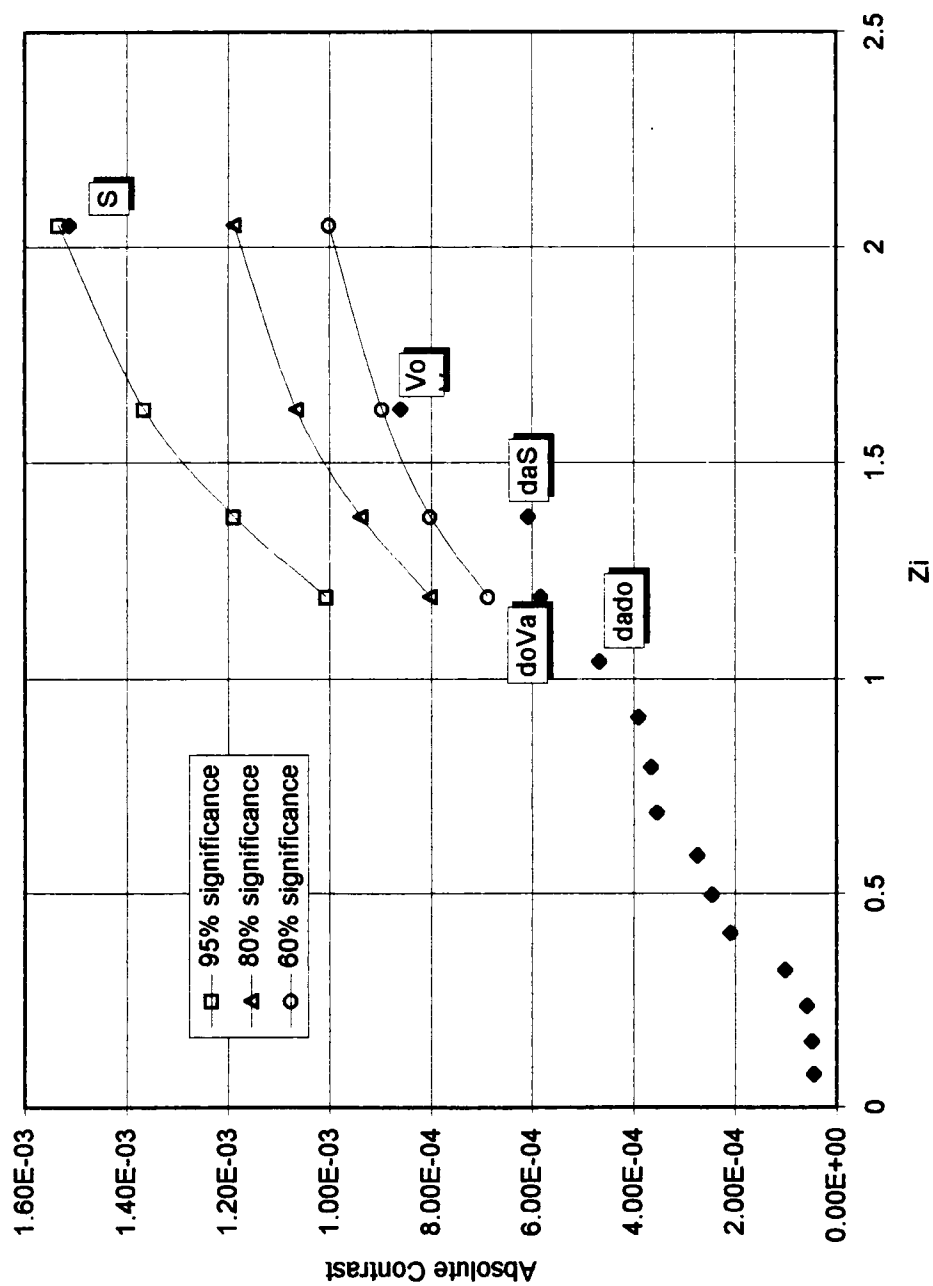


Figure 5-6. Half normal plot of uranium transfer rate after 40 minutes

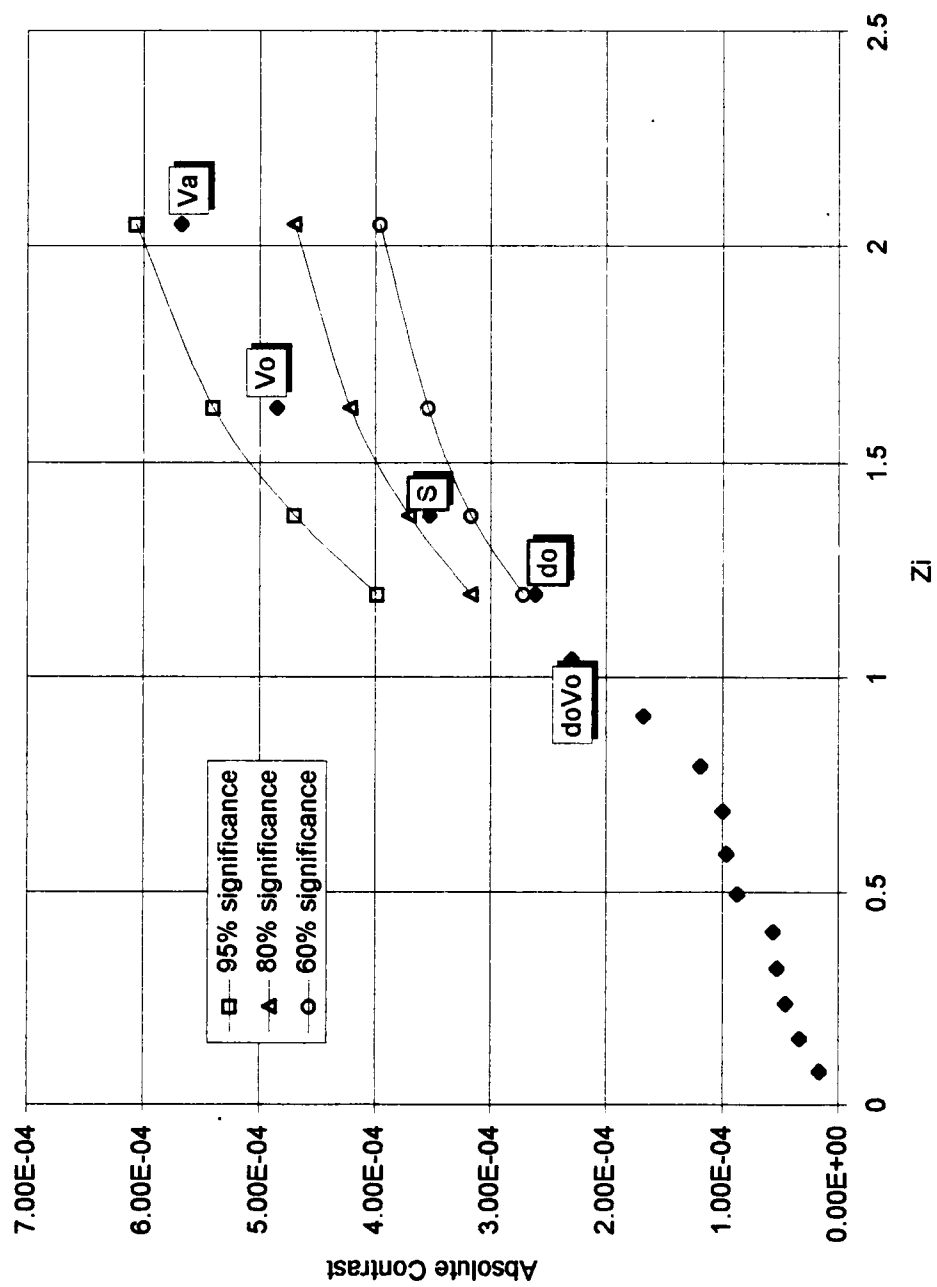


Figure 5-7. Half normal plot of uranium transfer rate after 80 minutes

insignificant is based on the observation that the bulk phases were thoroughly mixed, regardless of the diameter of the impeller present in the phase. The assumption that the $V_a V_o$ interaction generates a null contrast is based on the lack of either a physical or chemical relationship between these parameters vis a vis mass transfer between phases. The assumption in the ANOVA of uranium transfer data that these effects are null is supported by the results of the half normal plots in Figures 5-4 through 5-7. Complete results of the ANOVA are presented in Appendix A5.4c, and summarized graphically in Figure 5-8.

The results obtained from both the half normal plots and the ANOVA indicate the most significant effects on solute transfer rate are from interfacial area, organic phase volume, and the interaction effect of area and aqueous phase impeller diameter. Taken alone, the lack of a correlation between the rate of transfer and the impeller diameter in either phase does not indicate conclusively that the extraction process falls into the kinetic regime, due to the possible existence of a slip effect. However, determination of observed overall transfer coefficients which are consistently lower than film coefficients by an order of magnitude tends to exclude diffusion control, and supports the conclusion that the extraction process is controlled by kinetics.

From the reported solubility of DBC in water (McKay, 1952), it is estimated that the solvent is present in the bulk aqueous phase in near stoichiometric concentration with respect to uranium during the transfer tests. It is therefore likely that the solvation reaction occurs to some extent in the bulk aqueous solution. However, applying Danesi's criteria for evaluation of transfer regime (described in Section 3.7.1), the strong dependence of the transfer rate on interfacial area indicates that the source of kinetic control is not a bulk phase reaction. As explained by Danesi, no surface area effect on transfer rate is expected when a bulk phase

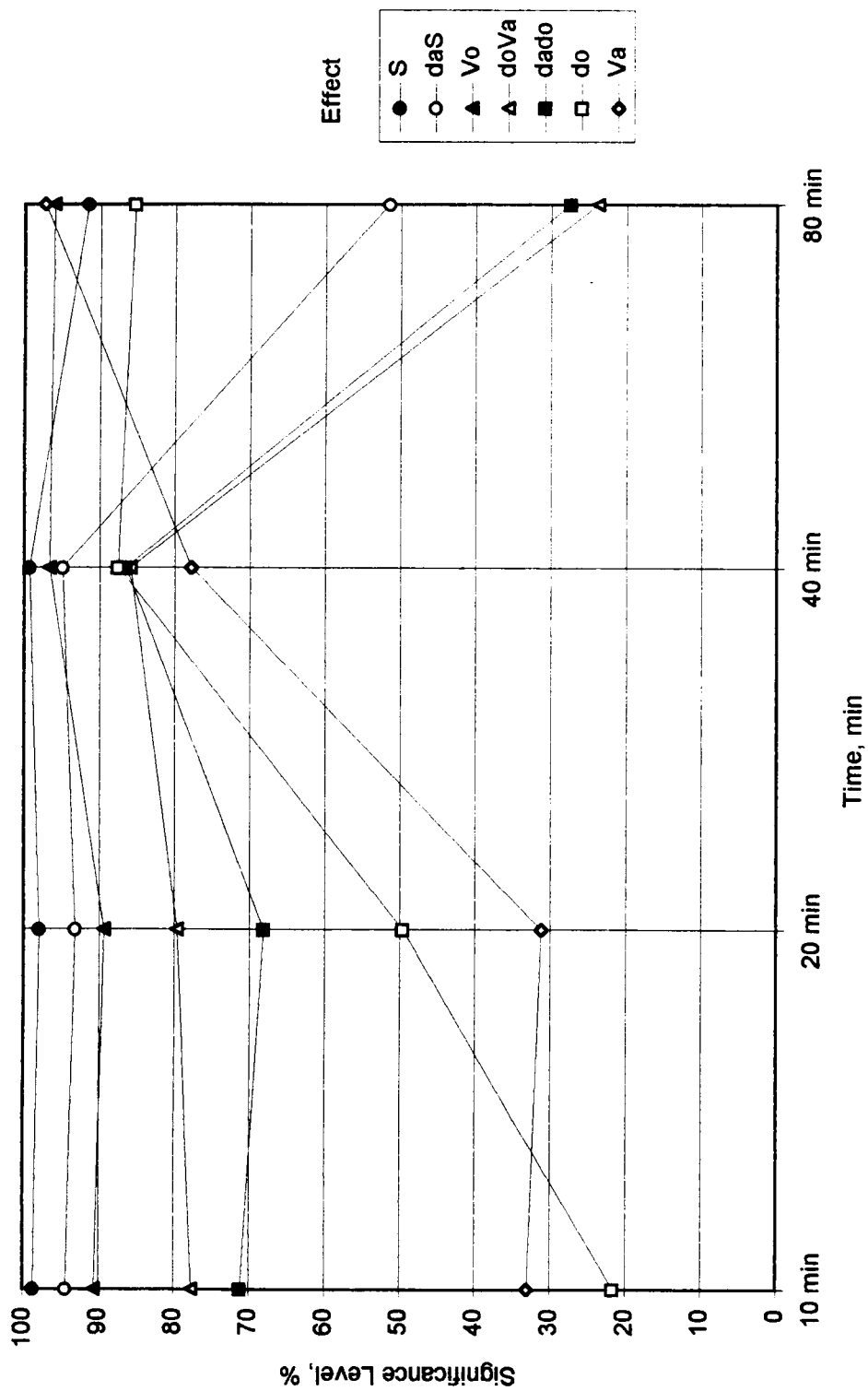


Figure 5-8. Results of ANOVA for uranium transfer

reaction controls the rate of transfer, as the process associated with solute transfer across the interface in such instances is fast relative to the rate of bulk phase reaction. A correlation between the bulk aqueous phase volume and the rate of solute transfer, which is expected in cases of controlling interfacial kinetics, is not indicated until transfer has been underway for 40 minutes or longer. The apparent lack of correlation could be due to the relatively small difference between the two volume levels used (350 and 450 ml).

The correlation between surface area and rate of transfer in the case of a slow reaction at the interface results from the increase in sites for chelation and solvent adsorption. The indication of significance of organic phase volume on the rate of transfer described as dC_o/dt results from dilution of transferred solute in the bulk organic, and provides no indication as the location of controlling kinetic effects. In any event, kinetic control of the transfer rate in the bulk phase would not be indicated by significance of the V_o variable, as the phase is homogeneous. In addition, the test apparatus is not a continuous flow system, therefore volume changes do not result in changes in residence or contact times.

Isolation of controlling extraction reactions at the interface is common in systems in which the solvent is not soluble in the aqueous phase and the solvent responsible for extraction is absorbed at the phase boundary (Danesi, 1980).

5.5 Comparison of Mass Transfer Coefficients

Overall coefficients K_a and K_o , based on organic phase uranium concentrations were calculated using equations (4-39) and (4-47). The results of the coefficient calculations are summarized in Tables 5.5A and 5.5B. These calculations were performed using a spreadsheet program, details of which are presented in Appendix A5.5a. A complete copy of the

Table 5.5A Overall uranium transfer coefficients, K_a .

Test No.	Overall Mass Transfer Coefficient, K_a , (Based on C_o), cm/s			
	10 min	20 min	40 min	80 min
1	9.76E-04	8.25E-04	6.71E-04	5.29E-04
2	3.99E-04	4.65E-04	5.29E-04	6.31E-04
3	4.48E-04	4.83E-04	5.31E-04	5.59E-04
4	1.08E-03	9.57E-04	9.66E-04	9.79E-04
5	4.97E-04	5.06E-04	5.24E-04	5.59E-04
6	8.92E-04	7.37E-04	7.21E-04	5.87E-04
7	7.11E-04	7.67E-04	6.18E-04	6.20E-04
8	6.31E-04	7.31E-04	6.61E-04	6.08E-04
9	1.304E-03	1.378E-03	1.488E-03	1.708E-03
10	1.0E-03	1.03E-03	1.096E-03	1.196E-03
11	7.55E-04	5.04E-04	5.09E-04	5.58E-04
12	1.17E-03	1.211E-03	1.244E-03	1.246E-03
13	9.88E-04	7.58E-04	7.01E-04	5.08E-04
14	7.5E-04	8.51E-04	9.43E-04	1.089E-03
15	1.457E-03	1.202E-03	1.173E-03	1.14E-03
16	8.84E-04	9.17E-04	1.056E-03	1.07E-03

Table 5.5B Overall uranium transfer coefficients, K_o .

Test No.	Overall Mass Transfer Coefficient, K_o , (Based on C_o), cm/s			
	10 min	20 min	40 min	80 min
1	1.95E-05	1.65E-05	1.34E-05	1.06E-05
2	7.98E-06	9.31E-06	1.06E-05	1.26E-05
3	8.96E-06	9.65E-06	1.06E-05	1.12E-05
4	2.16E-05	1.91E-05	1.93E-05	1.96E-05
5	9.95E-06	1.01E-05	1.05E-05	1.12E-05
6	1.78E-05	1.47E-05	1.44E-05	1.17E-05
7	1.42E-05	1.53E-05	1.24E-05	1.24E-05
8	1.26E-05	1.46E-05	1.32E-05	1.22E-05
9	2.61E-05	2.76E-05	2.98E-05	3.42E-05
10	2.00E-05	2.06E-05	2.19E-05	2.39E-05
11	1.51E-05	1.01E-05	1.02E-05	1.12E-05
12	2.34E-05	2.42E-05	2.49E-05	2.49E-05
13	1.98E-05	1.52E-05	1.40E-05	1.02E-05
14	1.50E-05	1.70E-05	1.89E-05	2.18E-05
15	2.91E-05	2.40E-05	2.35E-05	2.28E-05
16	1.77E-05	1.83E-05	2.11E-05	2.14E-05

spreadsheet in which the overall coefficients were determined and a listing of the typical individual cell formulas are presented in Appendix A5.5a.

The coefficients calculated from uranium transfer results represent total uranium transfer, not the transfer of specific species. Use of "true" overall coefficients which are related to film coefficients according to equations (4-8) and (4-14) is problematic for the uranium system under consideration, as the existence of the unreacted transferring aqueous-phase species in the organic phase is unlikely.

To isolate diffusion transfer and chemical reaction effects, the film transfer coefficients were calculated using equation (4-61) by expanding the dimensionless groups and separating the Sherwood number to isolate the film coefficient, k . The aqueous phase diffusion coefficient used in the calculation of k_a was estimated using the Nernst-Haskell equation which pertains to the diffusion of a salt through an electrolyte solution. The diffusion coefficient of the solvate in the organic solution used in the calculation of k_o was estimated by the method of Lusis and Ratcliff. Calculations of both diffusion coefficients are presented in Appendix A5.5b. The density of the aqueous solution was assumed to be that of an aqueous solution of 3.5M $\text{Ca}(\text{NO}_3)_2$ and 1.0M HNO_3 , and was determined from a plot of density as a function of calcium nitrate concentration (reference Figure A5-1, Appendix A5.5c). Data from which the plot was developed were obtained at a constant 25°C. as a part of this study, and are also presented in Appendix A5.5c. Other property data was obtained from the literature. Calculations of the film transfer coefficients are presented in Appendix A5.5d.

Comparison of predicted film coefficients and observed (with reaction) overall coefficients, which are presented in Table 5.5C and Figure 5-9, indicates that overall transfer coefficient values calculated from test data are consistently lower than either of the film

Table 5.5C. Comparison of observed overall transfer coefficients with predicted film coefficients

Test No.	predicted k_a , cm/s	Observed K_a , cm/s	predicted k_o , cm/s	Observed K_o , cm/s
1	4.604E-03	7.50E-04	1.92E-04	1.50E-05
2	4.604E-03	5.06E-04	1.92E-04	1.01E-05
3	4.68E-03	5.05E-04	1.95E-04	1.01E-05
4	4.68E-03	9.95E-04	1.95E-04	1.99E-05
5	5.267E-03	5.22E-04	2.16E-04	1.04E-05
6	5.267E-03	7.34E-04	2.16E-04	1.47E-05
7	5.221E-03	6.79E-04	2.18E-04	1.36E-05
8	5.221E-03	6.58E-04	2.18E-04	1.32E-05
9	4.604E-03	1.47E-03	1.92E-04	2.94E-05
10	4.604E-03	1.081E-03	1.92E-04	2.16E-05
11	4.68E-03	5.82E-04	1.95E-04	1.16E-05
12	4.68E-03	1.218E-03	1.95E-04	2.44E-05
13	5.267E-03	7.39E-04	2.16E-04	1.48E-05
14	5.267E-03	9.08E-04	2.16E-04	1.82E-05
15	5.221E-03	1.243E-03	2.18E-04	2.49E-05
16	5.221E-03	9.82E-04	2.18E-04	1.96E-05

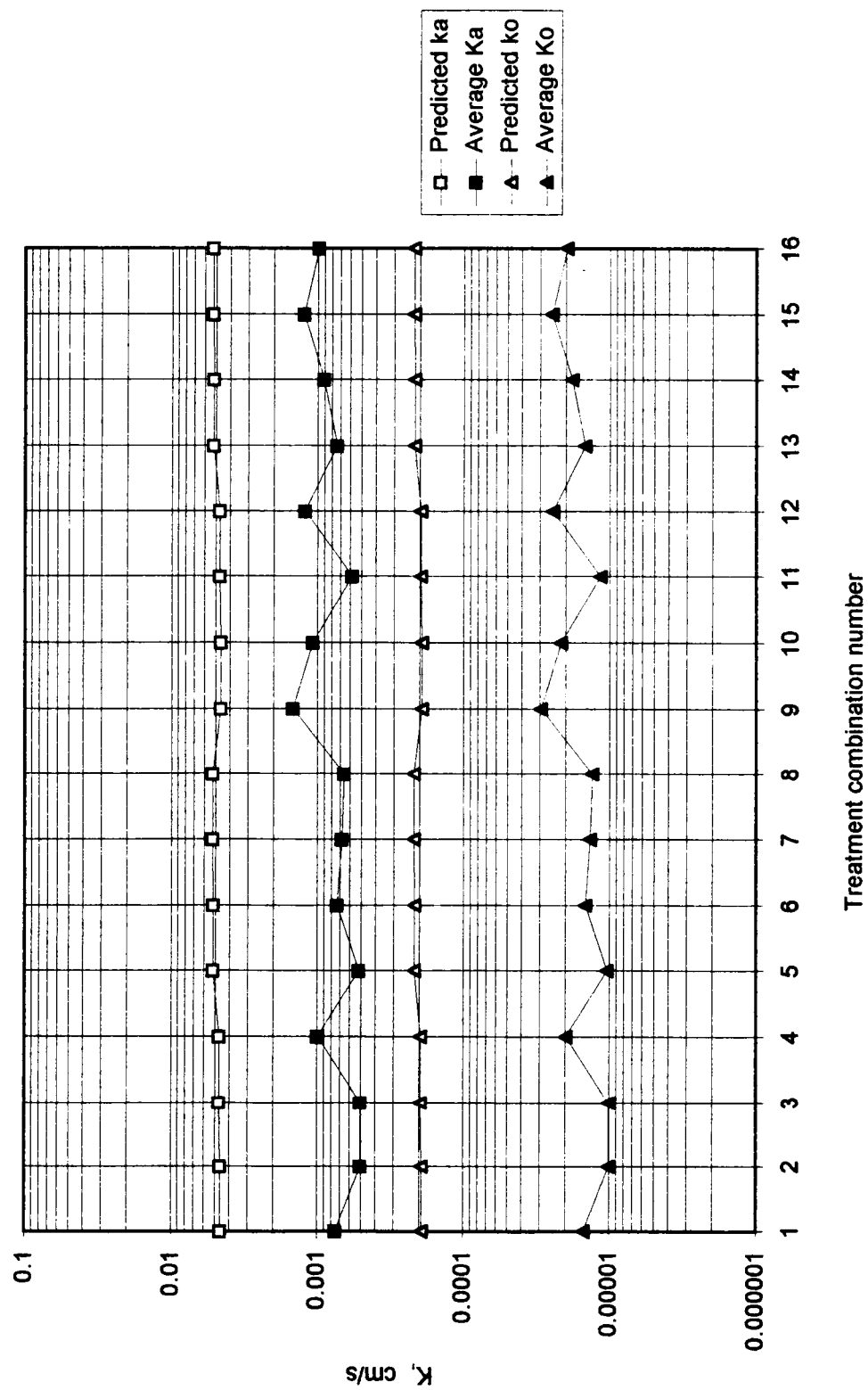


Figure 5.9 Comparison of predicted film and observed overall transfer coefficients

coefficients. This result indicates that neither of the diffusion film resistances individually controls the transfer rate. No comparison between the actual resistance to transfer and the summed film resistances can be made, as the overall coefficients calculated are for total uranium transfer, whereas the film coefficients are applicable to specific species. Under the conditions proposed for the system under system, the relationships between overall and film coefficients described in equations (4-8) and (4-14) are of little meaning, as the transferring species in the aqueous phase is not likely to exist in the bulk organic or the organic film.

5.6 Reaction Rate Expression

Results of transfer tests performed at different component initial concentration conditions are presented in Figure 5-10. The figure indicates a significant change in the rate of transfer (as indicated by the curve slope) only in response to changes in the initial aqueous phase uranium concentration. Analysis of the slopes between data points from tests in which the uranium concentration was varied indicates a first order relationship between uranium concentration and the transfer rate.

No significant rate change was observed in response to changes in the aqueous phase nitrate concentration. In the event that association of the uranyl ion controls the overall rate of reaction the lack of a rate response to changes in nitrate concentration could be an indication that the aqueous uranyl species is completely undissociated. On the other hand, the lack of correlation between nitrate concentration and transfer rate may indicate that complexation or solvent absorption at the interface rather than uranyl nitrate association controls the overall rate of transfer. As the uranium distribution coefficient increases over the range of nitrate

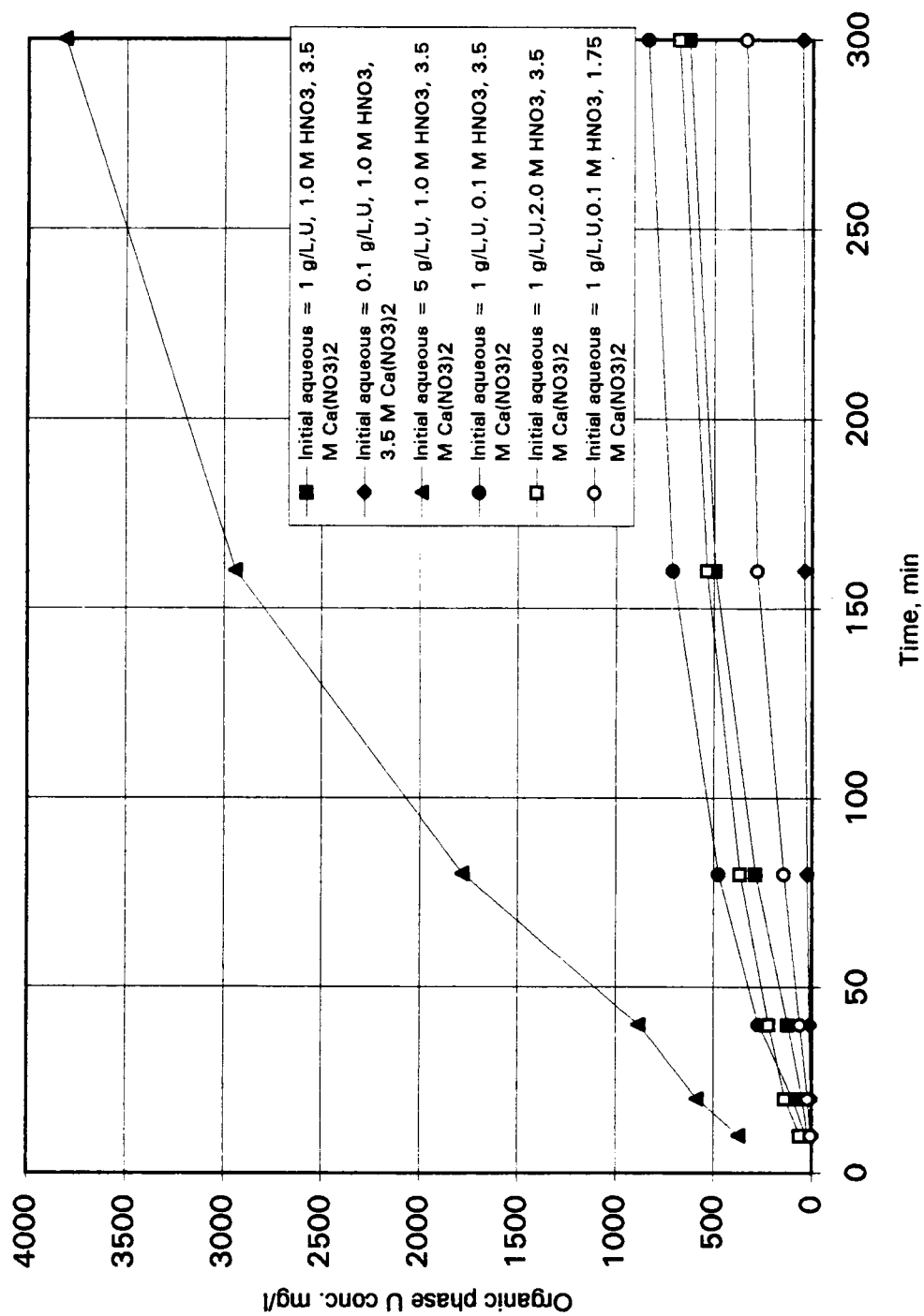


Figure 5-10. Lewis cell kinetic test results

concentrations evaluated without any indication of leveling out (ref. Figure 5-1), complete uranyl nitrate association in the aqueous phase under transfer test conditions seems unlikely.

Relative to the concentration of uranium present, water (in the aqueous phase) and DBC (in the bulk organic) are available at concentrations far exceeding the stoichiometric amounts. At an aqueous phase uranium concentration of 1g/L (0.0042 *M*), the stoichiometric concentrations of DBC and water are 0.0084 *M* and 0.0168 *M*, respectively. At the nominal aqueous phase calcium nitrate, uranium, and nitric acid concentration conditions used during testing (3.5 *M* Ca(NO₃)₂, 1gU/L, and 1.0 *M* HNO₃), the aqueous phase water concentration was 40.5 *M*. The concentration of DBC in the undiluted form as used in all testing was 4.06 *M*. As water and DBC are essentially undepleted during extraction and nitrate concentration was found to have no effect on transfer rate, the reaction may be described by a psuedo first-order rate expression.

5.7 Reaction Rate Constant Determination

Under conditions used during testing and in consideration of the high distribution coefficients for uranium observed, it is valid to assume that uranium transfer behavior observed during testing included only the effects of the forward extraction reaction. Therefore, the reaction rate constant determined from the data as the overall rate constant K_r may be considered equivalent to the forward rate constant, k_f .

As extraction of uranium in the system UO₂(NO₃)₂-HNO₃-H₂O-Ca(NO₃)₂-DBC is indicated to fall into the kinetic regime, the reaction rate constant has been determined by solving directly for the constant using the solution of equation (4-64), inserting rate and concentration values obtained experimentally according to the procedure described in Section

3.4.3. The values calculated, which are presented in Table 5.7 have then been averaged to obtain a single rate constant value. The spreadsheet used for calculation is located in Appendix A5.7a.

The rate constant has also been determined by combining volume, interfacial area, and uranium concentration values, and regressing the combined term against the experimentally determined rate. The results of the regression, which was performed using the data analysis tool in Microsoft Excel (version 5.0) are shown in Figure 5-11. The worksheet from which the regression plot was developed is presented in Appendix A5.7b. The slope value determined by the regression, $8.35\text{E-}04$ cm/s, is equivalent to the reaction rate constant. The standard error estimate for the slope of the regression is $3.62\text{E-}05$ cm/s.

In using the rate constant, it should be recognized that it was determined based on experiments at only one temperature (25°C.), and may not be a true kinetic constant.

Table 5.7. Directly calculated reaction rate constant without diffusion film correction.

Test No.	k_f values cm/s at 10 minutes	k_f values cm/s at 20 minutes	k_f values cm/s at 40 minutes	k_f values cm/s at 80 minutes
1	0.000974	0.000822	0.000667	0.000523
2	0.000399	0.000464	0.000527	0.000622
3	0.000448	0.000482	0.000528	0.000553
4	0.001077	0.000953	0.000957	0.000958
5	0.000497	0.000505	0.000523	0.000554
6	0.00089	0.000735	0.000717	0.000581
7	0.00071	0.000765	0.000615	0.000614
8	0.00063	0.00073	0.000658	0.000603
9	0.001299	0.001365	0.00145	0.001529
10	0.000997	0.001023	0.001078	0.001132
11	0.000753	0.000503	0.000506	0.00055
12	0.001166	0.001201	0.001222	0.001186
13	0.000986	0.000755	0.000696	0.000502
14	0.000749	0.000847	0.000933	0.00105
15	0.001452	0.001195	0.001158	0.001102
16	0.000882	0.000913	0.001044	0.001038

Average value is 8.37E-04 cm/s

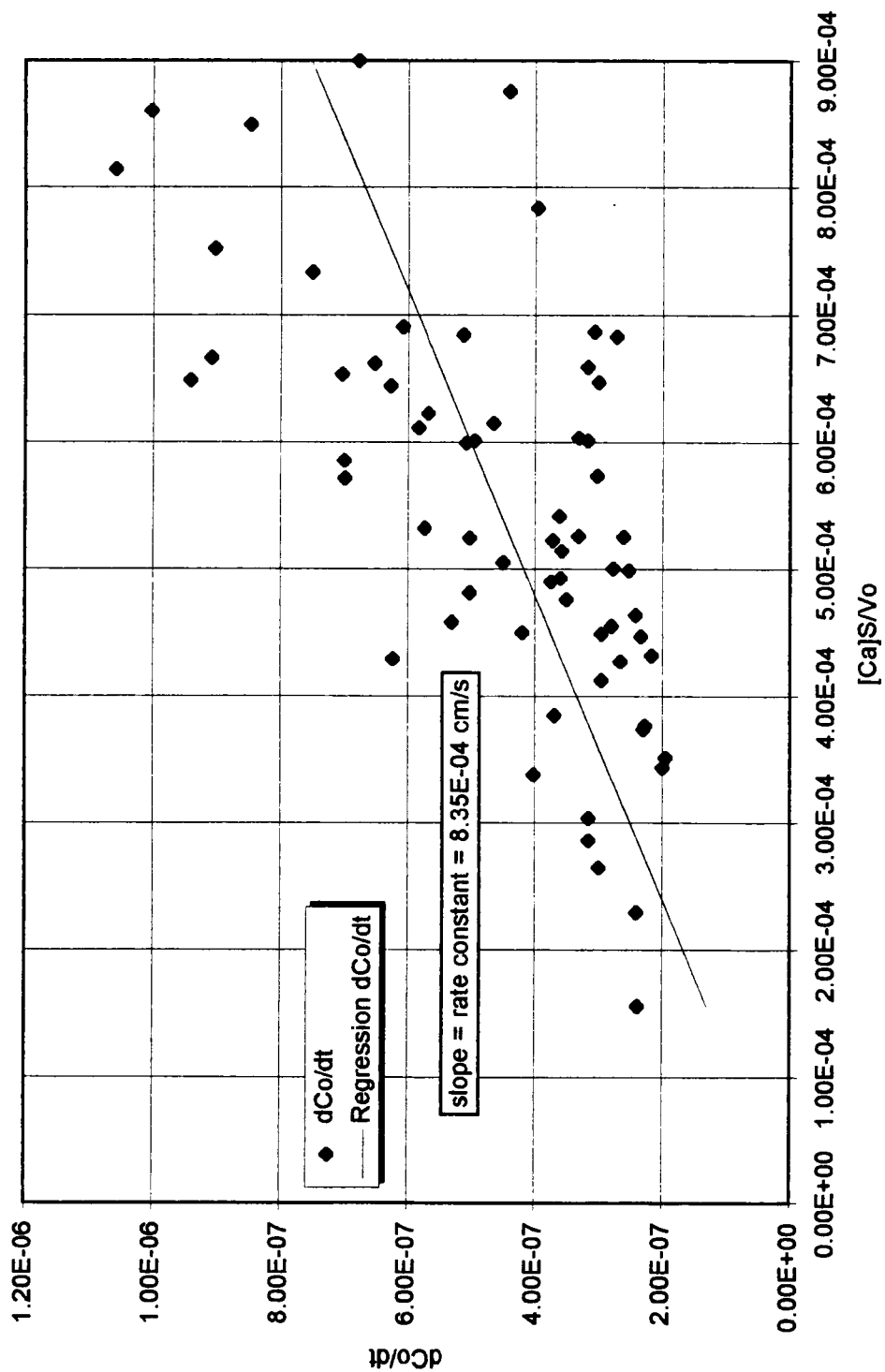


Figure 5-11. Regression to determine reaction rate constant

5.8 Transfer Modeling

Based on the results of the analysis of effect significance, the system was modeled using the reaction rate expression only. Based on the dominance of the forward reaction indicated by the high reaction equilibrium constant value, the model is based on an irreversible first order rate expression as given in equation (4-50). To compare model results with observed transfer rates, plots of dC_o/dt have been constructed using the value of k_f determined directly from the transfer data ($8.37\text{E-}04$ cm/s) as described in Section 5.7. Predictions using the value of k_f determined by regression of transfer rates ($8.35\text{E-}04$ cm/s) have not been included in the figures, due to the near equivalence of the two k_f values (which generate superimposed plot values). The comparison of predicted and observed transfer rates is presented in Figures 5-12 through 5-27. A tabulation of the rate values plotted in Figures 5-12 through 5-27 is presented in Appendix A5.8.

As the figures indicate, transfer rates determined by using a first order reaction rate expression generally track observed rates closely. In all cases, model rates are of the same order of magnitude as observed values. Deviations between predicted and observed rates range from as low as approximately 2% to in excess of 100%. The figures also indicate that the predicted values are generally higher than those observed for tests in which the interfacial area is at the lower test value, with the trend reversed for tests in which the area was at the higher value. There was no apparent correlation between any test variables and the degree of error between predicted and observed rate values.

The close fit between observed rates and those predicted using only a reaction rate expression further supports the conclusions reached from the results of the kinetic tests which

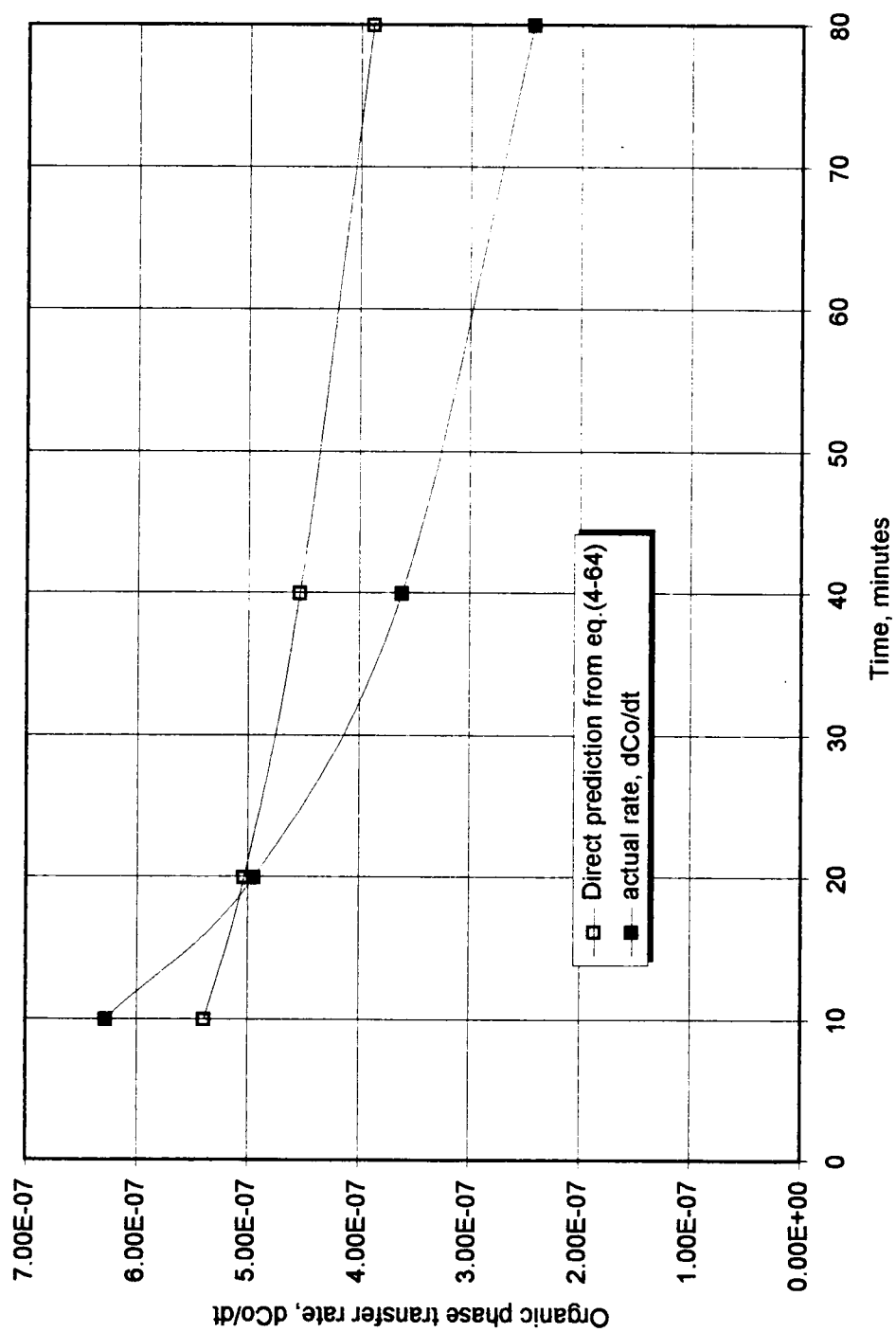


Figure 5-12. Comparison of predicted and actual transfer rates, Test 1

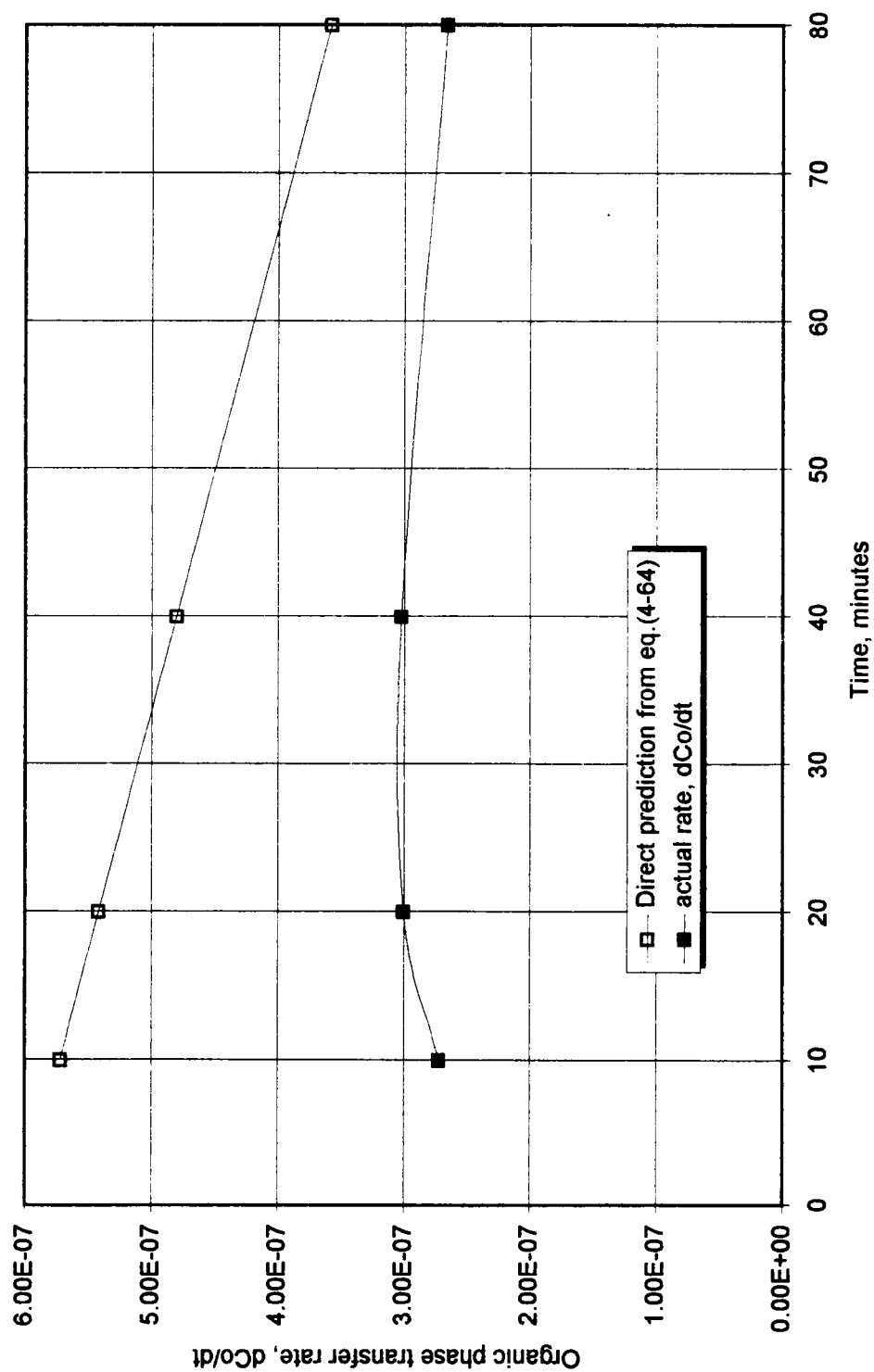


Figure 5-13. Comparison of predicted and actual transfer rates, Test 2

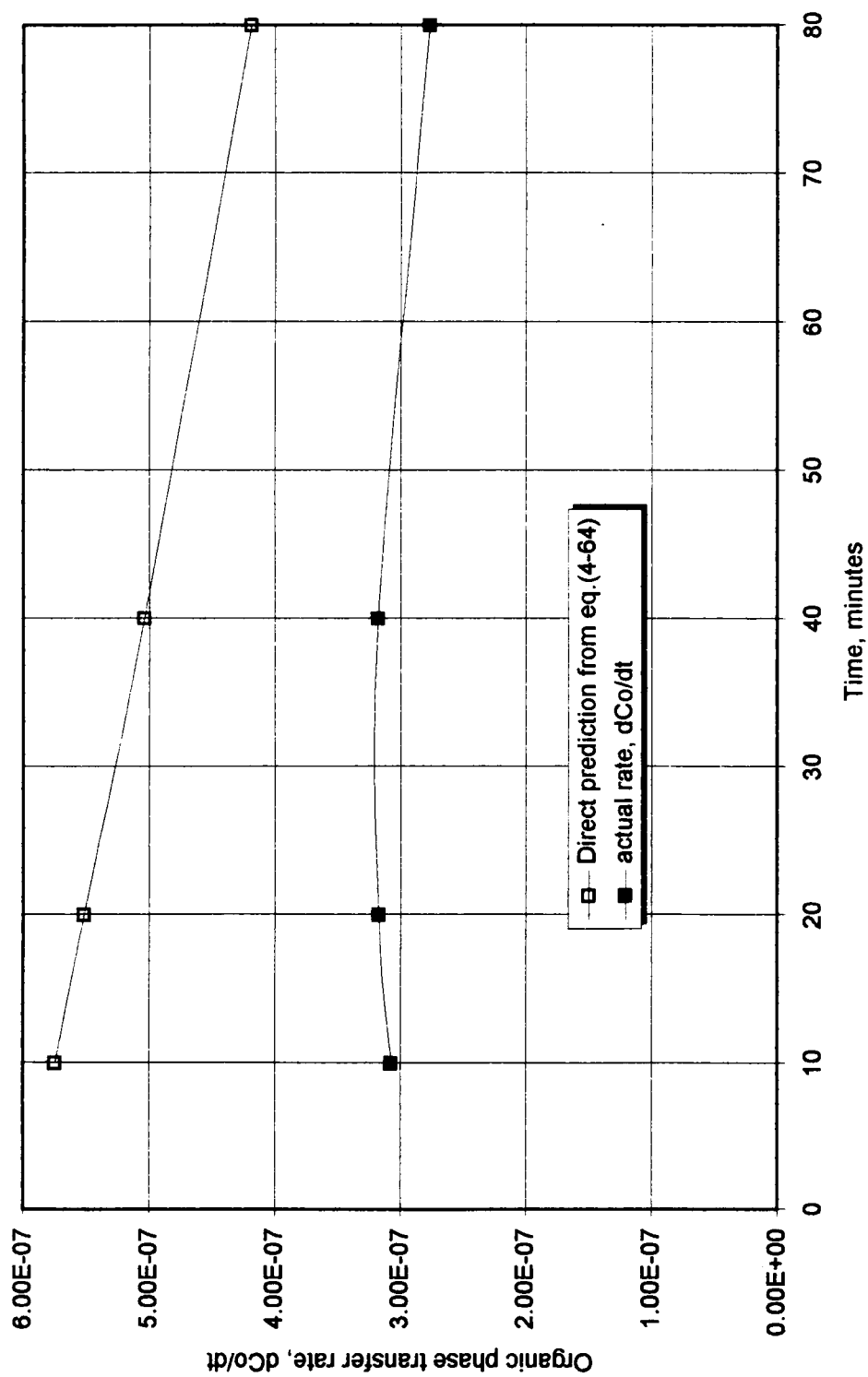


Figure 5-14. Comparison of predicted and actual transfer rates, Test 3

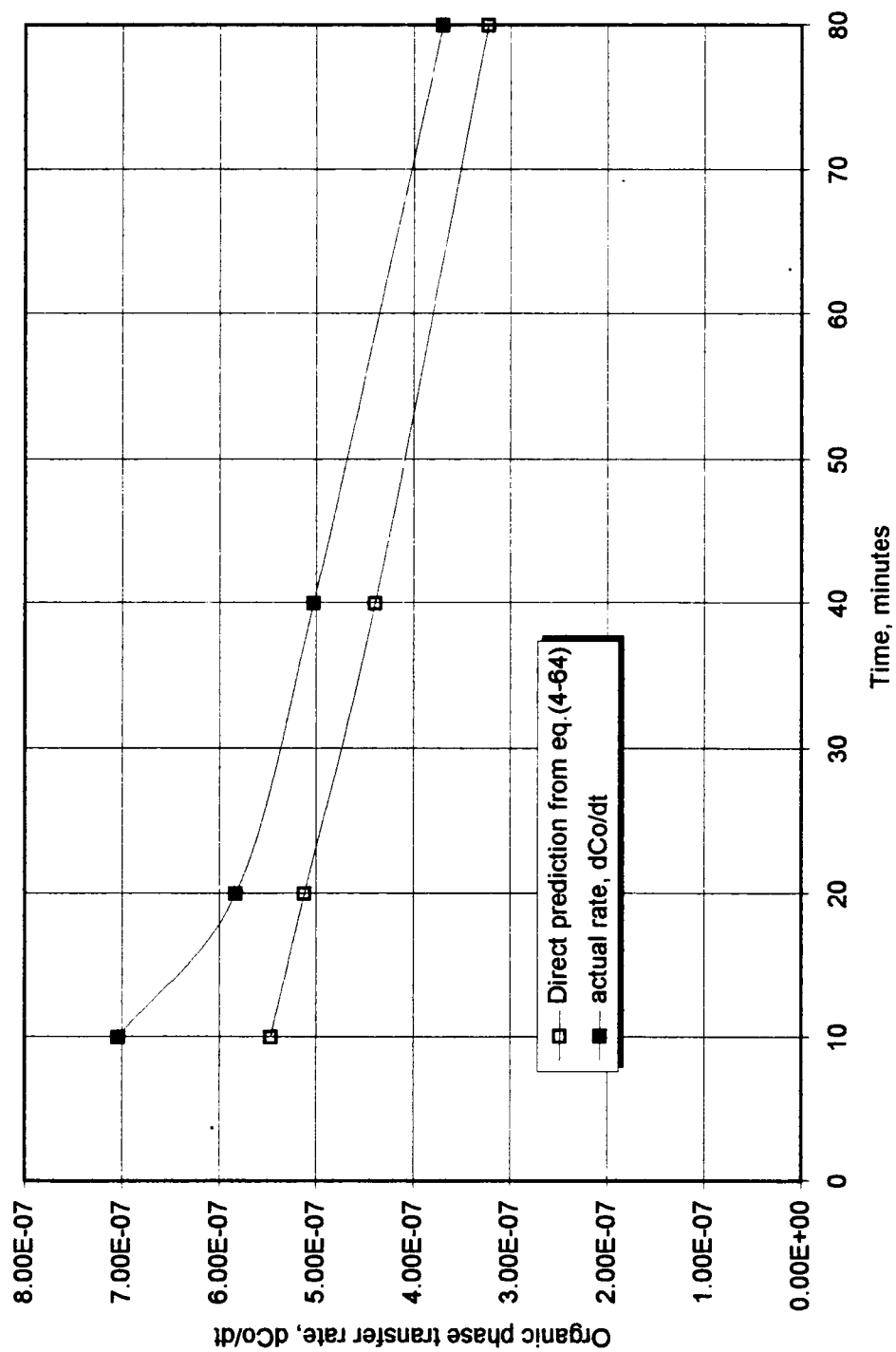


Figure 5-15. Comparison of predicted and actual transfer rates, Test 4

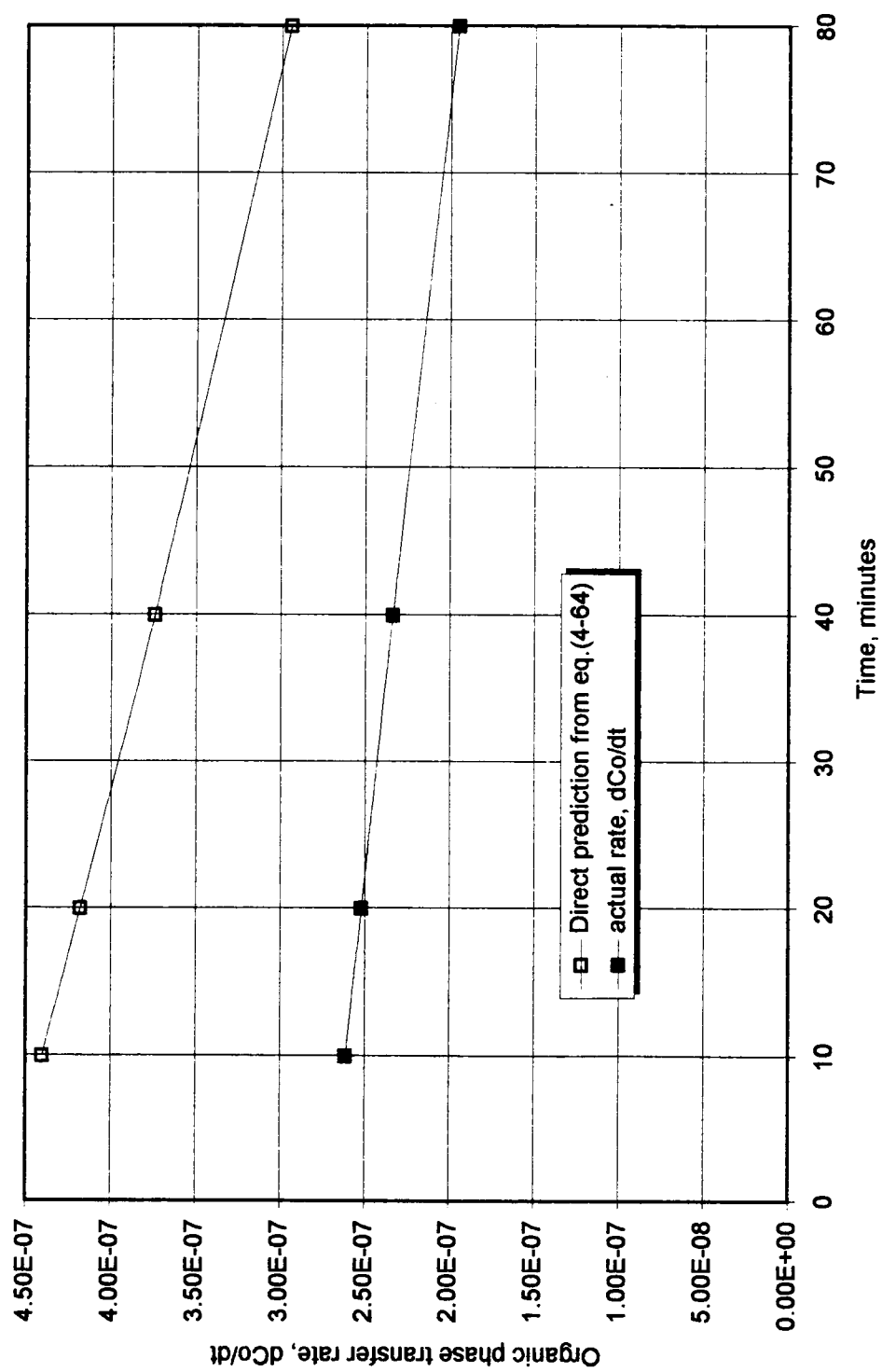


Figure 5-16. Comparison of predicted and actual transfer rates, Test 5

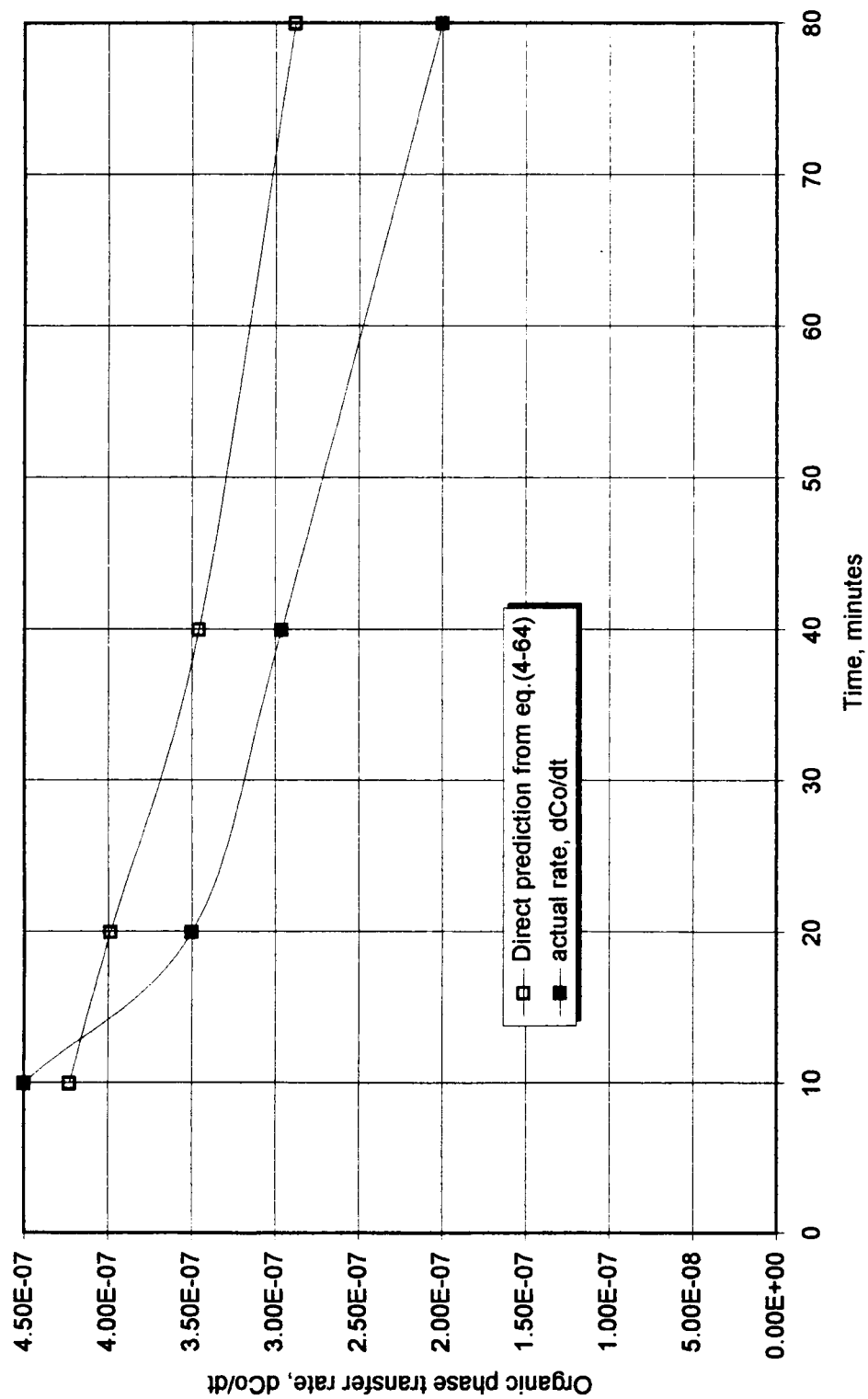


Figure 5-17. Comparison of predicted and actual transfer rates, Test 6

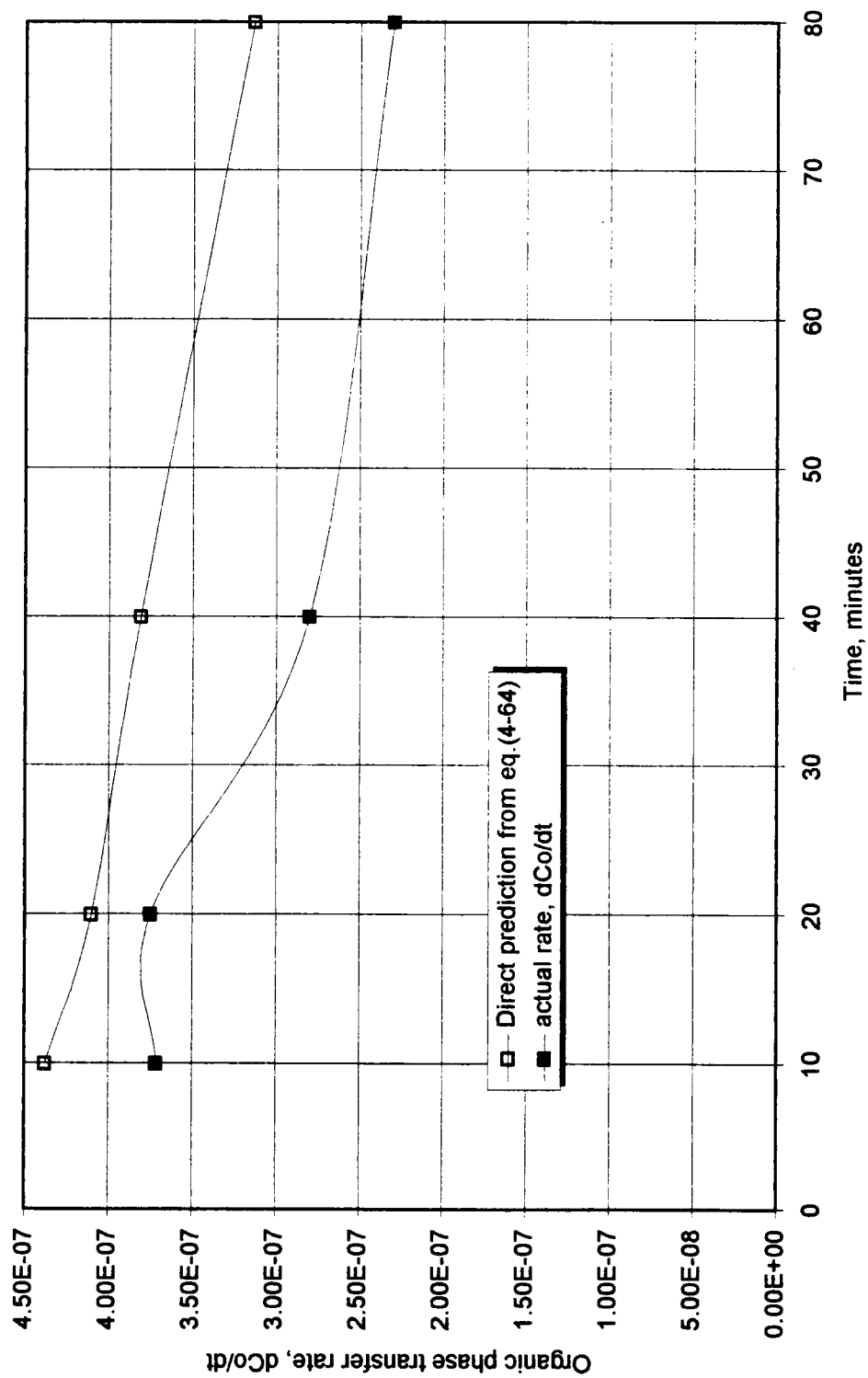


Figure 5-18. Comparison of predicted and actual transfer rates, Test 7

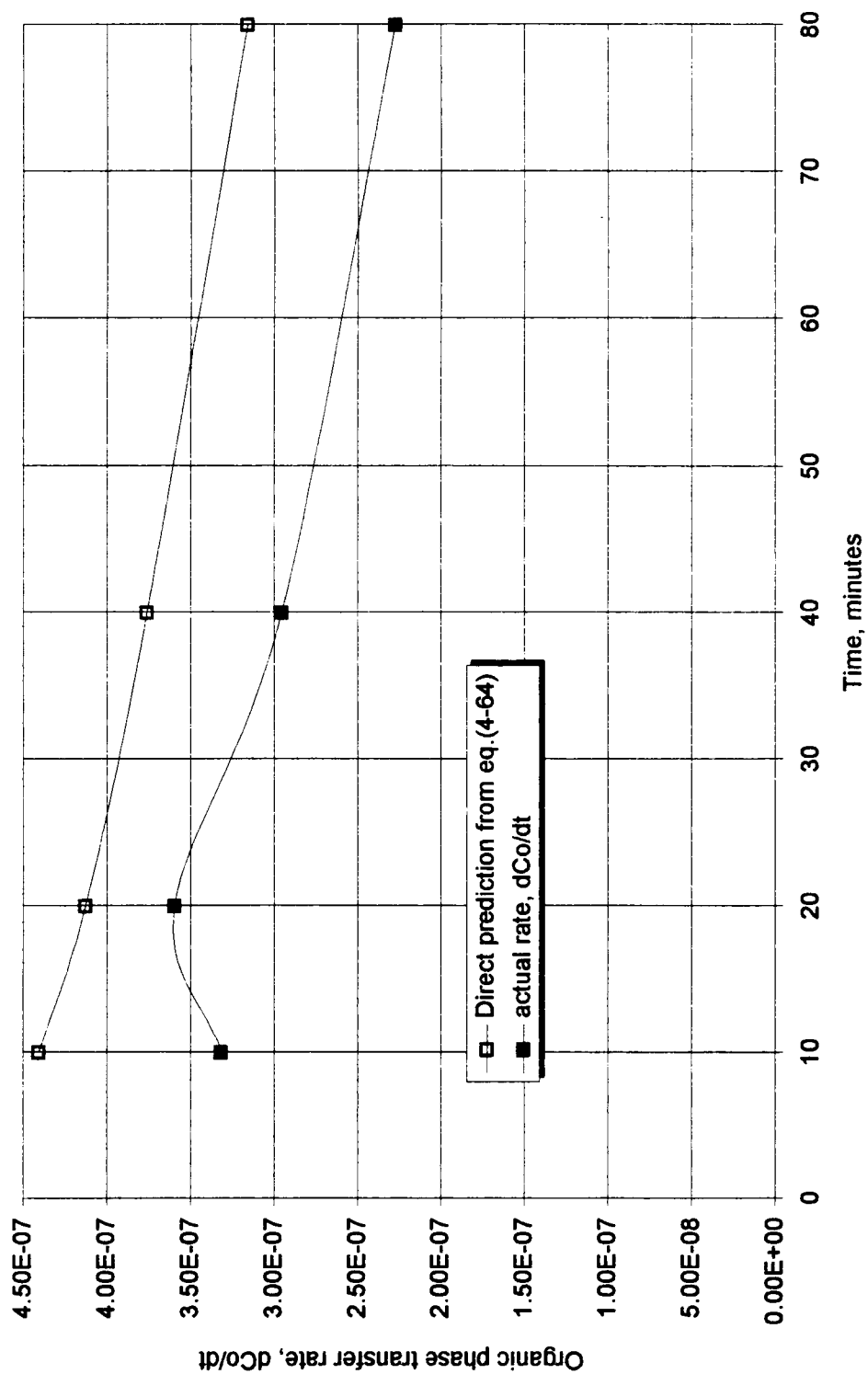


Figure 5-19. Comparison of predicted and actual transfer rates, Test 8

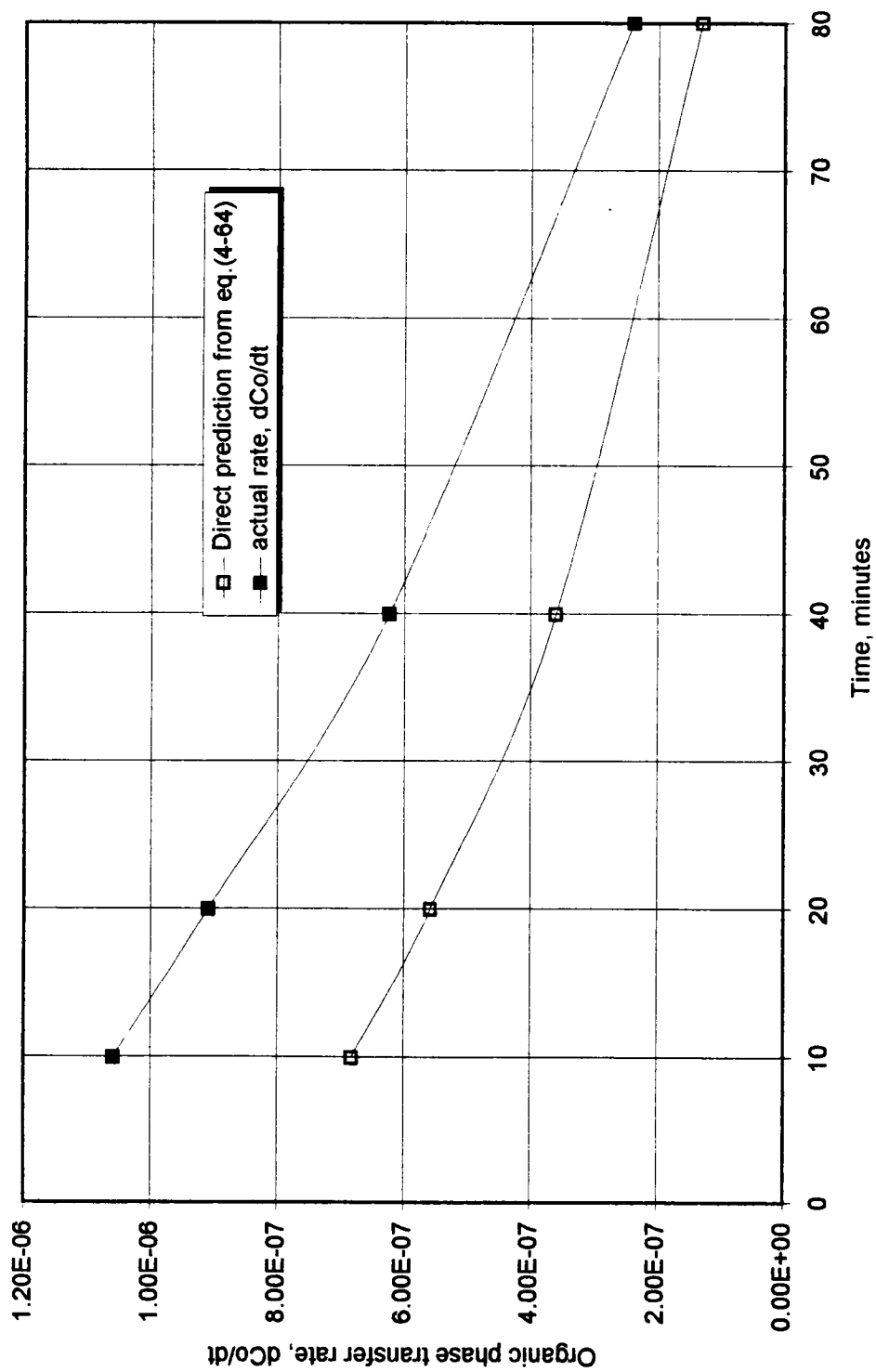


Figure 5-20. Comparison of predicted and actual transfer rates, Test 9

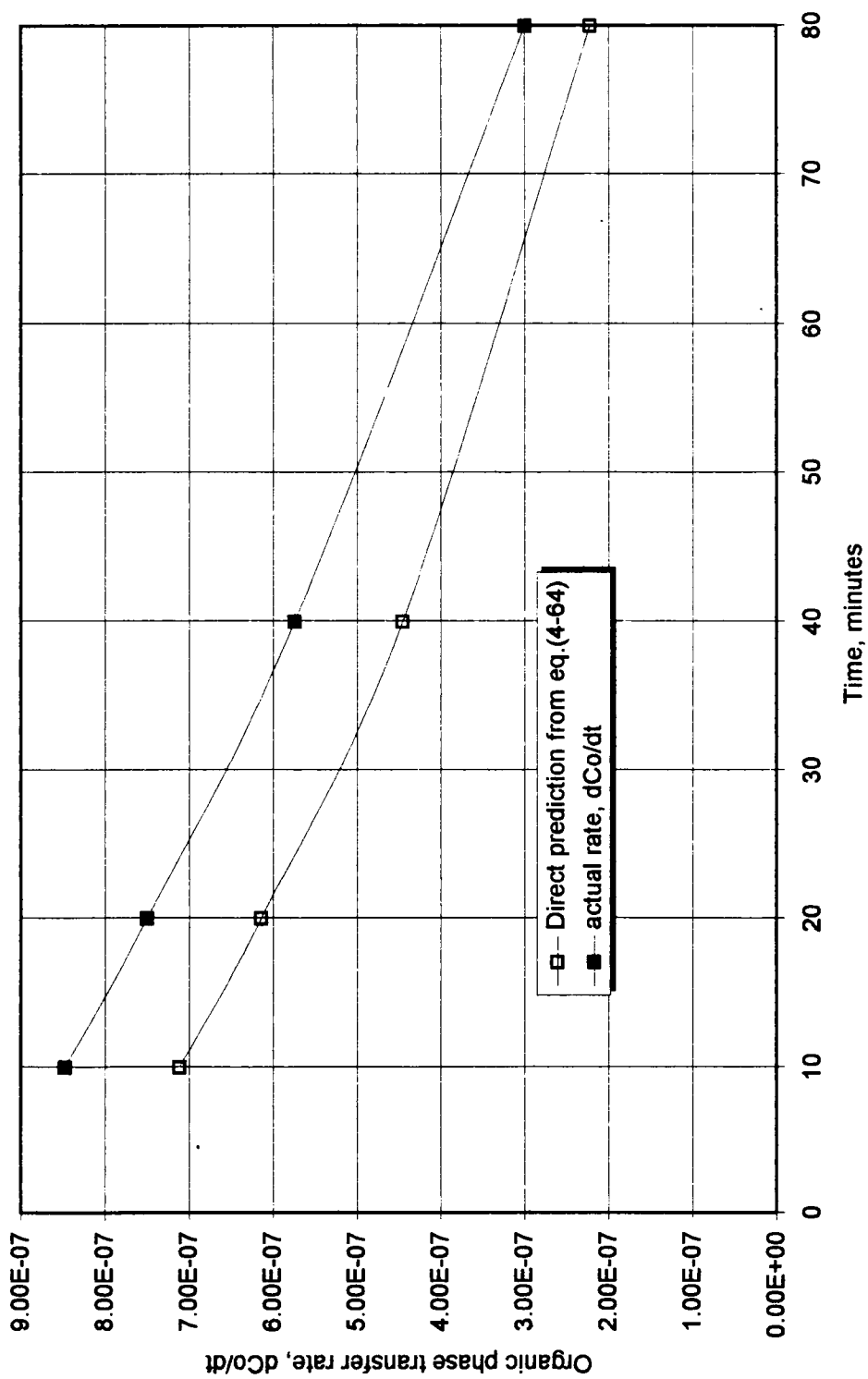


Figure 5-21. Comparison of predicted and actual transfer rates, Test 10

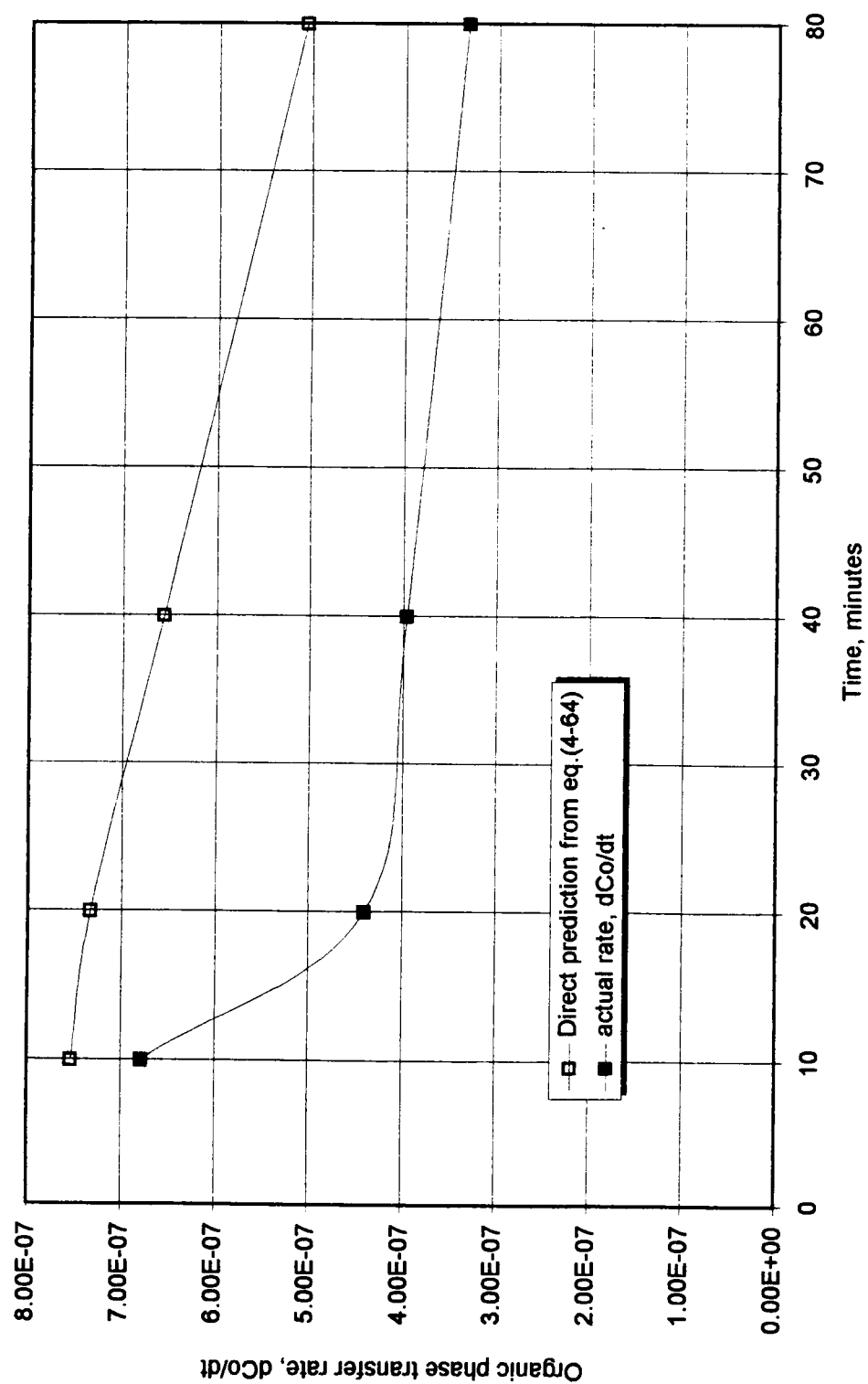


Figure 5-22. Comparison of predicted and actual transfer rates, Test 11

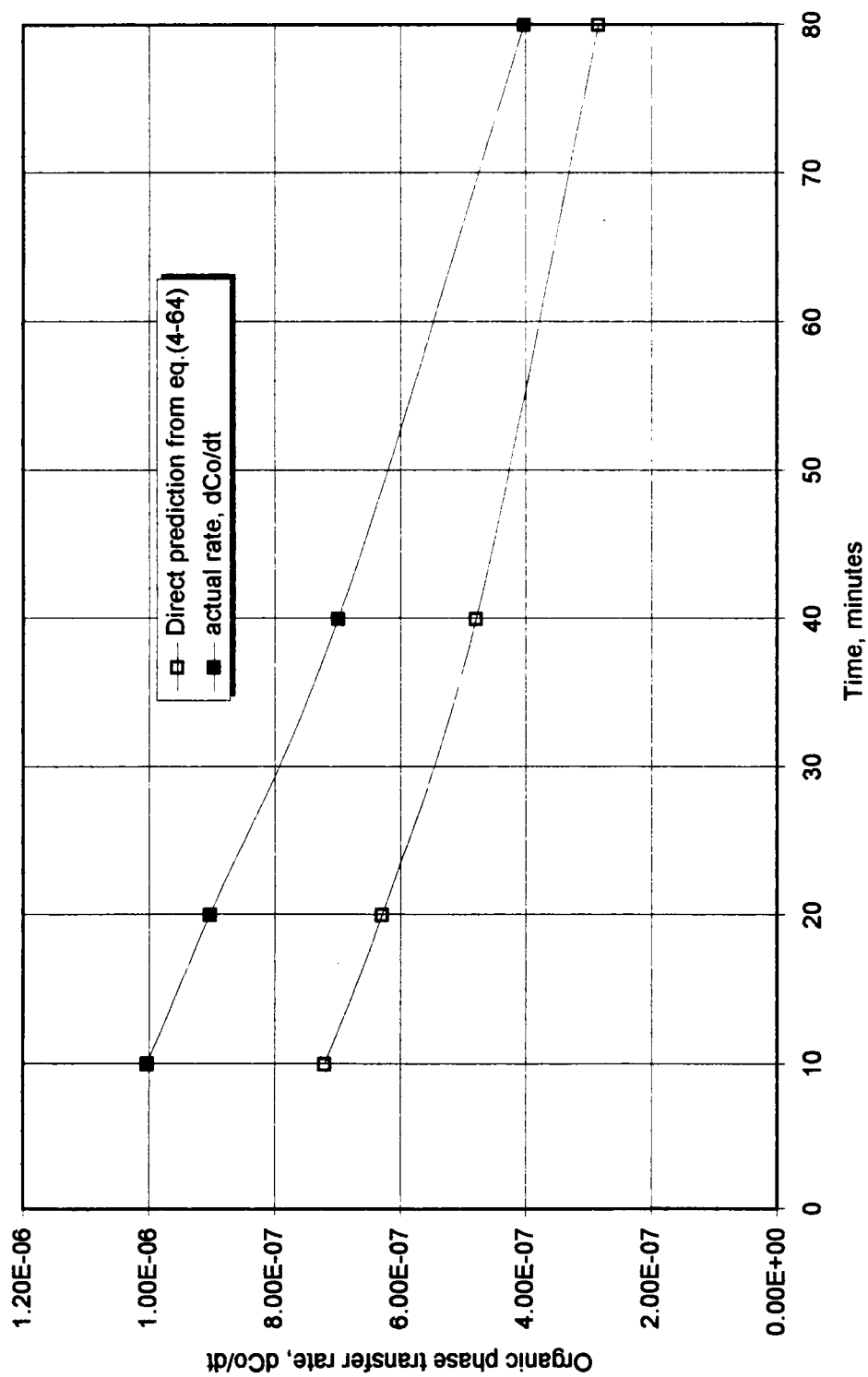


Figure 5-23. Comparison of predicted and actual transfer rates, Test 12

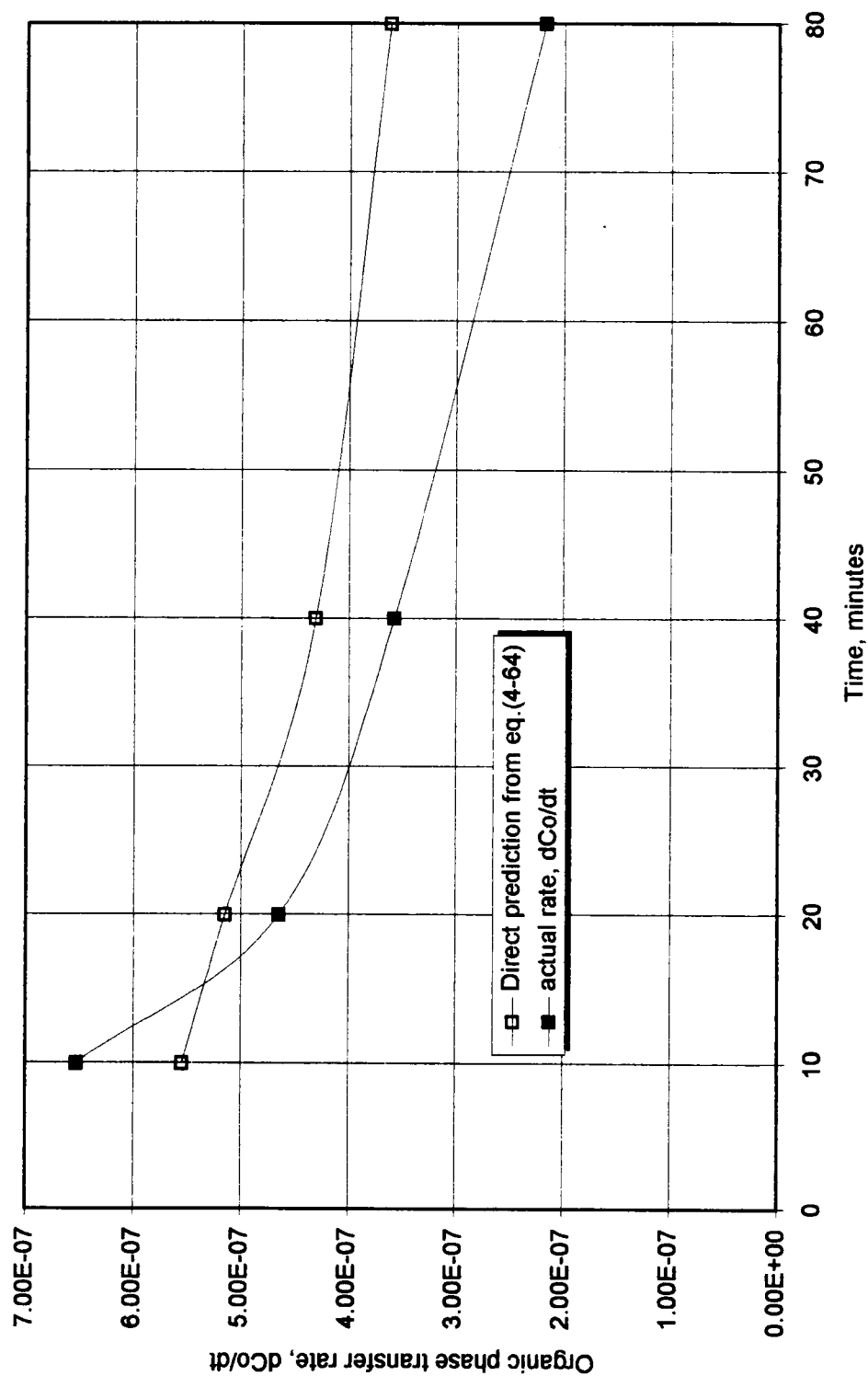


Figure 5-24. Comparison of predicted and actual transfer rates, Test 13

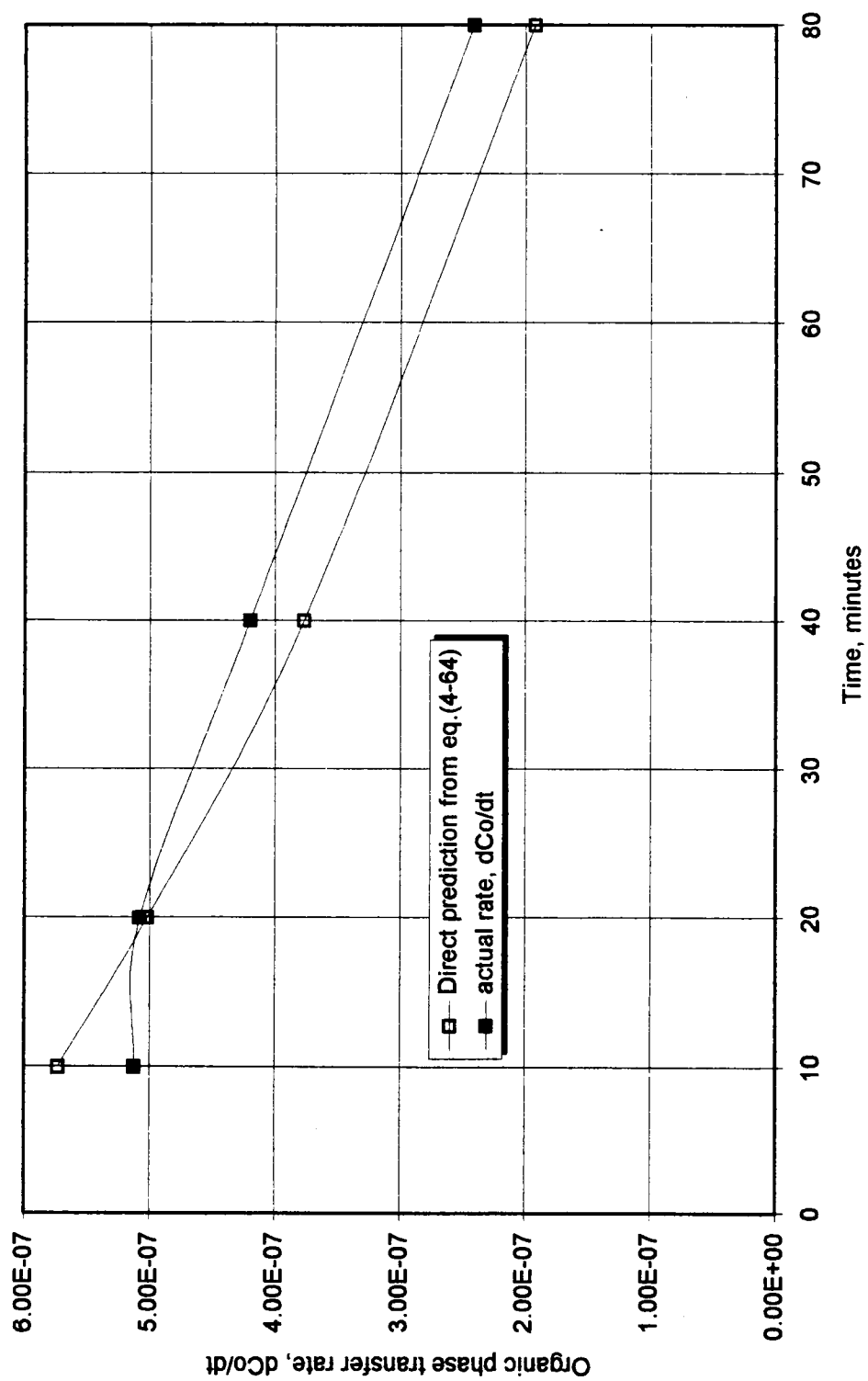


Figure 5-25. Comparison of predicted and actual transfer rates, Test 14

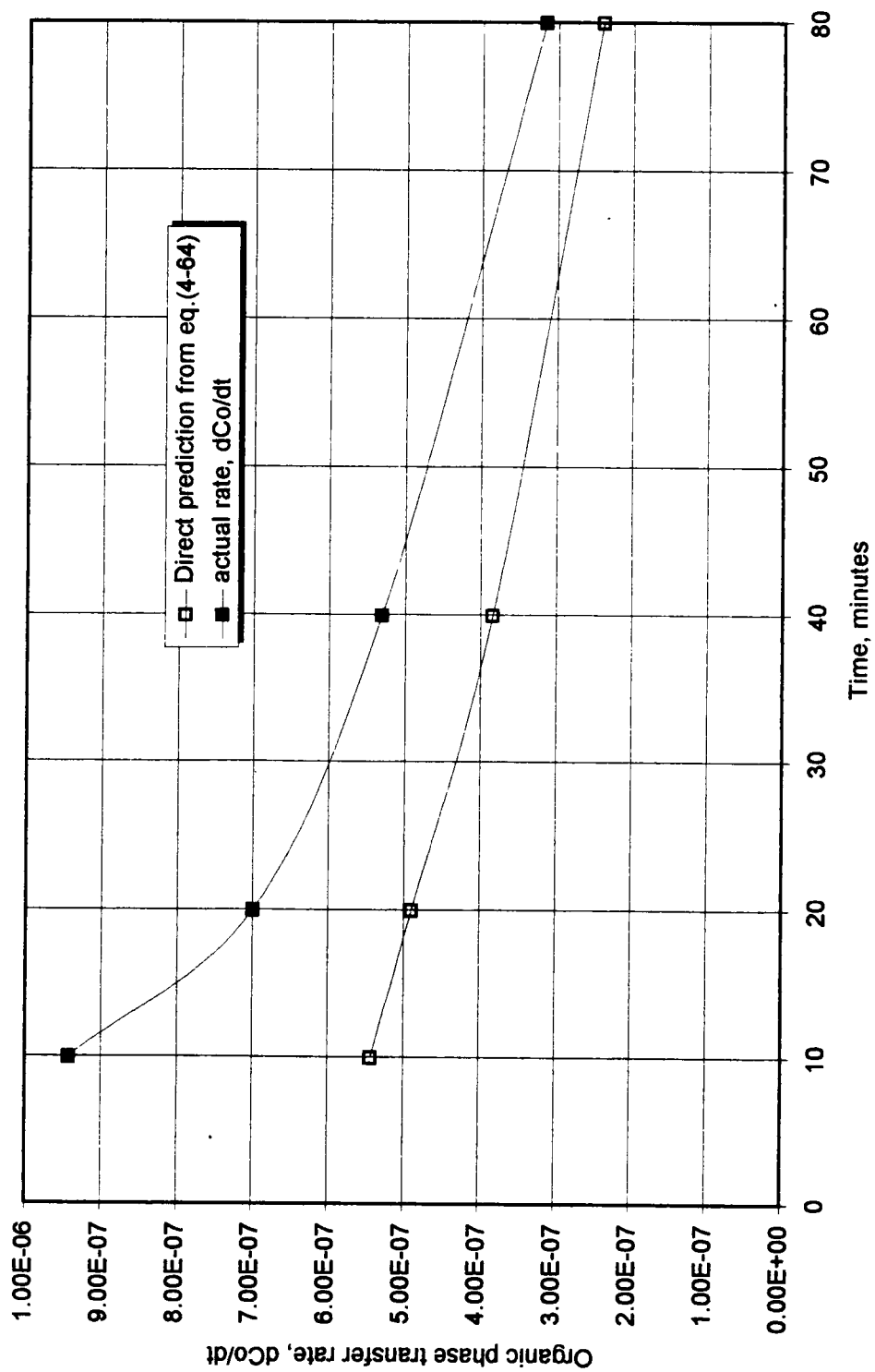


Figure 5-26. Comparison of predicted and actual transfer rates, Test 15

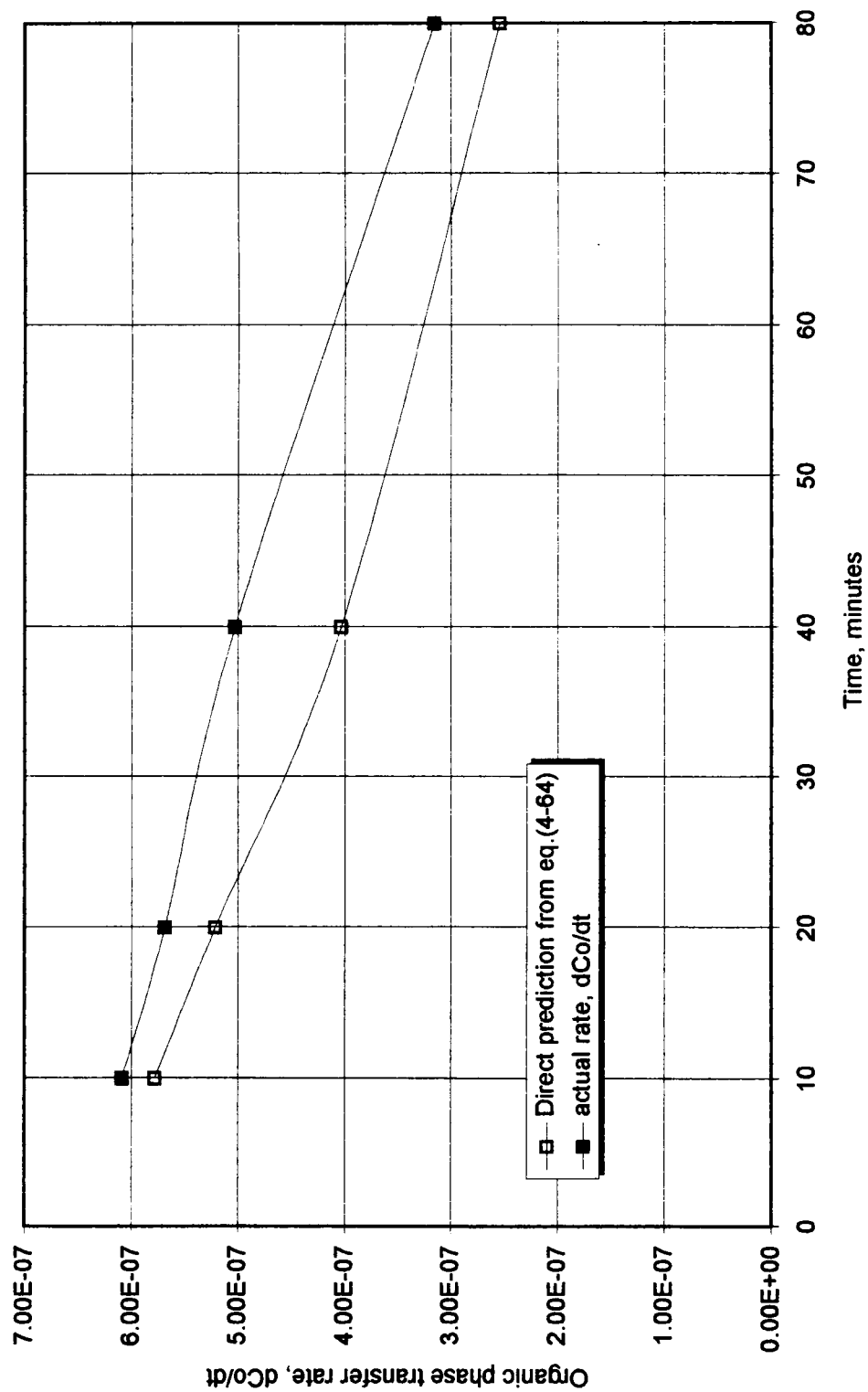


Figure 5-27. Comparison of predicted and actual transfer rates, Test 16

indicated a first order dependence of reaction rate on the aqueous phase uranium concentration.

The close comparison of observed transfer rates and those predicted from the reaction rate expression provides no indication as to the transfer regime in effect as both kinetics and diffusion are described by first order expressions under the conditions of the present study.

6. CONCLUSIONS

Several significant conclusions may be drawn from the various components of the study performed. Results of the equilibrium tests confirm the viability of salting using calcium nitrate to obtain high extraction coefficients. The results of these tests also indicate that the problem of nitric acid co-extraction is not entirely avoided by the use of the non-extracting salt, but may be effectively mitigated. The potential for a further reduction in HNO_3 co-extraction is considerable when the initial acid concentration in the aqueous phase is reduced below the 1.0 M values used in the subject study.

The solvation reaction under the conditions of the present study was determined to be pseudo first-order. This conclusion is supported both by the results of kinetic testing and in the similarity in observed and predicted transfer rate trends.

The rate of uranium transfer in the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$ in the apparatus used was indicated to be controlled by the rate of chemical reaction. This conclusion is supported by the lack of significance of agitation (impeller diameter) effects on the rate of transfer. Comparison of predicted film coefficients with observed overall transfer coefficients tends to indicate that rate of solute transfer is not controlled by diffusion in a single film layer on either side of the phase boundary. However, no conclusions regarding combined film resistances on the rate of transfer can be made based on this comparison, as overall coefficients and distribution coefficients determined are for total uranium transfer. Film coefficients calculated using the model described are for the uranyl ion in the aqueous film, and for the complexed solvate in the organic film.

The results of the significance tests indicate that the reaction which controls the rate of transfer occurs at the phase boundary, even though the occurrence of the reaction in the bulk aqueous phase is likely. This conclusion is supported by the strong correlation between surface area and transfer rate, and is similar to that reported by Lewis (1954c) for the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-DBC}$. Interfacial kinetic control in metal extraction processes is common, as Danesi (1980) reports that transfer in 65 of 82 systems for which extraction studies have been documented has been found to be controlled by the rate of a chemical reaction at the interface.

In light of the indicated kinetic control, design of systems for extraction of uranium in the system under study should be concerned primarily with the reaction rate expression and rate constant. Enhancement of the extraction rate should be sought by increases in interfacial area, which can be obtained through proper selection and design of process equipment.

The accuracy of the reaction rate model indicates that the reaction mechanism proposed in equations (4-65) through (4-67) may be applicable. However, no determination as to a unique mechanism can be made from the present study as a number of equally plausible reaction mechanisms can yield first order reaction rate expressions. Additional tests in which greater ranges of reactant concentrations are used are needed to obtain a better understanding of the reaction mechanism.

In addition to conclusions regarding the mass transfer in the system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O-Ca}(\text{NO}_3)_2\text{-DBC}$, findings regarding determination of the transfer regime merit mention. In the subject area of mass transfer accompanied by simultaneous chemical reaction it is commonly assumed that transfer in fluid-fluid systems is analogous to that in gas-liquid operations. In terms of the possible transfer regimes this concept is generally valid. Based on

the two-film theory, Levenspiel (1972) identifies eight transfer regimes for mass transfer of a slightly soluble gaseous species "A" which is absorbed into a liquid phase where it undergoes reaction with a reactant "B":

- A. Instantaneous reaction with respect to mass transfer,
- B. Instantaneous reaction with excess reactant "B" present,
- C. Fast reaction according to a second-order rate expression,
- D. Fast reaction with excess "B," hence psuedo first-order rate,
- E. Intermediate reaction with respect to mass transfer,
- F. Intermediate reaction with a high concentration of "B," psuedo first-order kinetics,
- G. Slow chemical reaction with respect to mass transfer,
- H. Infinitely slow chemical reaction.

These regimes describe gas-liquid systems in which reactant B is present in the liquid phase only. In practice, distinctions between instantaneous and fast reaction, and between slow and infinitely slow reaction are difficult to make. If these gradations are ignored, and without regard to the order of the reaction taking place, the eight regimes can be reduced to the three considered by Danesi: diffusion controlled (fast reaction), kinetic controlled (slow reaction), and diffusion-kinetic controlled (intermediate reaction).

Charpentier (1980) proposes a logic diagram for determining the applicable transfer regime. Eliminating the lesser distinctions of degree of reaction rate (fast versus instantaneous,

slow versus infinitely slow), and without consideration of the order of the reaction, the logic diagram of Charpentier is modified in accordance with the three regimes of Danesi in Figure 6-1.

Comparison of Figure 6-1 with the regime determination criteria of Danesi presented in Section 3.7.1 reveals some significant conflicts. Applying Charpentier's criteria, indication of an interfacial area effect on the rate of transfer is indicative of a diffusion controlled process. In contrast, Danesi states that interfacial area effects are indicative of interfacial kinetic control of the transfer process. The conflict can be attributed to a fundamental difference between gas-liquid absorption processes and liquid-liquid extraction of metals, namely that while absorbing gas components are generally soluble in the absorbing liquid, metals present in aqueous solutions as ionic groups are not likely to be transferred into organic solvents without undergoing reaction.

For the case of gas absorption it can be reasonably be assumed that any reaction which is sufficiently slow to control the overall rate of solute transfer will not remain restricted to the interface or the a film layer adjacent to the interface, but will extend into a bulk phase. For the particular case presented by Levenspiel and considered by Charpentier, a slow reaction will extend into the bulk liquid phase, as the reactant "B" is not present in the gas.

In metal extractions, analogous extension of the zone of chemical reaction into the bulk organic phase is highly improbable due the absence of the unreacted metal species in the bulk solvent. In those cases in which the solvent is significantly soluble in the aqueous phase the possibility of kinetic control in the bulk aqueous phase exists. However, as aqueous/solvent pairings are intentionally selected for their mutual insolubility, reaction control at the interface

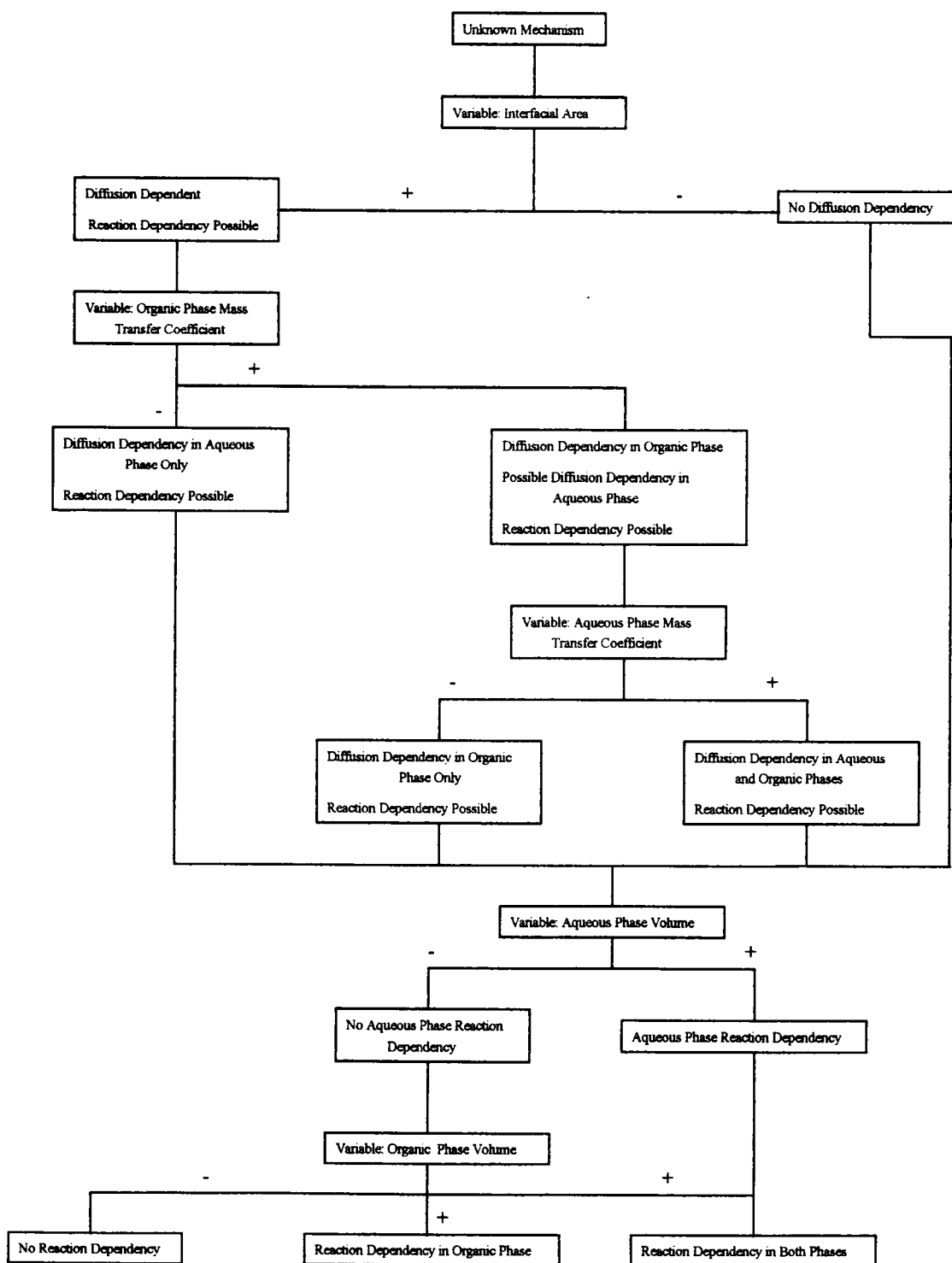


Figure 6-1. Logic diagram for determining controlling regime in gas-liquid absorption.

is more likely as the concentrations of solvent at the interface are considerably higher than those in the bulk aqueous solution, even when the latter contains solvent at the solubility limit. As surface area effects on transfer rate in extraction systems indicate kinetic control at the interface, indication of diffusion control in these systems in Lewis cell type devices must be by detection of film agitation (impeller size/speed) effects.

According to Danesi, no volume effect is to be anticipated in cases in which a slow reaction occurs in a bulk phase. For gas-liquid systems Charpentier proposes volume effects as an indicator of a reaction zone which extends into the bulk liquid phase. In this case, the difference in interpretation is due to differences between the test conditions. Charpentier's diagram is based on flow systems in which the two phases are continually being replaced. In this case the volume effect is actually volumetric flow rate, which controls contact time between gas and liquid elements at the interface. Regime determination criteria applied by Danesi are based on the use of batch contact devices, hence volume has no residence or contact time effects.

Finally, the use of true, single component overall transfer coefficients as defined in Section 4.1 and which are related to film coefficients by expressions (4-8) and (4-14) is probably not applicable to most metal extraction systems, as the aqueous phase transferring component is essentially nonexistent in the bulk organic phase. As a result, the aqueous phase concentration of the unreacted species "A" in equilibrium with the bulk organic phase "A" concentration, $C_{A,a}^*$, as defined by equation (4-2) does not exist since $C_{A,o} = 0$.

7. RECOMMENDATIONS

Additional information concerning reaction kinetics and the reaction mechanism could be obtained by performing rate tests in which the concentrations of all reactants, including the solvent and water, are varied. Variation of the solvent concentration will require use of an organic diluent which is determined to provide no extraction capability of its own. Considerable information stands to be gained by performing rate tests in which all reactants are present at or near stoichiometric concentrations.

Greater definition from effect tests stands to be gained by use of a transfer apparatus which allows independent control of impeller speeds in the two bulk phases, and which provides greater interface stability over a wide range of agitation conditions. The study reported was severely limited in the latter regard, as speeds lower than the 100 rpm speed used provided poor bulk phase mixing, and higher speeds resulted in interface instability.

Verification of the potential for minimizing co-extraction of nitric acid by using non-extracting salting agents should be attempted by performing additional equilibrium determinations for both uranium and HNO_3 , when the concentration of the latter is less than 1 M.

With regard to process applications, the results of this study indicate that devices used to facilitate uranium transfer in the system studied should be selected based on their ability to create a high degree of phase dispersion, as increasing the interfacial area will result in the greatest enhancement in the rate of solute transfer.

REFERENCES

REFERENCES

- Anderson, V. L., and R. A. McLean, "Design of Experiments," Marcel Dekker, Inc., New York (1974), Chapters 9 and 10.
- Baes, C. F., and R. E. Mesmer, "Hydrolysis of Cations," Krieger Publishing, Malabar, Fla., (1976).
- Benedict, M., T. H. Pigford, and H. W. Levi, "Nuclear Chemical Engineering," 2nd ed., Chap. 5, McGraw-Hill, New York (1981).
- Blankenship, J., and L. Folks, *Expected Values of Order Statistics from the Half-normal*, American Statistical Association Annual Meeting, 1965.
- Bulicka, J., and J. Prochazka, *Mass Transfer Between Two Turbulent Liquid Phases*, Chem. Eng. Sci., **31**, pp.137-146 (1976).
- Carberry, J. J., "Chemical and Catalytic Reaction Engineering," McGraw Hill, New York (1976).
- Charpentier, J., "Advances in Chemical Engineering," **11**, Thomas Drew, ed., Academic Press, New York (1981).
- Clewett, G. H., B. S. Weaver, W. B. Schaap, E. J. Lord, D. W. Kuhn, and C. M. Cobb, C-5.365.5 (Atomic Energy Commission Report), Jan. 22, 1946.
- Colburn, A. P., and D. G. Welsh, *Experimental Study of Individual Transfer Resistances in Countercurrent Liquid-Liquid Extraction*, Trans. Amer. Inst. Chem. Engrs., **38**, pp. 179-202 (1942).
- Cox, M. and D. S. Flett, "Proc. of Int. Solv. Extr. Conf.," ISEC 77, Toronto, 1977.
- Danckwerts, P. V., *Significance of Liquid-Film Coefficients in Gas Absorption*, Ind. Eng. Chem., **43**(6), pp. 1460-1467 (1951).
- Danesi, P. R., and Renato Chiarizia, *The Kinetics of Metal Solvent Extraction*, CRC Critical Reviews in Analytical Chemistry, CRC Press, **10**(1) November 1980.
- Daniel, C., *Use of Half-Normal Plots in Interpreting Factorial Two-Level Experiments*, Technometrics, **1**(4), pp. 311-341 (1959).
- Davies, J. T., "Turbulence Phenomena," Academic Press, New York (1972).
- DeMuth, S. F., *The Transport Dynamics of Zirconium Liquid-Liquid Extraction Based on the PUREX Process Used for Reprocessing Spent Nuclear Reactor Fuel* (Dissertation), The University of Tennessee, Knoxville (1989).

- Farber, H., D., W. Kuhn, L. J. Andrews, and J. W. Gates, Jr., *Observations on Dibutyl Carbitol Extraction*, C-1.365.2 (Atomic Energy Commission Report), August 10, 1945.
- Fisher, R. A., *The Correlation between Relative on the Supposition of Mendelian Inheritance*, Transactions of the Royal Society of Edinburgh, **52**, pp. 399-433 (1918).
- Fisher, R. A., "Statistical Methods for Research Workers," (1st ed.), Oliver and Boyd, Edinburgh (1925).
- Fisher, R. A., "The Design of Experiments," Oliver and Boyd, Edinburgh (1935).
- Gardner, A. W., H. A. C. McKay, and D. T. Warren, *The Partition of Uranyl Nitrate Between Water and Organic Solvents, Part III. -- The Water Content of the Organic Phase*, Trans. Faraday Soc., **48**, pp. 997-1004 (1952).
- Gilliland, E. R., and T. K. Sherwood, *Diffusion of Vapors into Air Streams*, Ind. Eng. Chem., **26**: p. 516 (1934).
- Glueckauf, E., H. A. C. McKay, and A. R. Mathieson, *The Partition of Uranyl Nitrate Between Water and Organic Solvents, Part II. -- The Partition Data and Their Interpretation*, Trans. Faraday Soc., **47**, pp. 437-449 (1951).
- Googin, J. M., and T. P. Sprague, *The Extraction of Uranium from Sodium Nitrate Solutions with Dibutyl Carbitol*, Y-331 (Atomic Energy Commission Report), January 26, 1949.
- Googin, J. M., and T. P. Sprague, *The Extraction of Small Amounts of Uranium from Magnesium Nitrate Solutions with Dibutyl Carbitol*, Y-327 (Atomic Energy Commission Report), January 20, 1949.
- Hanna, G. J., and R. D. Noble, *Measurement of Liquid-Liquid Interfacial Kinetics*, Chem. Rev., **85**, pp. 583-598 (1985).
- Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York (1943).
- Hatta, S., Tohoku Imperial U. Tech Rept., **8**, 1 (1928)
- Higbie, R., *The Rate of Absorption of a Pure Gas into a Still Liquid During Short Periods of Exposure*, Trans. AIChE, **31**, pp. 365-387 (1935).
- Huang, C., and C. Kuo, *General Mathematical Model for Mass Transfer Accompanied by Chemical Reaction*, A.I.Ch.E. J., **9**(2), pp. 161-167 (1963).

Jenkins, I. L., and H.A.C. McKay, *The Partition of Uranyl Nitrate Between Water and Organic Solvents, Part 6. - Salting-out by a Second Nitrate*. Trans. Faraday Soc., **49**, pp. 107-119 (1953).

Johnson, N. L. and F. C. Leone, *Statistics and Experimental Design*, Vol. 2., John Wiley & Sons, New York (1964), pp. 182-191.

Kishinevskii, M. Kh., and A. V. Pamfilov, Zhur. Priklad. Khim., **22**, 1173 (1949).

Kolar, V., *Heat and Mass Transfer in a Turbulent Medium*, Coll. Czech. Chem. Comm., **26**, 335 (1961)

Levenspiel, O., "Chemical Reaction Engineering," 2nd ed., John Wiley & Sons, New York, (1972).

Levich, V. G., "Physicochemical Hydrodynamics," Prentice-Hall, Englewood Cliffs, N.J., (1962).

Lewis, J. B., *The Mechanism of Mass Transfer of solutes across liquid-liquid interfaces --- Part I I - The determination of individual transfer coefficients for binary systems*, Chem. Eng. Sci., **3**, pp. 248-259 (1954).

Lewis, J. B., *The Mechanism of Mass Transfer of solutes across liquid-liquid interfaces --- Part II - The transfer of organic solutes between solvent and aqueous phases*, Chem. Eng. Sci., **3**, pp. 260-278 (1954).

Lewis, J. B., *The Mechanism of Mass Transfer of solutes across liquid-liquid interfaces --- Part III - The transfer of uranyl nitrate between solvent and aqueous phases*, Chem. Eng. Sci., **8**, pp. 295-308, (1958).

Lewis, W. K., and W. G. Whitman, Ind. Eng. Chem., **16**, 1215 (1924).

McKay, H.A.C., and A. R. Mathieson, *The Partition of Uranyl Nitrate Between Water and Organic Solvents, Part 1. - The State of the Uranyl Nitrate in the Organic Phase*, Trans. Faraday Soc., **47**, pp. 428-436 (1951).

McKay, H. A. C., *The Partition of Uranyl Nitrate Between Water and Organic Solvents. Part 5 - Calculation of the Activity of the Organic Solvent*, Trans. Faraday Soc., **48**, pp. 1103-1107 (1952).

Murdock, R., and H. R. C. Pratt, *Liquid- Liquid Extraction: Part VIII. The Extraction of Uranyl Nitrate in a Wetted Wall Column*, Trans. Instn. Chem. Engrs, **31**, pp. 307-326 (1953).

Nernst, W., Z. Phys. Chem., **47**, p. 52 (1904).

Nicholls, C. M., and R. Spence, *Chemical Processing of Nuclear Fuels*, Trans. Instn. Chem. Engrs., **35**, pp. 380-393 (1957).

Nicholls, C. M., *The Development of the BUTEX Process for the Industrial Separation of Plutonium from Nuclear Reactor Fuel*, Trans. Instn. Chem. Engrs., **36**, pp. 366-348 (1958).

Patton, F. S., J. M. Googin, and W. L. Griffith, "Enriched Uranium Processing," MacMillan, New York, 1963.

Seaborg, G. T., "Man-Made Transuranium Elements," Prentice-Hall, Englewood Cliffs, N. J., 1963.

Sherwood, T. K., R. L. Pigfor, and C. R. Wilke, "Mass Transfer", McGraw Hill, New York (1975).

Sprague, T. P., *Purification of Uranium with Dibutyl Carbitol*, Y-B66-31 (Atomic Energy Commission Report), September 20, 1954.

Sterling, C. V., and L. E. Scriven, *Interfacial Turbulence: Hydrodynamic Instability and the Marangoni Effect*, A.I.Ch.E. J., **4**(5), pp. 514-523 (1959).

Toor, H. L., and J. M. Marchello, *Film-penetration Model for Mass and Heat Transfer*, A.I.Ch.E. J., **4**(1), 97 (1958).

Tukey, J. W., "Index to Probability and Statistics: The Citation Index," R&D Press, Los Altos, CA (1973).

Van Name, R. G., and D. U. Hill, *On the Rate of Solution of Metals in Ferric Salts and Chromic Acid*, Amer. J. Sci., **42**, pp. 301-332 (1916).

Vivian, J. E., and C. J. King, *The Mechanism of Liquid-Phase Resistance to Gas Absorption in a Packed Column*, A.I.Ch.E. J., **10**, pg. 221 (1964)

Weaver, B. S., and C. E. Larson, *Factors Affecting the Extraction of Uranium with Dibutyl Carbitol*, AECD-3936 (Atomic Energy Commission Report), July 8, 1946.

Wei, J. C., thesis, Mass. Inst. Technol., Cambridge (1955).

Whitman, W.G., Chem. and Met. Engr., **29**, p. 146 (1923).

Wilcox, W. J., Jr., and T. F. Moore, CD-954-15 (Atomic Energy Commission report), Jan. 21, 1946.

Zahn, D. A., *Modifications of and Revised Critical Values for the Half-Normal Plot*, Technometrics, **17**(2), pp. 189-210 (1975).

Related Reading

Brenner, H., and L. G. Leal, *Interfacial Resistance to Interphase Mass Transfer in Quiescent Two-Phase Systems*, A.I.Ch.E. J., **24**(2), pp. 246-254 (1978).

Danckwerts, P. V., and A. M. Kennedy, *Kinetics of Liquid-Film Process in Gas Absorption. Part I: Models of the Absorption Process*, Trans. Instn. Chem. Engrs., **32** (supplement) p. S49 (1954).

Danckwerts, P. V., and A. M. Kennedy, *Kinetics of Liquid-Film Process in Gas Absorption. Part II: Models of the Absorption Process*, Trans. Instn. Chem. Engrs., **32** (supplement) p. S53 (1954).

Danckwerts, P. V., *Absorption by Simultaneous Diffusion and Chemical Reaction*, Trans. Faraday Soc., **46**, 300 (1950).

Danckwerts, P. V., and A. M. Kennedy, *The Kinetics of Absorption of Carbon Dioxide into Neutral and Alkaline Solutions*, Chem. Engr. Sci., **8** (3/4), 210 (1958).

Danesi, P.R., G. F. Vandegrift, E. P. Horwitz, and R. Chiarizia, *Simulation of Interfacial Two-Step Consecutive Reactions by Diffusion in the Mass-Transfer Kinetics of Liquid-Liquid Extraction of Metal Cations*, J. Phys. Chem. **84**, pp. 3582-3587 (1980).

Danesi, P. R., *The Relative Importance of Diffusion and Chemical Reaction in Liquid-Liquid Extraction Kinetics*, Solv. Ext. Ion Exch., **2**(1), pp. 29-44 (1984).

Gilliland, E. R., R. F. Baddour, and P. L. T. Brian, *Gas Absorption Accompanied by a Liquid-phase Chemical Reaction*, A.I.Ch.E. J., **4**(2), pp. 223-230 (1958).

Grady, H. R., G. M. Armstrong, and J. W. Gates, Jr., *The Dibutyl Carbitol-Tubanyl Nitrate Etherate*, AECD-3955 (Atomic Energy Commission Report), September 1945.

Guy, R. H., T. R. Aquino, and D. H. Honda, *Solute Transfer across Liquid-Liquid Interfaces. Kinetic and Thermodynamic Evaluation*, J. Phys. Chem., **86**, pp. 2861-2866 (1982).

Horner, D., J. Mailen, S. Thiel, T. Scott, and R. Yates, *Interphase Kinetics of Uraniium Using the Drop Method, Lewis Cell, and Kenics Mixer*, Ind. Eng. Chem. Fundam., **19**, pp. 103-109 (1980).

King, C. J., *Turbulent Liquid Phase Mass Transfer at a Free Gas-Liquid Interface*, Ind. Engr. Chem. Fund., **5**(1), pp. 1-8 (1966).

Kolar, V., *Contribution to the Theory of Mass and Heat Transfer in a Turbulent Medium*, Coll. Czech. Chem. Commun., **24**, pp. 3811-3815 (1959).

Olander, D. R., *Simultaneous Mass Transfer and Equilibrium Chemical Reaction*, A.I.Ch.E. J., **6**(2), pp. 233-239 (1960).

Olander, D. R., *The Mechanism of Extraction by Tributyl Phosphate-n-Hexane Solvents. Part II. Nitric Acid Extraction*, Nuc. Sci. Engrg, **15**, pp. 354-365 (1965).

Searle, S. R., F. M. Speed, and G. A. Milliken, *Population Marginal Means in the Linear Model: An Alternative to Least Squares Means*, Amer. Statistician, **34**(4), pp. 216-221 (1980).

Tavlarides, L. L., Stamatoudis, M., *The Analysis of Interphase Reactions and Mass Transfer in Liquid-Liquid Dispersions*, in "Advances in Chemical Engineering," **11**, Academic Press, New York (1981).

Toor, H. L., and S. H. Chiang, *Diffusion-controlled Chemical Reaction*, A.I.Ch.E. J., **5**(3), pp. 339-344 (1959).

Warren, B., E. C. Armstrong, and C. D. Susano, *The Reaction of Dibutyl Carbitol with Nitric Acid*, C.3.375.2 Series A (Atomic Energy Commission Report), August 23, 1945.

APPENDICES

Appendix A3.4.1 Acetic acid transfer test procedure

Procedure for Acetic Acid transfer testing in the Lewis cell

Test conditions are given in the grid below. Test variables are impeller diameter, volumes of the solution phases, and area of the interface. Variable codes are:

da1, small impeller in aqueous phase
da2, large impeller in aqueous phase
do1, small impeller in organic phase
do2, large impeller in organic phase
S1, smaller interfacial area (ring used)
S2, larger interfacial area (no ring)
Va1, smaller aqueous volume (350 ml)
Va2, larger aqueous volume (450 ml)
Vo1, smaller organic volume (350 ml)
Vo2, larger organic volume (450 ml)

Table A3.4.1-1 Conditions for acetic acid transfer tests.

Interfacial Area	Phase volume	Test name da1/do1	Test name da2/do1	Test name da1/do2	Test name da2/do2
S1	Va1/Vo1	Acid 1	x	x	Acid 2
S1	Va2/Vo1	x	Acid 3	Acid 4	x
S1	Va1/Vo2	X	Acid 5	Acid 6	x
S1	Va2/Vo2	Acid 7	x	x	Acid 8
S2	Va1/Vo1	x	Acid 9	Acid 10	x
S2	Va2/Vo1	Acid 11	x	x	Acid 12
S2	Va1/Vo2	Acid 13	x	x	Acid 14
S2	Va2/Vo2	x	Acid 15	Acid 16	x

Procedure:

Turn on the water bath and adjust the temperature to 25°C.

For a given set of conditions, place the appropriate volume of water in the beaker with longitudinal baffles.

Transfer the volume of isobutanol required for the test into the beaker.

If the S1 condition is called for, place the steel ring in the vessel such that the ring is split by the aqueous/organic interface.

Place the beaker into the water bath.

Attach the appropriate stirring disks to the stirring rod such that the blades on the disks oppose one another (blades on lower disk face downward; blades on upper disk face upward).

Insert the rod into the stirring motor.

Adjust the positions of the disks such that they are equal distances from the solution interface.

Allow thirty minutes for the solutions and equipment to come into thermal equilibrium. Inject 10 ml of acetic acid into the aqueous phase.

Initiate stirring at 150 rpm immediately after introducing the acetic acid. Start timing the run from the second the acetic acid was introduced.

Withdraw an organic phase sample after 1800 s (30 min).

Withdraw an organic sample after 2700 s (45 min).

Withdraw aqueous and organic samples at 3600 s (60 min).

Have all samples analyzed for acetic acid concentration only. Anticipated aqueous phase acetic acid concentrations should fall in the range 20 - 30 g/l. Organic phase acetic acid concentrations should be in the 4 - 8 g/l range.

Place the spent aqueous solution in a waste carboy. This solution is not a hazardous or RCRA waste. The isobutanol is a hazardous waste, and will have to be placed in a satellite accumulation area.

Appendix A3.4.2 Uranium mass transfer test procedure

Procedure for Uranium mass transfer tests

(Revision 1 -- supersedes procedure of 2/1/94)

Initial solutions for all tests will be undiluted dibutyl carbitol, and 1N HNO₃ containing calcium nitrate at a concentration of 3.5M.

A total of 16 tests will be performed. Condition sets for each test are given in the table below.

da1, small impeller in aqueous phase
da2, large impeller in aqueous phase
do1, small impeller in organic phase
do2, large impeller in organic phase
S1, smaller interfacial area (ring used)
S2, larger interfacial area (no ring)
Va1, smaller aqueous volume (300 ml)
Va2, larger aqueous volume (400 ml)
Vo1, smaller organic volume (300 ml)
Vo2, larger organic volume (400 ml)

Table A3.4.2-1 Conditions for uranium transfer tests

Interfacial Area	Phase volume	Test name da1/do1	Test name da2/do1	Test name da1/do2	Test name da2/do2
S1	Va1/Vo1	UDBC 1	x	x	UDBC 2
S1	Va2/Vo1	x	UDBC 3	UDBC 4	x
S1	Va1/Vo2	X	UDBC 5	UDBC 6	x
S1	Va2/Vo2	UDBC 7	x	x	UDBC 8
S2	Va1/Vo1	x	UDBC 9	UDBC 10	x
S2	Va2/Vo1	UDBC 11	x	x	UDBC 12
S2	Va1/Vo2	UDBC 13	x	x	UDBC 14
S2	Va2/Vo2	x	UDBC 15	UDBC 16	x

Procedure:

1. Turn on the Lewis cell water bath and adjust the temperature to 25°C.

2. Attach the appropriate impellers to the stirring rod such that the blades on the disks oppose one another (blades on lower disk face downward; blades on upper disk face upward).
3. With the mixing beaker outside the water bath, place the aqueous solution into the beaker.
4. Place the aqueous sample collection capillary tube into the beaker containing the aqueous solution. If the S1 condition is called for, place the interface ring in the beaker such that the ring breaks the liquid surface.
5. Adjust the sample capillary tube such that the bottom tip is at approximately the same depth as the aqueous phase impeller blades.
6. Place the appropriate volume of organic solution (dibutyl carbitol) into the beaker.
7. Place the beaker containing the two phases into the water bath.
8. Connect the impeller shaft to the variable speed stirrer. Adjust the positions of the impellers such that they are equal distances from the solution interface.
9. Stir the solutions in the beaker at a speed of 200 rpm for a minimum of 15 minutes to allow the acid concentration to equilibrate in the two phases.
10. After 15 minutes, reset the mixer speed to 100 rpm and stop mixing. Allow the two solutions phases to separate.
11. Withdraw 5 ml samples from both phases. (Note: there is no uranium in the system at this point.)
12. After sampling, inject a volume of the lower-concentration uranium spike solution into the aqueous phase to obtain an aqueous phase uranium concentration of 1 g/l. **The time at which uranium spike solution is first observed entering the aqueous phase becomes time $t = 0$.**
13. Withdraw 5 ml samples from both phase after 10 minutes. The organic sample is to be removed using a metering pipette. Aqueous samples are to be collected by the following procedure:

Insert the syringe through the sample collection capillary such that the tip is visible below the end of the capillary tube.

Slowly collect a small sample in the syringe (1-to-2 ml). Slowly flush this solution back into the aqueous phase. Do not bubble gas through the capillary tube into the aqueous phase.

Slowly collect a 5 ml sample.

If necessary, lower the interface ring so that it stays at the solution interface.

14. Repeat sampling of both phases after 20 minutes. Readjust the interface ring as needed.
15. Repeat sampling of both phases after 40 minutes. Readjust the interface ring as needed.
16. Repeat sampling of both phases after 80 minutes. Readjust the interface ring as needed.
17. Repeat sampling of both phases after 160 minutes. Readjust the interface ring as needed.
18. Repeat sampling of both phases after 300 minutes.

(Note: the sampling frequency may be reduced pending results of the first few tests.)

19. Have all samples analyzed for uranium and nitric acid concentrations.

Appendix A3.4.3 Procedure for evaluation of uranium solvation kinetics

Tests to determine effects of uranium and nitric acid concentrations on rate of U extraction into dibutyl carbitol

Initial solutions for all tests will be undiluted dibutyl carbitol, and 1N HNO₃ containing calcium nitrate at a concentration of 3.5M.

A total of five tests will be performed. The following conditions will remain unchanged for all five tests.

d_a – small impeller in aqueous phase

d_o – small impeller in organic phase

S – small interfacial area (interface ring is used)

V_a – small aqueous volume (300 ml)¹

V_o – small organic volume (300 ml)

Table A3.4.3-1 Conditions for uranium transfer kinetics tests

Test Name	U conc, g/l	HNO ₃ conc, M	Ca(NO ₃) ₂ conc, M	U spike volume, ml*
YKINETK-1	1	1	3.5	0.872 (345 g/l sol'n)
YKINETK-2	0.1	1	3.5	0.259 (116 g/l sol'n)
YKINETK-3	5	1	3.5	4.35 (345 g/l sol'n) ¹
YKINETK-4	1	0.1	3.5	0.872 (345 g/l sol'n)
YKINETK-5	1	2	3.5	0.872 (345 g/l sol'n)

*The concentration of the uranium spike solution to be used is given in parentheses.

¹Due to the significant spike solution volume, the pre-spike acid volume is to 296 ml, not 300 ml.

Procedure:

1. Turn on the Lewis cell water bath and adjust the temperature to 25°C.
2. Attach the small impellers to the stirring rod such that the blades on the disks oppose one another (blades on lower disk face downward; blades on upper disk face upward).
3. With the mixing beaker outside the water bath, place the aqueous solution into the beaker. (Don't forget the special condition for test YKINETK-3.)

4. Place the aqueous sample collection capillary tube into the beaker containing the aqueous solution. If the S1 condition is called for, place the interface ring in the beaker such that the ring breaks the liquid surface.
5. Adjust the sample capillary tube such that the bottom tip is at approximately the same depth as the aqueous phase impeller blades.
6. Place the appropriate volume of organic solution (dibutyl carbitol) into the beaker.
7. Place the beaker containing the two phases into the water bath.
8. Connect the impeller shaft to the variable speed stirrer. Adjust the positions of the impellers such that they are equal distances from the solution interface.
9. Stir the solutions in the beaker at a speed of 200 rpm for a minimum of 15 minutes to allow the acid concentration to equilibrate in the two phases.
10. After 15 minutes, reset the mixer speed to 100 rpm and stop mixing. Allow the two solutions phases to separate.
11. Withdraw 2 ml samples from both phases. (Note: there is no uranium in the system at this point.)
12. After sampling, inject the uranium spike solution into the aqueous phase to obtain the desired aqueous phase uranium concentration. **The time at which uranium spike solution is first observed entering the aqueous phase becomes time $t = 0$.**
13. Withdraw 3 ml samples from both phase after 10 minutes. The organic sample is to be removed using a metering pipette. Aqueous samples are to be collected by the following procedure:

Insert the syringe through the sample collection capillary such that the tip is visible below the end of the capillary tube.

Slowly collect a small sample in the syringe (1-to-2 ml). Slowly flush this solution back into the aqueous phase. Due not bubble gas through the capillary tube into the aqueous phase.

Slowly collect a 3 ml sample.

If necessary, lower the interface ring so that it stays at the solution interface.

14. Repeat sampling of both phases after 20 minutes. Readjust the interface ring as needed.
15. Repeat sampling of both phases after 40 minutes. Readjust the interface ring as needed.
16. Repeat sampling of both phases after 80 minutes. Readjust the interface ring as needed.
17. Repeat sampling of both phases after 160 minutes. Readjust the interface ring as needed.
18. Repeat sampling of both phases after 300 minutes.

(Note: the sampling frequency may be reduced pending results of the first few tests.)

19. Have all samples except those collect in step 11 analyzed for uranium and nitric acid concentrations. The samples collected in step 11 are to analyzed for nitric acid concentration only.

Appendix A3.6.1 Half Normal Plotting Technique

Half Normal Plotting Technique

Lacking prior knowledge of null effects and having no repeated treatment combinations, either of which could be used to generate an error estimate, significance of single and two-factor interaction effects on uranium transfer was evaluated by use of half normal plots. This technique, developed by Daniel (1959), can be used to estimate the error standard deviation, test significance of factors on yields, and make judgments regarding the validity of the data. Subsequently, the technique has been modified by Zahn (1975) to incorporate corrected significance guard rails and simplified plotting procedures.

Construction of half normal plots first requires determination of contrasts from the experimental yields (dependent variable values). In the case of the transfer experiments performed in the subject study, the yields are transfer rates. Single effects are the impeller diameters in the two bulk phases, the interfacial surface area, and the bulk phase volumes.

When manual calculations are performed, calculation of contrasts by application of Yates' technique is recommended (Johnson and Leone, 1964). This method results in calculation of contrasts and sums of squares for all main effects and interactions. Alternatively, when effects from interactions of greater than two factors are assumed to be zero, contrasts and sums of squares may be calculated using two-way tables, as described by Anderson and McLean (1974). For the subject study in which interaction effects higher than order 2 have been assumed insignificant and factors were applied at two levels, contrasts were calculated using a table of the form shown in Table A3.6.1-1. As indicated in the table, the levels of each factor are coded as either -1 (low level) or +1 (high level). Contrasts for each single effect are calculated by summing for each treatment combination (each combination of factor conditions) the product of the yields and the factor level of the effect. For two factor interaction contrasts,

the products of the two applicable factors and the yield for each treatment combination are summed.

Table A3.6.1. Typical factor level table for calculation of contrasts

Test No.	da	do	Va	Vo	S	Yield
1	-1	-1	-1	-1	-1	1.107
2	+1	+1	-1	-1	-1	1.549
3	+1	-1	+1	-1	-1	1.244
4	-1	+1	+1	-1	-1	1.289
5	+1	-1	-1	+1	-1	1.388
6	-1	+1	-1	+1	-1	1.388
7	-1	-1	+1	+1	-1	1.304
8	+1	+1	+1	+1	-1	1.684
9	+1	-1	-1	-1	+1	1.566
10	-1	+1	-1	-1	+1	1.249
11	-1	-1	+1	-1	+1	1.188
12	+1	+1	+1	-1	+1	1.569
13	-1	-1	-1	+1	+1	1.543
14	+1	+1	-1	+1	+1	1.955
15	+1	-1	+1	+1	+1	1.341
16	-1	+1	+1	+1	+1	1.226

The contrasts calculated in this manner are then ranked by magnitude, and are assigned order statistics which are referred to by Zahn as z-statistics. Z-statistics are defined as the means of the order statistics of random samples from the standard half-normal distribution. Z-values calculated by Blankenship and Folks (1965) are presented in Table A3.2.

Using the procedure recommended by Zahn, calculated contrasts are plotted by rank on the ordinate against an abscissa having dual scales of the z-statistic and the probability.

Significance of effects is based on comparisons against guard rails which are constructed on the

plots. Guard rails are based on percentiles of the t-statistics (the normalized contrasts), where t_i is the absolute contrast, x_i for the i th effect divided by the error.

$$t_i = x_i / \sigma$$

Table A3.6.1-2. Order statistics for 16 effects

i	1	2	3	4	5	6	7	8
z_i	0.079	0.158	0.239	0.322	0.408	0.496	0.589	0.688
i	9	10	11	12	13	14	15	
z_i	0.794	0.910	1.040	1.191	1.376	1.626	2.051	

z_i mean order statistic for rank i

Zahn developed two modifications to the plotting technique of Daniel, which he referred to as the "X" and "S" modifications. Zahn's research indicated that while the results of the X and S modifications of Daniel's procedure were comparable when only one real (significant) effect is present, the S modification is more powerful when from two to four effects are significant. Zahn states that in his studies in which four effects are significant (real), his second modification (the "S" version) detects 27% of the real effects, while the first modification (the "X" version) detects only 21%.

The X and S modifications of the plot technique differ in the initial error estimate used in the construction of significance guard rails. For the S-type half normal construction, the initial error estimate is the slope of the ordinary least squares regression line through the origin, as calculated by the expression

$$SL(a,n) = \frac{\sum_{i=1}^a x_i z_i}{\sum_{i=1}^a z_i^2}, \quad a \leq n$$

where n is the number of effects under consideration and a is given by the expression

$$a = 0.683(n + 1).$$

Using the S modification to the method of Daniel, guard rails for evaluating significance at the 0.05, 0.20 and 0.40 levels (95%, 80%, and 60% confidence levels) are established. For plots of 15 effects, guard rails corresponding to only the four highest rank order statistics are plotted. In analyses of 15 effects, the eleventh-ranked effect is taken as an estimate of the error as this observation occurs nearest one standard deviation from the mean for a normal distribution. As Zahn plots the contrast values directly, the critical values (which were calculated based on use of t statistics) must be corrected by multiplication by the error estimate prior to plotting against the corresponding z values. The critical values for the S method analysis were determined by generating a cumulative distribution from 999 simulations and estimating the 0.95, 0.80, and 0.60 quantiles. Critical values determined by Zahn for evaluation of 15 effects are presented in Table A3.6.1-3.

Table A3.6.1-3. Critical values for establishing significance guard rails.

Rank	0.05 level	0.20 level	0.40 level
15	3.37	2.61	2.20
14	3.00	2.34	1.97
13	2.61	2.06	1.76
12	2.21	1.76	1.51

Appendix A3.6.2 Analysis of Variance

Analysis of Variance

When prior knowledge of the experimental error exists or error can be estimated from null effect contrasts, significance of effects can be determined by an analysis of variance. As in the case of the half normal plot technique, contrasts are calculated from the data and factor level codes. In addition, sums of squares are calculated. Significance of an effect is determined by calculation of an F statistic, which is the sum of squares for each effect divided by the residual sum of squares.

For a factorial experiment in which there is one data point for each treatment combination and no reasonable error estimate exists, a pooled estimate of the residual can be obtained if it is assumed that specific effects are zero. In the case of a full factorial experiment, this is usually accomplished by pooling the sums of squares of multiple (e.g. 4- and 5- factor interactions) to obtain an estimate of the residual.

In the case of a fractional factorial experiment, such as the half-factorial transfer experiments used in this study, there are no degrees of freedom available if all main and two-factor interaction effects are included in the analysis. With no prior error estimate available, a residual can be calculated by pooling the sums of squares for any effects which can reasonably be assumed to be zero.

In the acetic acid transfer rate evaluation performed in this study, it has been assumed that the single factor phase volume effects and all two-factor interaction effects involving a bulk phase volume are zero. This assumption is based on the lack of any chemical reaction in the transfer of acetic acid as reported by Lewis (1954), and the observed complete mixing of the bulk phases. As a result phase volumes cannot affect either the rate of reaction or diffusion. In the transfer of uranium from aqueous nitric acid into dibutyl carbitol, interaction effects

between a bulk phase volume and the diameter of the impeller in the same phase have been assumed to be null, as the bulk phases were thoroughly mixed regardless of impeller diameter. Hence, the volume effect relates only to the rate of chemical reaction whereas the impeller diameter relates to diffusion mass transfer. In addition, the interaction effect between the two bulk phase volumes, V_1 and V_0 has been assumed to be null do to physical separation.

Sums of squares are calculated by the expression

$$SS(A) = \frac{\left[\sum_i^n a_i x_i \right]^2}{n \sum_i^n a_i^2},$$

where $SS(A)$ is the sum of squares for an effect A , a_i 's are the coded coefficients from a factor level table equal to either +1 or -1 (ref. Table A3.6.1-2), x_i is the yield for the same treatment combination, and n is the number of replications. For a fractional two-level experiment with k factors, the divisor becomes $n2^k$, where k is the number of factors and n is the fraction.

An estimate of the residual sum of squares is obtained by pooling the sums of squares for the treatment combinations assumed to produce zero effects, and dividing by the number of effects pooled.

$$\sigma^2 = \frac{\sum SS(\text{zero effects})}{\text{no. of zero effects}}.$$

F statistics are then calculated for the non-zero effects by dividing their respective sums of squares by the estimated residual

$$F_i = \frac{SS_i}{\sigma^2}.$$

To evaluate significance at various levels of confidence, the F values calculated are compared against percentage points of the F distribution.

In the study performed, analysis of variance was performed using the SAS statistical analysis software package (SAS Institute, Cary, North Carolina). Printouts of the results and a sample program code used are presented in Appendixes A5.2b and A5.5.

Appendix A5.1. Distribution data for uranium and nitric acid.

				U equilibrium data with calcium nitrate in aqueous phase			
U, g/L, aq	9.5	9.5	9.27	9.27	8.34	8.11	6.26
U, g/L, org	0.6	0.6	0.93	0.93	1.76	1.76	3.4
H, mol/L aq	0.7	0.8	0.74	0.8	0.82	0.76	0.7
H, mol/L or	0.2	0.2	0.14	0.14	0.2	0.2	0.28
U dist. coeff.	0.063157895	0.063157895	0.100323625	0.094929881	0.211031175	0.21701603	0.54313099
HNO3 dist. coeff.	0.285714286	0.25	0.189189189	0.175	0.243902439	0.263157895	0.4
Ca, aqueous conc., mol/L	0.101562566	0.101562566	0.247584163	0.247584163	0.501757358	0.501757358	0.996891806
Ca, target conc.	2.3615	2.3615	5.9038	5.9038	11.8075	11.8075	23.615
Ca wt	2.3984	2.3984	5.8467	5.8467	11.849	11.849	23.5416
Free DBC	3.851957983	3.851957983	3.909184874	3.909605042	3.842210084	3.842210084	3.748428571
NO3 total	0.903125132	1.003125132	1.235168325	1.295168325	1.823514715	1.763514715	2.693783612
Ku/DBCf ²	0.004256617	0.004256617	0.006564941	0.006210652	0.014295008	0.014700415	0.038655038
Kh/DBCf	0.07417378	0.064902058	0.048396071	0.044761555	0.063479725	0.068491282	0.106711384
	10.1	10.1	10.2	10.15	10.1	9.87	9.66
U, g/L, aq	6.49	2.36	2.36	0.08	0.08		
U, g/L, org	3.42	8.9	10.2	11.7	12.3		
H, mol/L aq	0.66	0.46	0.48	0.11	0.11		
H, mol/L or	0.32	0.54	0.56	0.86	0.86		
U dist. coeff.	0.526964561	3.771186441	4.322033898	146.25	153.75		
HNO3 dist. coeff.	0.484848485	1.173913043	1.166666667	7.818181818	7.818181818		
Ca, aqueous conc., mol/L	0.996891806	1.998729621	1.998729621	4.001693839	4.001693839		
Ca, target conc.	23.615	47.23	47.23	94.46	94.46		
Ca wt	23.5416	47.2	47.2	94.5	94.5		
Free DBC	3.708260504	3.442210084	3.411285714	3.098680672	3.093638655		
NO3 total	2.653783612	4.457459242	4.477459242	8.113387677	8.113387677		
Ku/DBCf ²	0.038321362	0.318275536	0.371408619	15.23148434	16.0648233		
Kh/DBCf	0.130748227	0.341034888	0.342002038	2.523067926	2.527180026		
	9.91	11.26	12.56	11.78	12.38		

U equilibrium data without calcium nitrate addition									
U, g/L, aq	4.54	4.54	4.54	2.4	2.4	2.4	2.4	2.4	2.4
U, g/L, org	0.48	0.49	0.49	0.35	0.34	0.35	0.35	0.41	0.38
Initial aq HNO3, mol/L	1.12	1.2	1.2	1.3	1.3	1.3	1.3	1.34	1.4
U dist. coef.	0.105727	0.10793	0.10793	0.145833	0.141667	0.145833	0.145833	0.170833	0.158333
U, g/L, aq	2.4	2.23	2.23	2.23	2.92	2.92	2.92	2.92	1.77
U, g/L, org	0.4	0.58	0.59	0.57	2.3	2.27	2.27	2.31	3.04
Initial aq HNO3, mol/L	1.4	1.7	1.7	1.7	2.46	2.5	2.5	2.54	3.46
U dist. coef.	0.166667	0.26009	0.264574	0.255605	0.787671	0.777397	0.777397	0.791096	1.717514
U, g/L, aq	1.8	1.8	1.25	1.25					
U, g/L, org	3.11	3.12	3.53	3.53					
Initial aq HNO3, mol/L	3.5	3.5	4.9	4.9					
U dist. coef.	1.727778	1.733333	2.824	2.824					

	A	B	C	D
1	Typical cell formulas			
2	U dist. data with calcium			
3				
4	U, g/L, aq	9.5	9.5	9.27
5	U, g/L, org	0.6	0.6	0.93
6	H, mol/L aq	0.7	0.8	0.74
7	H, mol/L or	0.2	0.2	0.14
8	U dist. coeff.	= B\$5/B\$4	= C\$5/C\$4	= D\$5/D\$4
9	HNO3 dist. coeff.	= B\$7/B\$6	= C\$7/C\$6	= D\$7/D\$6
10	Ca, aqueous conc., mol/L	= B12/236.15/0.1	= C12/236.15/0.1	= D12/236.15/0.1
11	Ca, target conc.	2.3615	2.3615	5.9038
12	Ca wt	2.3984	2.3984	5.8467
13	Free DBC	= 4.057-B5/238*2-B7	= 4.057-C5/238*2-C7	= 4.057-D5/238*2-D7
14	NO3 total	= B4/238*0+B6+2*B10	= C4/238*0+C6+2*C10	= D4/238*0+D6+2*D10
15	Ku/DBCf^2	= B8/B13^2	= C8/C13^2	= D8/D13^2
16	Kh/DBCf	= B9/B13	= C9/C13	= D9/D13
17				
18				
19	U dist. data without calcium			
20				
21	U, g/L, aq	4.54	4.54	4.54
22	U, g/L, org	0.48	0.49	0.49
23	Initial aq HNO3, mol/L	1.12	1.2	1.2
24	U dist. coeff.	= B22/B21	= C22/C21	= D22/D21

Data for nitric acid distribution without calcium nitrate addition										
H, aq	1.12	1.2	1.2	1.3	1.3	1.3	1.34	1.4	1.4	
H, or	0.08	0.12	0.1	0.2	0.2	0.3	0.3	0.3	0.26	1.7
Kh/DBCf	0.071429	0.1000	0.083333	0.153846	0.153846	0.230769	0.223881	0.214286	0.185714	0.4
										0.235294
H, aq	1.7	1.7	2.46	2.5	2.54	3.46	3.5	3.5	4.9	
H, or	0.4	0.4	0.9	0.74	1	1.7	1.64	1.7	2.6	2.5
Kh/DBCf	0.235294	0.235294	0.365854	0.296	0.393701	0.491329	0.468571	0.485714	0.510204	0.530612

Appendix A5.2a. Calculation of overall transfer coefficients for acetic acid transfer.

		A
1	Typical formula for calculating overall coefficients	
2		
3	K at 30 min from organic phase concentration data	
4	$=\$C4/(-\$F4*(1/\$K\$21+\$C4/\$B4)*H4*60)*LN((\$G4-(1/\$K\$21+\$C4/\$B4)*I4)/\$G4)$	
5	$=\$C5/(-\$F5*(1/\$K\$21+\$C5/\$B5)*H5*60)*LN((\$G5-(1/\$K\$21+\$C5/\$B5)*I5)/\$G5)$	
6	$=\$C6/(-\$F6*(1/\$K\$21+\$C6/\$B6)*H6*60)*LN((\$G6-(1/\$K\$21+\$C6/\$B6)*I6)/\$G6)$	
7	$=\$C7/(-\$F7*(1/\$K\$21+\$C7/\$B7)*H7*60)*LN((\$G7-(1/\$K\$21+\$C7/\$B7)*I7)/\$G7)$	
8	$=\$C8/(-\$F8*(1/\$K\$21+\$C8/\$B8)*H8*60)*LN((\$G8-(1/\$K\$21+\$C8/\$B8)*I8)/\$G8)$	
9	$=\$C9/(-\$F9*(1/\$K\$21+\$C9/\$B9)*H9*60)*LN((\$G9-(1/\$K\$21+\$C9/\$B9)*I9)/\$G9)$	
10	$=\$C10/(-\$F10*(1/\$K\$21+\$C10/\$B10)*H10*60)*LN((\$G10-(1/\$K\$21+\$C10/\$B10)*I10)/\$G10)$	
11	$=\$C11/(-\$F11*(1/\$K\$21+\$C11/\$B11)*H11*60)*LN((\$G11-(1/\$K\$21+\$C11/\$B11)*I11)/\$G11)$	
12	$=\$C12/(-\$F12*(1/\$K\$21+\$C12/\$B12)*H12*60)*LN((\$G12-(1/\$K\$21+\$C12/\$B12)*I12)/\$G12)$	
13	$=\$C13/(-\$F13*(1/\$K\$21+\$C13/\$B13)*H13*60)*LN((\$G13-(1/\$K\$21+\$C13/\$B13)*I13)/\$G13)$	
14	$=\$C14/(-\$F14*(1/\$K\$21+\$C14/\$B14)*H14*60)*LN((\$G14-(1/\$K\$21+\$C14/\$B14)*I14)/\$G14)$	
15	$=\$C15/(-\$F15*(1/\$K\$21+\$C15/\$B15)*H15*60)*LN((\$G15-(1/\$K\$21+\$C15/\$B15)*I15)/\$G15)$	
16	$=\$C16/(-\$F16*(1/\$K\$21+\$C16/\$B16)*H16*60)*LN((\$G16-(1/\$K\$21+\$C16/\$B16)*I16)/\$G16)$	
17	$=\$C17/(-\$F17*(1/\$K\$21+\$C17/\$B17)*H17*60)*LN((\$G17-(1/\$K\$21+\$C17/\$B17)*I17)/\$G17)$	
18	$=\$C18/(-\$F18*(1/\$K\$21+\$C18/\$B18)*H18*60)*LN((\$G18-(1/\$K\$21+\$C18/\$B18)*I18)/\$G18)$	

	A		B		C		D		E		F		G		H		I		J		K		L	
	Acetic acid tests		ml	Aq. Vol	ml	Org. Vol	cm	Aq. Dia	cm	Org. Dia	cm2	Interface	Initial Aq.	Time	Sample 1	Time	conc.	Time	Sample 2	Time	conc.	Time	Sample 3	Time
1																								
2																								
3	Test No.																							
4	1		350		350	4.4958	4.4958	59.242	0.485228	30	0.12	47	0.17	60										
5	2		350		350	5.85978	5.85978	59.242	0.485228	30	0.16	45	0.19	60										
6	3		450		350	5.85978	4.4958	59.242	0.379743	30	0.11	45	0.15	60										
7	4		450		350	4.4958	5.85978	59.242	0.379743	30	0.11	45	0.15	60										
8	5		350		450	5.85978	4.4958	59.242	0.485228	30	0.12	45	0.15	60										
9	6		350		450	4.4958	5.85978	59.242	0.485228	30	0.12	45	0.15	60										
10	7		450		450	4.4958	4.4958	59.242	0.379743	30	0.11	45	0.11	60										
11	8		450		450	5.85978	5.85978	59.242	0.379743	30	0.11	45	0.14	60										
12	9		350		350	5.85978	4.4958	81.352	0.485228	30	0.19	45	0.23	60										
13	10		350		350	4.4958	5.85978	81.352	0.485228	30	0.17	45	0.2	60										
14	11		450		350	4.4958	4.4958	81.352	0.379743	30	0.14	45	0.16	60										
15	12		450		350	5.85978	5.85978	81.352	0.379743	30	0.16	45	0.19	60										
16	13		350		450	4.4958	4.4958	81.352	0.485228	30	0.15	45	0.18	60										
17	14		350		450	5.85978	5.85978	81.352	0.485228	30	0.17	45	0.2	60										
18	15		450		450	5.85978	4.4958	81.352	0.379743	30	0.12	45	0.15	60										
19	16		450		450	4.4958	5.85978	81.352	0.379743	30	0.11	45	0.14	60										
20			volume Acetic acid injected at time = 0 was 10 ml																					
21			moles acetic acid injected =																					
22			molecular weight acetic acid =																					
23			density acetic acid at 20 C =																					
24			viscosity at 25 C =																					
25																								
26																								

	M	N	O	P	Q
1	SAMPLES				
2		Organic-based K at time			Avg K
3	conc.	30 min	45 min	60 min	
4	0.19	0.00107	0.001151	0.001102	0.001107
5	0.22	0.001831	0.001489	0.001519	0.001539
6	0.16	0.001265	0.001343	0.001126	0.001244
7	0.17	0.001265	0.001343	0.00126	0.001289
8	0.17	0.001461	0.001387	0.001315	0.001388
9	0.17	0.001461	0.001387	0.001315	0.001388
10	0.14	0.0015	0.001146	0.001266	0.001304
11	0.16	0.001719	0.001889	0.001645	0.001684
12	0.24	0.001804	0.001664	0.001428	0.001565
13	0.23	0.001313	0.001185	0.001248	0.001249
14	0.19	0.001311	0.001093	0.001161	0.001188
15	0.21	0.00164	0.001548	0.001519	0.001589
16	0.21	0.001515	0.001443	0.001672	0.001543
17	0.22	0.001915	0.001893	0.002057	0.001955
18	0.16	0.001428	0.001399	0.001198	0.001341
19	0.16	0.001252	0.00123	0.001198	0.001226
20					
21					
22					
23					
24					
25					
26					
28					

Appendix A5.2b. SAS printouts for acetic acid transfer experiment ANOVA

```

options ls=80 ps=56;
data urate;
infile 'd:\phdfile\acetacid\60data.txt';
input rate Va Vo da do S;
run;
proc print;
proc univariate data=urate normal;
var rate;
run;
proc glm;
model rate=da do Va Vo S da*do da*Vo da*S do*Va do*S Va*S Vo*S;
run;

```

SAS 10:47 Wednesday, April 19, 1995 22

OBS	RATE	VA	VO	DA	DO	S
1	0.49200	-1	-1	-1	-1	-1
2	0.55300	-1	-1	1	1	-1
3	0.44600	1	-1	1	-1	-1
4	0.44582	1	-1	-1	1	-1
5	0.45600	-1	1	1	-1	-1
6	0.45600	-1	1	-1	1	-1
7	0.39800	1	1	-1	-1	-1
8	0.41600	1	1	1	1	-1
9	0.54738	-1	-1	1	-1	1
10	0.55661	-1	-1	-1	1	1
11	0.49206	1	-1	-1	-1	1
12	0.49666	1	-1	1	1	1
13	0.48000	-1	1	-1	-1	1
14	0.46333	-1	1	1	1	1
15	0.42844	1	1	1	-1	1
16	0.41598	1	1	-1	1	1

SAS 10:47 Wednesday, April 19, 1995 23

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.471454	Sum	7.543271
Std Dev	0.049308	Variance	0.002431
Skewness	0.491298	Kurtosis	-0.62025
USS	3.592778	CSS	0.036469
CV	10.45871	Std Mean	0.012327
T:Mean=0	38.24565	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.934437	Prob<W	0.2850

Quantiles(Def=5)

100% Max	0.556609	99%	0.556609
75% Q3	0.494361	95%	0.556609
50% Med	0.459665	90%	0.553
25% Q1	0.437126	10%	0.415976
0% Min	0.398	5%	0.398
		1%	0.398
Range	0.158609		
Q3-Q1	0.057235		
Mode	0.456		

Extremes

Lowest	Obs	Highest	Obs
0.398(	7)	0.492059(	11)
0.415976(	16)	0.496663(	12)
0.416(	8)	0.547382(	9)
0.428436(	15)	0.553(	2)
0.445817(	4)	0.556609(	10)

SAS 10:47 Wednesday, April 19, 1995 24
General Linear Models Procedure
Number of observations in data set = 16

SAS 10:47 Wednesday, April 19, 1995 25

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	0.00465388	0.00077565	0.22	0.9607
Error	9	0.03181536	0.00353504		
Corrected Total	15	0.03646924			
	R-Square	C.V.	Root MSE	RATE Mean	
	0.127611	12.61123	0.0594562	0.47145444	

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00030931	0.00030931	0.09	0.7741
DO	1	0.00025215	0.00025215	0.07	0.7954
S	1	0.00296037	0.00296037	0.84	0.3840
DA*DO	1	0.00009424	0.00009424	0.03	0.8739
DA*S	1	0.00048419	0.00048419	0.14	0.7199
DO*S	1	0.00055363	0.00055363	0.16	0.7015

Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00030931	0.00030931	0.09	0.7741
DO	1	0.00025215	0.00025215	0.07	0.7954
S	1	0.00296037	0.00296037	0.84	0.3840
DA*DO	1	0.00009424	0.00009424	0.03	0.8739
DA*S	1	0.00048419	0.00048419	0.14	0.7199
DO*S	1	0.00055363	0.00055363	0.16	0.7015

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.4714544375	31.72	0.0001	0.01486405
DA	0.0043968125	0.30	0.7741	0.01486405
DO	0.0039698125	0.27	0.7954	0.01486405
S	0.0136023125	0.92	0.3840	0.01486405
DA*DO	0.0024269375	0.16	0.8739	0.01486405
DA*S	-0.0055010625	-0.37	0.7199	0.01486405
DO*S	-0.0058823125	-0.40	0.7015	0.01486405

SAS 10:47 Wednesday, April 19, 1995 26

OBS	RATE	VA	VO	DA	DO	S
1	0.35500	-1	-1	-1	-1	-1
2	0.36500	-1	-1	1	1	-1
3	0.33200	1	-1	1	-1	-1
4	0.33156	1	-1	-1	1	-1
5	0.32000	-1	1	1	-1	-1
6	0.32000	-1	1	-1	1	-1
7	0.27700	1	1	-1	-1	-1
8	0.29000	1	1	1	1	-1
9	0.29214	-1	-1	1	-1	1
10	0.35533	-1	-1	-1	1	1
11	0.33111	1	-1	-1	-1	1
12	0.30049	1	-1	1	1	1
13	0.29500	-1	1	-1	-1	1
14	0.24588	-1	1	1	1	1
15	0.28460	1	1	1	-1	1
16	0.28981	1	1	-1	1	1

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.311557	Sum	4.984918
Std Dev	0.032607	Variance	0.001063
Skewness	-0.07455	Kurtosis	-0.4377
USS	1.569036	CSS	0.015948
CV	10.46568	Std Mean	0.008152
T:Mean=0	38.22017	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.960487	Prob<W	0.6466

Quantiles(Def=5)

100% Max	0.365	99%	0.365
75% Q3	0.331778	95%	0.365
50% Med	0.310245	90%	0.355332
25% Q1	0.289905	10%	0.277
0% Min	0.245883	5%	0.245883
		1%	0.245883
Range	0.119117		
Q3-Q1	0.041873		
Mode	0.32		

Extremes

Lowest	Obs	Highest	Obs
0.245883(	14)	0.331557(	4)
0.277(	7)	0.332(	3)
0.284596(	15)	0.355(	1)
0.289811(	16)	0.355332(	10)
0.29(	8)	0.365(	2)

SAS 10:47 Wednesday, April 19, 1995 28

General Linear Models Procedure

Number of observations in data set = 16

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	0.00556931	0.00092822	0.80	0.5905
Error	9	0.01037854	0.00115317		
Corrected Total	15	0.01594785			

R-Square	C.V.	Root MSE	RATE Mean
0.349220	10.89955	0.0339584	0.31155738

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00097188	0.00097188	0.84	0.3825
DO	1	0.00000788	0.00000788	0.01	0.9359
S	1	0.00240580	0.00240580	2.09	0.1825
DA*DO	1	0.00027187	0.00027187	0.24	0.6389
DA*S	1	0.00184011	0.00184011	1.60	0.2383
DO*S	1	0.00007177	0.00007177	0.06	0.8086

Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00097188	0.00097188	0.84	0.3825
DO	1	0.00000788	0.00000788	0.01	0.9359
S	1	0.00240580	0.00240580	2.09	0.1825
DA*DO	1	0.00027187	0.00027187	0.24	0.6389
DA*S	1	0.00184011	0.00184011	1.60	0.2383
DO*S	1	0.00007177	0.00007177	0.06	0.8086

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.3115573750	36.70	0.0001	0.00848959
DA	-.0077937500	-0.92	0.3825	0.00848959
DO	0.0007017500	0.08	0.9359	0.00848959
S	-.0122622500	-1.44	0.1825	0.00848959
DA*DO	-.0041221250	-0.49	0.6389	0.00848959
DA*S	-.0107241250	-1.26	0.2383	0.00848959
DO*S	-.0021178750	-0.25	0.8086	0.00848959

SAS 10:47 Wednesday, April 19, 1995 30

OBS	RATE	VA	VO	DA	DO	S
1	0.27400	-1	-1	-1	-1	-1
2	0.24000	-1	-1	1	1	-1
3	0.24800	1	-1	1	-1	-1
4	0.24466	1	-1	-1	1	-1
5	0.23200	-1	1	1	-1	-1
6	0.23200	-1	1	-1	1	-1
7	0.21700	1	1	-1	-1	-1
8	0.20500	1	1	1	1	-1
9	0.19165	-1	-1	1	-1	1
10	0.21910	-1	-1	-1	1	1
11	0.22537	1	-1	-1	-1	1
12	0.18482	1	-1	1	1	1
13	0.15500	-1	1	-1	-1	1
14	0.11340	-1	1	1	1	1
15	0.20512	1	1	1	-1	1
16	0.20512	1	1	-1	1	1

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.212016	Sum	3.392254
Std Dev	0.038568	Variance	0.001487
Skewness	-1.08059	Kurtosis	1.893313
USS	0.741524	CSS	0.022312
CV	18.19105	Std Mean	0.009642
T:Mean=0	21.98883	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.929868	Prob<W	0.2427

Quantiles(Def=5)

100% Max	0.274	99%	0.274
75% Q3	0.236	95%	0.274
50% Med	0.218052	90%	0.248
25% Q1	0.198325	10%	0.155
0% Min	0.113401	5%	0.113401
		1%	0.113401
Range	0.160599		
Q3-Q1	0.037675		
Mode	0.205122		

Extremes

Lowest	Obs	Highest	Obs
0.113401(	14)	0.232(	6)
0.155(	13)	0.24(	2)
0.184822(	12)	0.244664(	4)
0.19165(	9)	0.248(	3)
0.205(	8)	0.274(	1)

SAS 10:47 Wednesday, April 19, 1995 32

General Linear Models Procedure

Number of observations in data set = 16

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	0.01372590	0.00228765	2.40	0.1150
Error	9	0.00858636	0.00095404		
Corrected Total	15	0.02231226			
	R-Square	C.V.	Root MSE		RATE Mean
	0.615173	14.56850	0.0308875		0.21201587

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00144902	0.00144902	1.52	0.2490
DO	1	0.00067634	0.00067634	0.71	0.4216
S	1	0.00965670	0.00965670	10.12	0.0112
DA*DO	1	0.00166203	0.00166203	1.74	0.2195
DA*S	1	0.00028003	0.00028003	0.29	0.6011
DO*S	1	0.00000179	0.00000179	0.00	0.9664

Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00144902	0.00144902	1.52	0.2490
DO	1	0.00067634	0.00067634	0.71	0.4216
S	1	0.00965670	0.00965670	10.12	0.0112
DA*DO	1	0.00166203	0.00166203	1.74	0.2195
DA*S	1	0.00028003	0.00028003	0.29	0.6011
DO*S	1	0.00000179	0.00000179	0.00	0.9664

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.2120158750	27.46	0.0001	0.00772188
DA	-.0095165000	-1.23	0.2490	0.00772188
DO	-.0065016250	-0.84	0.4216	0.00772188
S	-.0245671250	-3.18	0.0112	0.00772188
DA*DO	-.0101920000	-1.32	0.2195	0.00772188
DA*S	-.0041835000	-0.54	0.6011	0.00772188
DO*S	-.0003346250	-0.04	0.9664	0.00772188

Appendix A5.3. Determination of p values from the correlation of Bulicka and Prochazka.

	A	B	C	D	E
1	p-value determination				
2					
3					
4	Acetic acid tests				
5		ft	ft	cm2	K from Co data
6	Test No.	Aq. Dia	Org. Dia	Interface	at 30 min
7 1		0.1475	0.1475	59.242	0.0010700929265887
8 2		0.19225	0.19225	59.242	0.0016310388920875
9 3		0.19225	0.1475	59.242	0.0012847634794550
10 4		0.1475	0.19225	59.242	0.0012647634794550
11 5		0.19225	0.1475	59.242	0.0014612947003355
12 6		0.1475	0.19225	59.242	0.0014612947003355
13 7		0.1475	0.1475	59.242	0.0014999293868972
14 8		0.19225	0.19225	59.242	0.0017190639032829
15 9		0.19225	0.1475	81.352	0.0016043293494668
16 10		0.1475	0.19225	81.352	0.0013127716597637
17 11		0.1475	0.1475	81.352	0.0013109898452781
18 12		0.19225	0.19225	81.352	0.0016399138993935
19 13		0.1475	0.1475	81.352	0.0015146846981831
20 14		0.19225	0.19225	81.352	0.0019148567047352
21 15		0.19225	0.1475	81.352	0.0014277101075726
22 16		0.1475	0.19225	81.352	0.0012518534732801
23			constants		
24			Aqueous diff. coeff.	1.5166349777144E-04ft2/s	
25			Organic diff. coeff.	4.84032178084358E-04ft2/s	
26			Aqueous viscosity	0.000598	lb/fts
27			Organic viscosity	0.00271	lb/fts
28			aqueous density	62.21904	lb/ft3
29			organic density	50.0448	lb/ft3
30			impeller speed	1.6667	1/s
31					
32					
33			distribution coeff.	1.28	

	F	G	H
1			
2			
3			
4			
5	K from Co data	K from Co data	
6	at 45 min	at 80 min	p-value
7	0.0011506708516718	0.0011015445227883	0.0411226448221535
8	0.0014687260303817	0.0015185527126253	0.0496559952926416
9	0.0013426815472257	0.0011259771407402	0.0398322262547842
10	0.0013426815472257	0.0012601218549334	0.0428061825142835
11	0.0013866584468968	0.0013147549259277	0.0465103719998428
12	0.0013866584468968	0.0013147549259277	0.0465103719998428
13	0.0011460426021886	0.0012664458774507	0.0472787099636762
14	0.0016885945032677	0.0016445468101699	0.0537759459947549
15	0.0016638471372549	0.0014283153470838	0.0505276510594375
16	0.0011852780273553	0.0012478853529412	0.0423905100651757
17	0.0010932759329290	0.0011608044355582	0.0433349243031028
18	0.0015477392474109	0.0015189990281613	0.049670589545879
19	0.0014428354634303	0.0016722700247119	0.0624288577088277
20	0.0018933794620408	0.0020569522537056	0.0672614197571132
21	0.0013986391032579	0.0011975887762819	0.0423655377814268
22	0.0012296651042701	0.0011975887762819	0.0406819416184877
23		avg p=	0.0477690981134489
24			
25	0.00001409	cm2/s	
26	0.000004311	cm2/s	
27	0.0088893700787401	g/cms	
28	0.0403299212598425	g/cms	
29	0.9971	g/cm3	
30	0.802	g/cm3	
31			
32			
33			

1	
2	
3	
4	
5	
6	p-value formula
7	$= (G7/30.48*B7/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B7^2*$D$29/$D$27)^0.75*((1+(C7/B7)^2)*($D$30/$D$29)*($D$28*D29$
8	$= (G8/30.48*B8/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B8^2*$D$29/$D$27)^0.75*((1+(C8/B8)^2)*($D$30/$D$29)*($D$28*D29$
9	$= (G9/30.48*B9/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B9^2*$D$29/$D$27)^0.75*((1+(C9/B9)^2)*($D$30/$D$29)*($D$28*D29$
10	$= (G10/30.48*B10/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B10^2*$D$29/$D$27)^0.75*((1+(C10/B10)^2)*($D$30/$D$29)*($D$28*D29$
11	$= (G11/30.48*B11/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B11^2*$D$29/$D$27)^0.75*((1+(C11/B11)^2)*($D$30/$D$29)*($D$28*D29$
12	$= (G12/30.48*B12/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B12^2*$D$29/$D$27)^0.75*((1+(C12/B12)^2)*($D$30/$D$29)*($D$28*D29$
13	$= (G13/30.48*B13/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B13^2*$D$29/$D$27)^0.75*((1+(C13/B13)^2)*($D$30/$D$29)*($D$28*D29$
14	$= (G14/30.48*B14/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B14^2*$D$29/$D$27)^0.75*((1+(C14/B14)^2)*($D$30/$D$29)*($D$28*D29$
15	$= (G15/30.48*B15/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B15^2*$D$29/$D$27)^0.75*((1+(C15/B15)^2)*($D$30/$D$29)*($D$28*D29$
16	$= (G16/30.48*B16/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B16^2*$D$29/$D$27)^0.75*((1+(C16/B16)^2)*($D$30/$D$29)*($D$28*D29$
17	$= (G17/30.48*B17/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B17^2*$D$29/$D$27)^0.75*((1+(C17/B17)^2)*($D$30/$D$29)*($D$28*D29$
18	$= (G18/30.48*B18/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B18^2*$D$29/$D$27)^0.75*((1+(C18/B18)^2)*($D$30/$D$29)*($D$28*D29$
19	$= (G19/30.48*B19/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B19^2*$D$29/$D$27)^0.75*((1+(C19/B19)^2)*($D$30/$D$29)*($D$28*D29$
20	$= (G20/30.48*B20/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B20^2*$D$29/$D$27)^0.75*((1+(C20/B20)^2)*($D$30/$D$29)*($D$28*D29$
21	$= (G21/30.48*B21/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B21^2*$D$29/$D$27)^0.75*((1+(C21/B21)^2)*($D$30/$D$29)*($D$28*D29$
22	$= (G22/30.48*B22/$D$25)/((($D$27/$D$29/$D$25)^0.5*($D$31*B22^2*$D$29/$D$27)^0.75*((1+(C22/B22)^2)*($D$30/$D$29)*($D$28*D29$
23	$= AVERAGE(I7:I22)$
24	
25	
26	
27	
28	
29	
30	
31	
32	
33	

Appendix A5.4a. Calculation of uranium diffusion coefficient.

Calculation of uranium diffusion coefficients

Diffusion coefficients for uranyl nitrate in the aqueous phase were calculated by two methods, the Nernst-Haskell equation which pertains to the diffusion of a salt through an electrolyte solution and the more general Wilke-Chang correlation.

Nernst-Haskell equation:

$$D_{AB}^{\circ} = \frac{RT}{F^2} \frac{1/n_+ + 1/n_-}{1/\lambda_+^{\circ} + 1/\lambda_-^{\circ}}$$

where

D_{AB}° = the diffusion coefficient at infinite dilution based on molecular concentration, cm^2/s

T = temperature, K

R = gas constant, 8.314 J/gmol K

λ_+° , λ_-° = limiting (zero concentration) ionic conductances, $(\text{A}/\text{cm}^2)(\text{V}/\text{cm})(\text{g-equivalent}/\text{cm}^3)$

n_+ , n_- = valences of the cationic and anionic species, respectively

F = faraday (=96,500 C/g-equivalent).

Values for the limiting ionic conductances of several cations and anions are presented by Reid, Prausnitz, and Sherwood (1977). Values for U^{+6} and UO_2^{++} are not available, and a value of 100 was estimated from the available data for other cations.

For the diffusion of uranyl nitrate in water

$$D_{AB}^o = \frac{8.314(298)}{96,500^2} \frac{1/2 + 1/1}{1/100 + 1/71.4} = 1.662 \times 10^{-5} \text{ cm}^2/\text{s}$$

Method of Wilke-Chang:

$$D_{AB}^o = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2} T}{\mu_B V_A^{0.6}}$$

where

D_{AB}^o = mutual diffusion coefficient of solute A at very low concentrations in solvent B, cm^2/s

M_B = molecular weight of the solvent B

T = absolute temperature, K

μ_B = viscosity of the solvent B, cp

V_A = molal volume of the solute A at its normal boiling temperature, cm^3/gmol

ϕ = association factor of solvent B, dimensionless

Absent experimental data for uranyl nitrate, additive volumes were used from Le Bas for nitrogen and oxygen (Reid, Prausnitz and Sherwood). The volume used for the uranium contribution was taken from a regression performed by Demuth (1989).

$$D_{AB}^o = 7.4 \times 10^{-8} \frac{(2.6(18.015))^{1/2} 298}{0.95(146.007)^{0.6}} = 7.987 \times 10^{-6} \text{ cm}^2/\text{s}$$

The method of Lusis-Ratcliff for infinite dilution diffusion in organic solvents was used to estimate the coefficient for diffusion of the solvated uranyl nitrate tetrahydrate complex in dibutyl carbitol.

$$D_{AB}^{\circ} = \frac{(8.52 \times 10^{-8})T}{\mu_B V_B^{1/3}} \left[1.40 \left(\frac{V_B}{V_A} \right)^{1/3} + \frac{V_B}{V_A} \right]$$

Application of this method requires knowledge of the viscosity of the solvent. As this data was not available for DBC, an estimation was made using the method of Van Velzen, Cardozo, and Langenkamp.

$$\log \mu_L = B \left[\frac{1}{T} - \frac{1}{T_o} \right]$$

where

μ_L = liquid viscosity, cp

T = temperature, K

and the factors B, and T_o are related to molecular structure of the solvent. The method for calculating these parameters is described in detail in Reid, Prausnitz, and Sherwood (1976).

For DBC (diethylene glycol dibutyl ether)

$$B=1625.661$$

$$T_o = 507.651$$

$$\log \mu_L = 1625.661 \left[\frac{1}{298} - \frac{1}{507.651} \right] = 2.253$$

$$\mu_L = 179 \text{ cp}$$

Volume contributions are

$$\text{UO}_2(\text{NO}_3)_2 = 146.007$$

$$\text{H}_2\text{O} = 18.7$$

$$\text{DBC} = 301.1$$

So for the solvate complex $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot 2\text{DBC}$, the molal volume is $823.007 \text{ cm}^3/\text{gmol}$, and the diffusion coefficient by the method of Lusis and Ratcliff is

$$D_{AB}^o = \frac{(8.52 \times 10^{-8})298}{179(301.1)^{1/3}} \left[1.40 \left(\frac{301.1}{823.007} \right)^{1/3} + \frac{301.1}{823.007} \right] = 2.893 \times 10^{-8} \text{ cm}^2/\text{s}$$

Appendix A5.4b. Determination of aqueous solution density

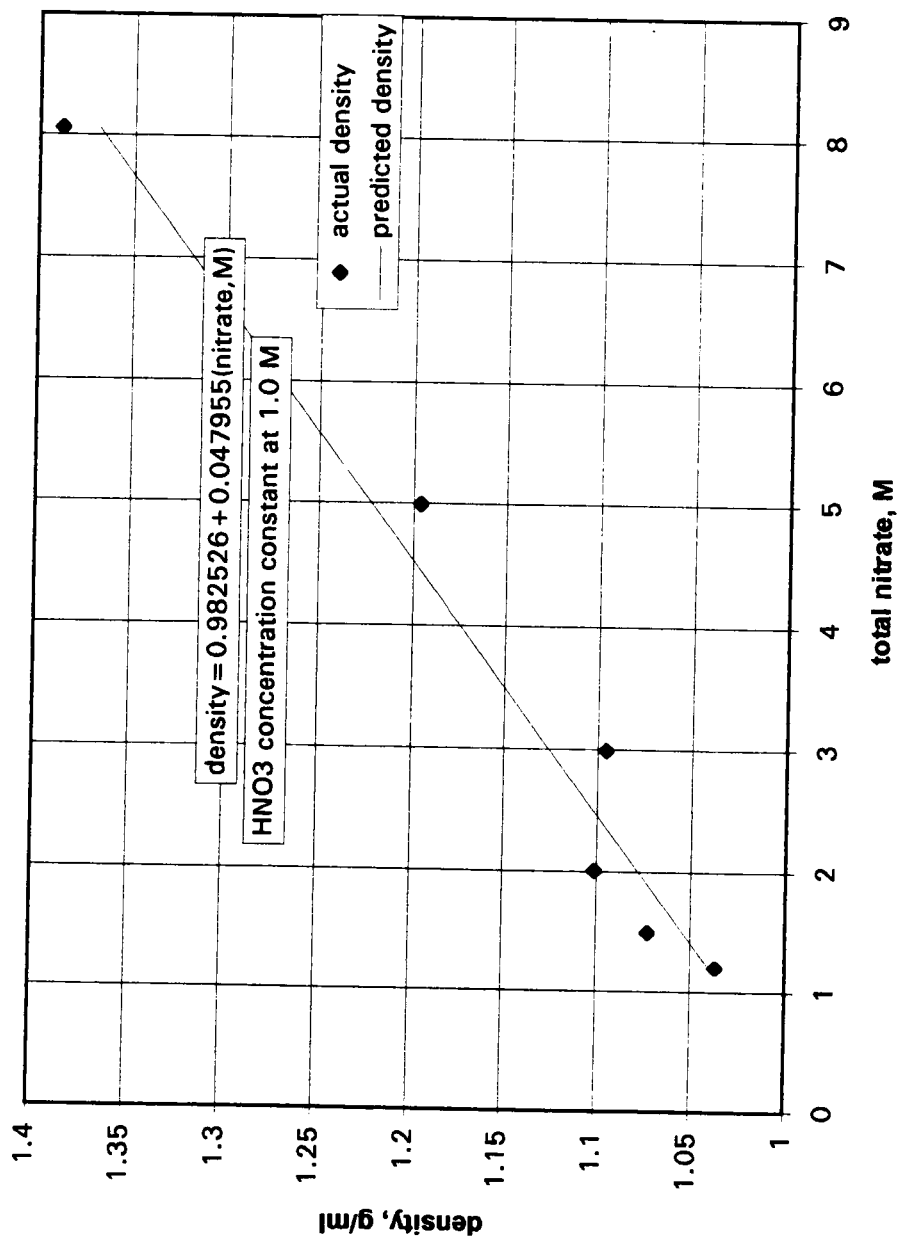


Figure A5-1. Density of aqueous calcium nitrate-nitric acid solutions

	Calcium	Density	
	nitrate, M	g/ml	
	1.203125	1.037	
	1.495168	1.07256	
	2.003515	1.10098	
	2.993784	1.095775	
	4.997459	1.19599	
	8.06	1.388055	
All solutions contained HNO ₃ at 1.0 M			

SUMMARY OUTPUT							
Regression Statistics							
Multiple R	0.982879083						
R Square	0.966051291						
Adjusted R Square	0.957564114						
Standard Error	0.026521852						
Observations	6						
ANOVA							
	df	SS	MS	F	Significance F		
Regression	1	0.080065349	0.080065349	113.8248041	0.000437179		
Residual	4	0.002813634	0.000703409				
Total	5	0.082878983					
Coefficients		Standard Error	t Stat	P-value	Lower 95%	Upper 95%	
Intercept	0.982526205	0.018945677	51.86018037	8.27445E-07	0.929924465	1.035127944	
X Variable 1	0.047954523	0.004494808	10.6688708	0.000437179	0.03547491	0.060434135	
RESIDUAL OUTPUT							
Observation	Predicted Y	Residuals					
1	1.040221496	-0.003221496					
2	1.054226288	0.018333712					
3	1.078603796	0.022378204					
4	1.126091669	-0.030316669					
5	1.222176977	-0.026186977					
6	1.369039657	0.019015226					

Appendix A5.4c. Calculation of overall transfer coefficients for uranium.

	A		B	C	D		E		F	G	H	I	J
1	Uranium results										ORGANIC	SAMPLES	ORGANIC
2		ml		ml	cm		cm		cm ²		Sample 1	conc.	Sample 2
3	Test No.	Aq. Vol	Org. Vol	Aq. Dia	Aq. Dia	Org. Dia	Org. Dia	Interface	Initial Aq.		Time		Time
4	1	350	350	=1.77*2.54	=2.307*2.54	=1.77*2.54	=2.307*2.54	59.242	1000	10	94.3	20	20
5	2	350	350	=2.307*2.54	=2.307*2.54	=1.77*2.54	=2.307*2.54	59.242	1000	10	39.7	20	20
6	3	450	350	=2.307*2.54	=2.307*2.54	=1.77*2.54	=2.307*2.54	59.242	1000	10	44.7	20	20
7	4	450	350	=1.77*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	59.242	1000	10	105	20	20
8	5	350	450	=2.307*2.54	=1.77*2.54	=1.77*2.54	=2.307*2.54	59.242	1000	10	38.3	20	20
9	6	350	450	=1.77*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	59.242	1000	10	67.3	20	20
10	7	450	450	=1.77*2.54	=2.307*2.54	=1.77*2.54	=2.307*2.54	59.242	1000	10	54.6	20	20
11	8	450	450	=2.307*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	59.242	1000	10	48.6	20	20
12	9	350	350	=2.307*2.54	=2.307*2.54	=1.77*2.54	=1.77*2.54	81.352	1000	10	166	20	20
13	10	350	350	=1.77*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	81.352	1000	10	130	20	20
14	11	450	350	=1.77*2.54	=1.77*2.54	=1.77*2.54	=1.77*2.54	81.352	1000	10	101	20	20
15	12	450	350	=2.307*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	81.352	1000	10	153	20	20
16	13	350	450	=1.77*2.54	=1.77*2.54	=1.77*2.54	=1.77*2.54	81.352	1000	10	100	20	20
17	14	350	450	=2.307*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	81.352	1000	10	77.2	20	20
18	15	450	450	=2.307*2.54	=2.307*2.54	=1.77*2.54	=1.77*2.54	81.352	1000	10	146	20	20
19	16	450	450	=1.77*2.54	=2.307*2.54	=2.307*2.54	=2.307*2.54	81.352	1000	10	91.3	20	20
20											Distribution coefficient		
21													

1	K		L		M		N		O		P		Q	
	SAMPLES	ORGANIC SAMPLES	Sample 3	Time	conc.	Sample 4	Time	conc.	SAMPLES	at 10 min	Ka based on Co	at 20 min		
2	conc.													
3	154	40	238	80	348	80	348	348		0.000976279530483587	0.000824814610821705			
4	90.1	40	193	80	399	80	399	399		0.00039904587111622	0.000485315327886428			
5	94.3	40	198	80	381	80	381	381		0.000448183439097986	0.000482660027945021			
6	180	40	337	80	589	80	589	589		0.00107977893745178	0.000956657549356475			
7	75.9	40	149	80	283	80	283	283		0.000497419631710585	0.000505951459123939			
8	108	40	197	80	284	80	284	284		0.000891797514839123	0.000736910980747706			
9	114	40	177	80	323	80	323	323		0.000711226520347554	0.000767136395428608			
10	109	40	188	80	318	80	318	318		0.000631046603565812	0.000731425009108103			
11	318	40	580	80	840	80	840	840		0.00130411894332142	0.00137819152090895			
12	249	40	455	80	729	80	729	729		0.00100003701041663	0.0010298886353285			
13	133	40	254	80	491	80	491	491		0.000755064779566505	0.000504079680179111			
14	296	40	533	80	840	80	840	840		0.00117004089298907	0.00121057516284324			
15	148	40	251	80	335	80	335	335		0.000987920207435536	0.000758088679231347			
16	164	40	317	80	543	80	543	543		0.00075020195051595	0.000850713320204434			
17	229	40	397	80	623	80	623	623		0.00145743865959964	0.0012022358245187			
18	180	40	366	80	600	80	600	600		0.000883522134313323	0.000916726296392852			
19														
20														
21	50													

	R	S
1		
2		
3	at 40 min	at 80 min
4	0.00067110259891823	0.000529086195349753
5	0.000528077682412854	0.000630530047468407
6	0.000530507051310088	0.000559023065855138
7	0.00088623141505196	0.00097818573044838
8	0.000524435639736534	0.000559046550712564
9	0.000720792789733292	0.000586975548119847
10	0.000617822598284753	0.000620076154901844
11	0.000660601216888866	0.000608320671074093
12	0.00148816513497937	0.00170783479016573
13	0.001083245249868	0.00119590565142051
14	0.000508822569254061	0.000558498351181577
15	0.00124430834469276	0.00124604670695787
16	0.000700849173800328	0.000507671349423458
17	0.000943099119405014	0.00108949588899586
18	0.0011729461398876	0.00114010605214132
19	0.00105595770508022	0.00108964128308659
20		
21		

T	
1	TYPICAL FORMULA FOR Ka
2	Ka based on Co
3	at 10 min
4	= \$C4/(-\$F4*(1/\$K\$21+\$C4/\$B4)*H4*60)*LN((\$G4-(1/\$K\$21+\$C4/\$B4)*I4)/\$G4)
5	= \$C5/(-\$F5*(1/\$K\$21+\$C5/\$B5)*H5*60)*LN((\$G5-(1/\$K\$21+\$C5/\$B5)*I5)/\$G5)
6	= \$C6/(-\$F6*(1/\$K\$21+\$C6/\$B6)*H6*60)*LN((\$G6-(1/\$K\$21+\$C6/\$B6)*I6)/\$G6)
7	= \$C7/(-\$F7*(1/\$K\$21+\$C7/\$B7)*H7*60)*LN((\$G7-(1/\$K\$21+\$C7/\$B7)*I7)/\$G7)
8	= \$C8/(-\$F8*(1/\$K\$21+\$C8/\$B8)*H8*60)*LN((\$G8-(1/\$K\$21+\$C8/\$B8)*I8)/\$G8)
9	= \$C9/(-\$F9*(1/\$K\$21+\$C9/\$B9)*H9*60)*LN((\$G9-(1/\$K\$21+\$C9/\$B9)*I9)/\$G9)
10	= \$C10/(-\$F10*(1/\$K\$21+\$C10/\$B10)*H10*60)*LN((\$G10-(1/\$K\$21+\$C10/\$B10)*I10)/\$G10)
11	= \$C11/(-\$F11*(1/\$K\$21+\$C11/\$B11)*H11*60)*LN((\$G11-(1/\$K\$21+\$C11/\$B11)*I11)/\$G11)
12	= \$C12/(-\$F12*(1/\$K\$21+\$C12/\$B12)*H12*60)*LN((\$G12-(1/\$K\$21+\$C12/\$B12)*I12)/\$G12)
13	= \$C13/(-\$F13*(1/\$K\$21+\$C13/\$B13)*H13*60)*LN((\$G13-(1/\$K\$21+\$C13/\$B13)*I13)/\$G13)
14	= \$C14/(-\$F14*(1/\$K\$21+\$C14/\$B14)*H14*60)*LN((\$G14-(1/\$K\$21+\$C14/\$B14)*I14)/\$G14)
15	= \$C15/(-\$F15*(1/\$K\$21+\$C15/\$B15)*H15*60)*LN((\$G15-(1/\$K\$21+\$C15/\$B15)*I15)/\$G15)
16	= \$C16/(-\$F16*(1/\$K\$21+\$C16/\$B16)*H16*60)*LN((\$G16-(1/\$K\$21+\$C16/\$B16)*I16)/\$G16)
17	= \$C17/(-\$F17*(1/\$K\$21+\$C17/\$B17)*H17*60)*LN((\$G17-(1/\$K\$21+\$C17/\$B17)*I17)/\$G17)
18	= \$C18/(-\$F18*(1/\$K\$21+\$C18/\$B18)*H18*60)*LN((\$G18-(1/\$K\$21+\$C18/\$B18)*I18)/\$G18)
19	= \$C19/(-\$F19*(1/\$K\$21+\$C19/\$B19)*H19*60)*LN((\$G19-(1/\$K\$21+\$C19/\$B19)*I19)/\$G19)
20	
21	

Appendix A5.4d. Calculation of film and predicted overall (without reaction) transfer coefficients for uranium.

	A		B		C		D		E		F	G	H
	Uranium results		ml	Aq. Vol	ml	Org. Vol	cm	Aq. Dia	cm	Org. Dia	cm2	p-value	extrapolated ka
1													
2													
3	Test No.												
4	1	350	350	350	350	350	350	=1.77*2.54	=1.77*2.54	=2.307*2.54	59.242	0.0411226448221535	0.00460414515909682
5	2	350	350	350	350	350	350	=2.307*2.54	=2.307*2.54	=2.307*2.54	59.242	0.049659952926416	0.00460414515909682
6	3	450	450	450	450	450	450	=2.307*2.54	=2.307*2.54	=2.307*2.54	59.242	0.0398322262547842	0.00467953020387424
7	4	450	450	450	450	450	450	=1.77*2.54	=2.307*2.54	=2.307*2.54	59.242	0.0428081825142835	0.00467953020387424
8	5	350	350	350	450	450	450	=2.307*2.54	=1.77*2.54	=2.307*2.54	59.242	0.0465103719998428	0.00516679017623704
9	6	350	350	350	450	450	450	=1.77*2.54	=2.307*2.54	=2.307*2.54	59.242	0.046620611335958	0.00516679017623704
10	7	450	450	450	450	450	450	=1.77*2.54	=1.77*2.54	=1.77*2.54	59.242	0.0472787099636762	0.00522060989614804
11	8	450	450	450	450	450	450	=2.307*2.54	=2.307*2.54	=2.307*2.54	59.242	0.0537759459947549	0.00522060989614804
12	9	350	350	350	350	350	350	=2.307*2.54	=1.77*2.54	=2.307*2.54	81.352	0.0505276510594375	0.00460414515909682
13	10	350	350	350	350	350	350	=1.77*2.54	=2.307*2.54	=2.307*2.54	81.352	0.0423905100651757	0.00460414515909682
14	11	450	450	450	450	450	450	=1.77*2.54	=1.77*2.54	=1.77*2.54	81.352	0.0433349243031028	0.00467953020387424
15	12	450	450	450	450	450	450	=2.307*2.54	=2.307*2.54	=2.307*2.54	81.352	0.049670589545879	0.00467953020387424
16	13	350	350	450	450	450	450	=1.77*2.54	=1.77*2.54	=1.77*2.54	81.352	0.0624288577088277	0.00516679017623704
17	14	350	350	450	450	450	450	=2.307*2.54	=2.307*2.54	=2.307*2.54	81.352	0.0672814197571132	0.00516679017623704
18	15	450	450	450	450	450	450	=2.307*2.54	=1.77*2.54	=1.77*2.54	81.352	0.042365537814268	0.00522060989614804
19	16	450	450	450	450	450	450	=1.77*2.54	=2.307*2.54	=2.307*2.54	81.352	0.0406819416184877	0.00522060989614804
20													Distribution coefficient, Kd =
21													
22													
23													
24													
25													
26													
27													

	I	J
1		
2		
3	extrapolated ko	Ka without rxn
4	0.00019209130839556	0.00311223267848429
5	0.00019209130839556	0.00311223267848429
6	0.000185236476800197	0.00316319019431364
7	0.000195236476800197	0.00316319019431364
8	0.000215565637238378	0.00349256000271523
9	0.000215565637238378	0.00349256000271523
10	0.000217811070442142	0.00352894015261623
11	0.000217811070442142	0.00352894015261623
12	0.00019209130839556	0.00311223267848429
13	0.00019209130839556	0.00311223267848429
14	0.000195236476800197	0.00316319019431364
15	0.000195236476800197	0.00316319019431364
16	0.000215565637238378	0.00349256000271523
17	0.000215565637238378	0.00349256000271523
18	0.000217811070442142	0.00352894015261623
19	0.000217811070442142	0.00352894015261623
20		
21		50
22		
23	p-value	0.0477690981134489
24		
25		
26		
27		

1	K
2	
3	extrapolated ka
4	=J\$23*\$P\$21/B4*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B4^2*\$P\$25/\$P\$23)^0.75*(1+(C4/B4)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
5	=J\$23*\$P\$21/B5*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B5^2*\$P\$25/\$P\$23)^0.75*(1+(C5/B5)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
6	=J\$23*\$P\$21/B6*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B6^2*\$P\$25/\$P\$23)^0.75*(1+(C6/B6)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
7	=J\$23*\$P\$21/B7*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B7^2*\$P\$25/\$P\$23)^0.75*(1+(C7/B7)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
8	=J\$23*\$P\$21/B8*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B8^2*\$P\$25/\$P\$23)^0.75*(1+(C8/B8)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
9	=J\$23*\$P\$21/B9*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B9^2*\$P\$25/\$P\$23)^0.75*(1+(C9/B9)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
10	=J\$23*\$P\$21/B10*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B10^2*\$P\$25/\$P\$23)^0.75*(1+(C10/B10)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
11	=J\$23*\$P\$21/B11*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B11^2*\$P\$25/\$P\$23)^0.75*(1+(C11/B11)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
12	=J\$23*\$P\$21/B12*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B12^2*\$P\$25/\$P\$23)^0.75*(1+(C12/B12)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
13	=J\$23*\$P\$21/B13*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B13^2*\$P\$25/\$P\$23)^0.75*(1+(C13/B13)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
14	=J\$23*\$P\$21/B14*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B14^2*\$P\$25/\$P\$23)^0.75*(1+(C14/B14)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
15	=J\$23*\$P\$21/B15*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B15^2*\$P\$25/\$P\$23)^0.75*(1+(C15/B15)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
16	=J\$23*\$P\$21/B16*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B16^2*\$P\$25/\$P\$23)^0.75*(1+(C16/B16)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
17	=J\$23*\$P\$21/B17*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B17^2*\$P\$25/\$P\$23)^0.75*(1+(C17/B17)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
18	=J\$23*\$P\$21/B18*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B18^2*\$P\$25/\$P\$23)^0.75*(1+(C18/B18)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
19	=J\$23*\$P\$21/B19*(((\$P\$23/\$P\$25/\$P\$21)^0.5*(N\$27*B19^2*\$P\$25/\$P\$23)^0.75*(1+(C19/B19)^2*((\$P\$26/\$P\$25)*(\$P\$24*\$P\$25/\$P\$25
20	
21	
22	
23	
24	
25	
26	
27	

1	
2	
3	extrapolated ko
4	= \$J\$23*\$P\$22/C4* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C4^2*\$P\$28/\$P\$24)^0.75*((1+(B4/C4)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
5	= \$J\$23*\$P\$22/C5* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C5^2*\$P\$28/\$P\$24)^0.75*((1+(B5/C5)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
6	= \$J\$23*\$P\$22/C6* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C6^2*\$P\$28/\$P\$24)^0.75*((1+(B6/C6)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
7	= \$J\$23*\$P\$22/C7* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C7^2*\$P\$28/\$P\$24)^0.75*((1+(B7/C7)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
8	= \$J\$23*\$P\$22/C8* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C8^2*\$P\$28/\$P\$24)^0.75*((1+(B8/C8)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
9	= \$J\$23*\$P\$22/C9* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C9^2*\$P\$28/\$P\$24)^0.75*((1+(B9/C9)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
10	= \$J\$23*\$P\$22/C10* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C10^2*\$P\$28/\$P\$24)^0.75*((1+(B10/C10)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
11	= \$J\$23*\$P\$22/C11* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C11^2*\$P\$28/\$P\$24)^0.75*((1+(B11/C11)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
12	= \$J\$23*\$P\$22/C12* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C12^2*\$P\$28/\$P\$24)^0.75*((1+(B12/C12)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
13	= \$J\$23*\$P\$22/C13* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C13^2*\$P\$28/\$P\$24)^0.75*((1+(B13/C13)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
14	= \$J\$23*\$P\$22/C14* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C14^2*\$P\$28/\$P\$24)^0.75*((1+(B14/C14)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
15	= \$J\$23*\$P\$22/C15* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C15^2*\$P\$28/\$P\$24)^0.75*((1+(B15/C15)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
16	= \$J\$23*\$P\$22/C16* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C16^2*\$P\$28/\$P\$24)^0.75*((1+(B16/C16)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
17	= \$J\$23*\$P\$22/C17* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C17^2*\$P\$28/\$P\$24)^0.75*((1+(B17/C17)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
18	= \$J\$23*\$P\$22/C18* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C18^2*\$P\$28/\$P\$24)^0.75*((1+(B18/C18)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
19	= \$J\$23*\$P\$22/C19* ((\$P\$24/\$P\$28/\$P\$22)^0.5*(N\$27*C19^2*\$P\$28/\$P\$24)^0.75*((1+(B19/C19)^2*(N\$25/\$P\$26)*(\$P\$23*\$P\$26/\$P\$
20	
21	
22	
23	
24	
25	
26	
27	

	M	N	O	P	Q	R	S
1							
2							
3	Ka without rxn						
4	=1/(1/H4+1/\$J\$21/L4)						
5	=1/(1/H5+1/\$J\$21/L5)						
6	=1/(1/H6+1/\$J\$21/L6)						
7	=1/(1/H7+1/\$J\$21/L7)						
8	=1/(1/H8+1/\$J\$21/L8)						
9	=1/(1/H9+1/\$J\$21/L9)						
10	=1/(1/H10+1/\$J\$21/L10)						
11	=1/(1/H11+1/\$J\$21/L11)						
12	=1/(1/H12+1/\$J\$21/L12)						
13	=1/(1/H13+1/\$J\$21/L13)						
14	=1/(1/H14+1/\$J\$21/L14)						
15	=1/(1/H15+1/\$J\$21/L15)						
16	=1/(1/H16+1/\$J\$21/L16)						
17	=1/(1/H17+1/\$J\$21/L17)						
18	=1/(1/H18+1/\$J\$21/L18)						
19	=1/(1/H19+1/\$J\$21/L19)						
20							
21	Diffaq	1.78896191125716E-08	ft2/s	0.00001662	cm2/s		
22	Difforg	3.11399928355412E-11	ft2/s	0.00000002893	cm2/s		
23	muuaq	0.00102144	lb/fts	0.0152	g/cms	1.52	cp
24	muorg	0.120286	lb/fts	1.79	g/cms	179	cp
25	rhoaq	85.3632	lb/ft3	1.368	g/cm		
26	rhoorg	55.24272	lb/ft3	0.8853	g/cm		
27	rot speed	1.6666666666667	1/s				

Appendix A5.5a. Calculation of uranium transfer rates from concentration data.

	K		L		M		N		O	
	SAMPLES	ORGANIC	SAMPLES	ORGANIC	SAMPLES	ORGANIC	SAMPLES	ORGANIC	SAMPLES	ORGANIC
1	Co at	Ka based on Co								
2	80 min, mg/L	at 10 min	at 20 min	(cm/s)	at 40 min	at 80 min				
3	348	0.000976278530483587	0.000824814610921705	0.00067110259691823	0.000529066195349753					
4	399	0.00039904587111622	0.000465315327886426	0.000529077682412854	0.000630530047488407					
5	381	0.000448183439097986	0.000482660027945021	0.000530507051310068	0.000559023065855138					
6	589	0.00107977893745178	0.000956657549356475	0.00086623141505196	0.00097918573044838					
7	283	0.000497419631710585	0.000505951459123939	0.000524435639736534	0.000559046550712584					
8	294	0.000891797514839123	0.000736810980747706	0.000720792789733292	0.000586975548119847					
9	323	0.000711226520347554	0.000767136395428606	0.000617822588284753	0.000620076154901844					
10	318	0.000631046603565612	0.000731425009108103	0.000660601216888866	0.000808320671074093					
11	840	0.00130411894332142	0.00137819152090985	0.00148816513497937	0.00170783479016573					
12	729	0.00100003701041663	0.00102988863533285	0.0010963245249888	0.00119590565142051					
13	491	0.000755084779566505	0.000504079960179111	0.00050822569254061	0.00058498351181577					
14	840	0.00117004069296907	0.00121057516284324	0.00124430934469276	0.00124604670695787					
15	335	0.000987920207435536	0.000758088679231347	0.000700949173800328	0.000507671349423458					
16	543	0.00075020195051595	0.000850713320204434	0.000943099119405014	0.00108949568899566					
17	623	0.00145743865959684	0.00120222358245187	0.0011729461398876	0.00114010605214132					
18	600	0.000883522134313323	0.000916726296392652	0.00105595770508022	0.00106964128308659					
19										
20										
21	50									

	P	Q	R	S
1				
2	dCo/dt	(mol/s)	at 40 min	at 80 min
3	at 10 min	at 20 min		
4	6.27535007471016E-07	4.94455730386796E-07	3.61415834882472E-07	2.42706479280298E-07
5	2.72304756070889E-07	3.00514054778682E-07	3.02200660458523E-07	2.65925410480079E-07
6	3.07376312553943E-07	3.17438477822177E-07	3.17693693466195E-07	2.76727803593982E-07
7	7.03599706848616E-07	0.000005826635788713	5.02425517288583E-07	3.6916020023849E-07
8	2.61386238349557E-07	2.5212963207805E-07	2.33652404386578E-07	1.94967173576915E-07
9	4.4994669078389E-07	3.50138418358375E-07	2.96147134636566E-07	2.0004401281445E-07
10	3.71502595459434E-07	3.7499675742634E-07	2.80047557949407E-07	2.29990534163144E-07
11	3.31757612456849E-07	3.59603462855915E-07	2.95338422147726E-07	2.27346445493847E-07
12	1.05797204051967E-06	9.09385781975387E-07	6.23202425859411E-07	2.3884277432962E-07
13	8.47146895916733E-07	7.50350142438863E-07	5.73780942356899E-07	2.99482911775142E-07
14	6.77990317631679E-07	4.4005725433588E-07	3.96229188937194E-07	3.31784885992608E-07
15	1.00320349327675E-06	9.03082647116752E-07	6.98484224329051E-07	4.01417208606284E-07
16	6.52430928074283E-07	4.64558120439173E-07	3.57936720255617E-07	2.16945236154217E-07
17	5.12404221085077E-07	5.07818781723646E-07	4.19855025293294E-07	2.4082025090177E-07
18	9.42192046257798E-07	6.99891687477142E-07	5.30172981720663E-07	3.15696090566409E-07
19	6.0861569597955E-07	5.68488192539681E-07	5.02656290293739E-07	3.15245318139348E-07
20				
21				

T		U	
1	Calculation formulas		
2	dCo/dt	(mol/s)	
3	at 10 min	at 20 min	
4	=F4/\$C4*L4*(1/238-(C4/\$B4+1/\$K\$21)*H4/1000/238)	=F4/\$C4*M4*(1/238-(C4/\$B4+1/\$K\$21)*I4/1000/238)	
5	=F5/\$C5*L5*(1/238-(C5/\$B5+1/\$K\$21)*H5/1000/238)	=F5/\$C5*M5*(1/238-(C5/\$B5+1/\$K\$21)*I5/1000/238)	
6	=F6/\$C6*L6*(1/238-(C6/\$B6+1/\$K\$21)*H6/1000/238)	=F6/\$C6*M6*(1/238-(C6/\$B6+1/\$K\$21)*I6/1000/238)	
7	=F7/\$C7*L7*(1/238-(C7/\$B7+1/\$K\$21)*H7/1000/238)	=F7/\$C7*M7*(1/238-(C7/\$B7+1/\$K\$21)*I7/1000/238)	
8	=F8/\$C8*L8*(1/238-(C8/\$B8+1/\$K\$21)*H8/1000/238)	=F8/\$C8*M8*(1/238-(C8/\$B8+1/\$K\$21)*I8/1000/238)	
9	=F9/\$C9*L9*(1/238-(C9/\$B9+1/\$K\$21)*H9/1000/238)	=F9/\$C9*M9*(1/238-(C9/\$B9+1/\$K\$21)*I9/1000/238)	
10	=F10/\$C10*L10*(1/238-(C10/\$B10+1/\$K\$21)*H10/1000/238)	=F10/\$C10*M10*(1/238-(C10/\$B10+1/\$K\$21)*I10/1000/238)	
11	=F11/\$C11*L11*(1/238-(C11/\$B11+1/\$K\$21)*H11/1000/238)	=F11/\$C11*M11*(1/238-(C11/\$B11+1/\$K\$21)*I11/1000/238)	
12	=F12/\$C12*L12*(1/238-(C12/\$B12+1/\$K\$21)*H12/1000/238)	=F12/\$C12*M12*(1/238-(C12/\$B12+1/\$K\$21)*I12/1000/238)	
13	=F13/\$C13*L13*(1/238-(C13/\$B13+1/\$K\$21)*H13/1000/238)	=F13/\$C13*M13*(1/238-(C13/\$B13+1/\$K\$21)*I13/1000/238)	
14	=F14/\$C14*L14*(1/238-(C14/\$B14+1/\$K\$21)*H14/1000/238)	=F14/\$C14*M14*(1/238-(C14/\$B14+1/\$K\$21)*I14/1000/238)	
15	=F15/\$C15*L15*(1/238-(C15/\$B15+1/\$K\$21)*H15/1000/238)	=F15/\$C15*M15*(1/238-(C15/\$B15+1/\$K\$21)*I15/1000/238)	
16	=F16/\$C16*L16*(1/238-(C16/\$B16+1/\$K\$21)*H16/1000/238)	=F16/\$C16*M16*(1/238-(C16/\$B16+1/\$K\$21)*I16/1000/238)	
17	=F17/\$C17*L17*(1/238-(C17/\$B17+1/\$K\$21)*H17/1000/238)	=F17/\$C17*M17*(1/238-(C17/\$B17+1/\$K\$21)*I17/1000/238)	
18	=F18/\$C18*L18*(1/238-(C18/\$B18+1/\$K\$21)*H18/1000/238)	=F18/\$C18*M18*(1/238-(C18/\$B18+1/\$K\$21)*I18/1000/238)	
19	=F19/\$C19*L19*(1/238-(C19/\$B19+1/\$K\$21)*H19/1000/238)	=F19/\$C19*M19*(1/238-(C19/\$B19+1/\$K\$21)*I19/1000/238)	
20			
21			

	V	W
1		
2		
3	at 40 min	at 80 min
4	=F4/\$C4*N4*(1/238-(\$C4/\$B4+1/\$K\$21)*J4/1000/238)	=F4/\$C4*O4*(1/238-(\$C4/\$B4+1/\$K\$21)*K4/1000/238)
5	=F5/\$C5*N5*(1/238-(\$C5/\$B5+1/\$K\$21)*J5/1000/238)	=F5/\$C5*O5*(1/238-(\$C5/\$B5+1/\$K\$21)*K5/1000/238)
6	=F6/\$C6*N6*(1/238-(\$C6/\$B6+1/\$K\$21)*J6/1000/238)	=F6/\$C6*O6*(1/238-(\$C6/\$B6+1/\$K\$21)*K6/1000/238)
7	=F7/\$C7*N7*(1/238-(\$C7/\$B7+1/\$K\$21)*J7/1000/238)	=F7/\$C7*O7*(1/238-(\$C7/\$B7+1/\$K\$21)*K7/1000/238)
8	=F8/\$C8*N8*(1/238-(\$C8/\$B8+1/\$K\$21)*J8/1000/238)	=F8/\$C8*O8*(1/238-(\$C8/\$B8+1/\$K\$21)*K8/1000/238)
9	=F9/\$C9*N9*(1/238-(\$C9/\$B9+1/\$K\$21)*J9/1000/238)	=F9/\$C9*O9*(1/238-(\$C9/\$B9+1/\$K\$21)*K9/1000/238)
10	=F10/\$C10*N10*(1/238-(\$C10/\$B10+1/\$K\$21)*J10/1000/238)	=F10/\$C10*O10*(1/238-(\$C10/\$B10+1/\$K\$21)*K10/1000/238)
11	=F11/\$C11*N11*(1/238-(\$C11/\$B11+1/\$K\$21)*J11/1000/238)	=F11/\$C11*O11*(1/238-(\$C11/\$B11+1/\$K\$21)*K11/1000/238)
12	=F12/\$C12*N12*(1/238-(\$C12/\$B12+1/\$K\$21)*J12/1000/238)	=F12/\$C12*O12*(1/238-(\$C12/\$B12+1/\$K\$21)*K12/1000/238)
13	=F13/\$C13*N13*(1/238-(\$C13/\$B13+1/\$K\$21)*J13/1000/238)	=F13/\$C13*O13*(1/238-(\$C13/\$B13+1/\$K\$21)*K13/1000/238)
14	=F14/\$C14*N14*(1/238-(\$C14/\$B14+1/\$K\$21)*J14/1000/238)	=F14/\$C14*O14*(1/238-(\$C14/\$B14+1/\$K\$21)*K14/1000/238)
15	=F15/\$C15*N15*(1/238-(\$C15/\$B15+1/\$K\$21)*J15/1000/238)	=F15/\$C15*O15*(1/238-(\$C15/\$B15+1/\$K\$21)*K15/1000/238)
16	=F16/\$C16*N16*(1/238-(\$C16/\$B16+1/\$K\$21)*J16/1000/238)	=F16/\$C16*O16*(1/238-(\$C16/\$B16+1/\$K\$21)*K16/1000/238)
17	=F17/\$C17*N17*(1/238-(\$C17/\$B17+1/\$K\$21)*J17/1000/238)	=F17/\$C17*O17*(1/238-(\$C17/\$B17+1/\$K\$21)*K17/1000/238)
18	=F18/\$C18*N18*(1/238-(\$C18/\$B18+1/\$K\$21)*J18/1000/238)	=F18/\$C18*O18*(1/238-(\$C18/\$B18+1/\$K\$21)*K18/1000/238)
19	=F19/\$C19*N19*(1/238-(\$C19/\$B19+1/\$K\$21)*J19/1000/238)	=F19/\$C19*O19*(1/238-(\$C19/\$B19+1/\$K\$21)*K19/1000/238)
20		
21		

Appendix A5.5b. Calculations for construction of uranium transfer half normal plots

A		B	C	D	E	F	G	H	I	J	K	L
1	Half normal plot at 10 minutes											
2	Test No.	da	do	Va	Vo	S	Yield			Contrast	absContrast	SS
3		1	-1	-1	-1	-1	0.000827535		da	0.00012695	0.00012695	1.00727E-09
4		2	1	1	-1	-1	0.000272305		do	-0.000546527	0.000546527	1.86683E-08
5		10	-1	1	-1	-1	0.000847147		Va	0.000265111	0.000265111	4.39274E-09
6		9	1	-1	-1	1	0.001057972		Vo	-0.001366893	0.001366893	1.16775E-07
7		4	-1	1	1	-1	0.0007036		S	0.002976547	0.002976547	5.53738E-07
8		3	1	-1	1	-1	0.000307376		dado	-0.000729107	0.000729107	3.32248E-08
9		11	-1	-1	1	-1	0.00067799		daVa	0.000318693	0.000318693	6.34781E-09
10		12	1	1	1	-1	0.001003203		daVo	0.00055778	0.00055778	1.94449E-08
11		5	-1	1	-1	1	0.000261396		daS	0.001332226	0.001332226	1.10927E-07
12		6	1	-1	-1	1	0.000449947		doVa	0.001242758	0.001242758	9.65279E-08
13		13	-1	-1	-1	1	0.00052431		doVo	-0.00085729	0.00085729	4.59341E-08
14		14	1	1	1	1	0.000512404		doS	-0.000171903	0.000171903	1.84691E-09
15		7	-1	-1	1	-1	0.000371503		VaVo	0.000490689	0.000490689	1.50485E-08
16		8	1	1	1	-1	0.000331758		VaS	5.89839E-05	5.89839E-05	2.17444E-10
17		16	-1	1	1	1	0.000608616		VoS	-0.000374447	0.000374447	8.76317E-09
18		15	1	-1	1	1	0.000942192					

1	M	N	O	P	Q	R	S	T	U	V
2	SAS SS	zi		xizi	zi ²	Rank zi	xi		Test statistics	80% significance
3	0.25050025	0.794		0.006104897	4.208601	15	2.051	0.002976547	95% significance	0.002080339
4	0.094249	0.589		0.002222567	2.643876	14	1.626	0.001366893	0.002388206	0.001847201
5	0.050625	0.079		0.001833143	1.893376	13	1.376	0.001332226	0.002060339	0.001626168
6	0.071289	0.688		0.001480125	1.418481	12	1.191	0.001242758	0.001744579	0.001389348
7	0.029241	2.051		0.000891581	1.0816	11	1.04	0.00085729	#N/A	#N/A
8	0.091204	1.376		0.000663487	0.8281	10	0.91	0.000729107	#N/A	#N/A
9	0.007225	0.158		0.000442878	0.630436	9	0.794	0.00055778	#N/A	#N/A
10	0.002209	0.322		0.000376011	0.473344	8	0.688	0.000546527	#N/A	#N/A
11	0.012544	1.626		0.000289016	0.349921	7	0.589	0.000490689	#N/A	#N/A
12	0.00148225	1.04		0.000185726	0.248016	6	0.496	0.000374447	#N/A	#N/A
13	0.00099225	0.91		0.000130027	0.166464	5	0.408	0.000318693	#N/A	#N/A
14	0.01600225	0.239		8.53657E-05	0.103684	4	0.322	0.000265111	#N/A	#N/A
15	0.01808025	1.191		4.10848E-05	0.057121	3	0.239	0.000171903	#N/A	#N/A
16	0.07263025	0.486		2.00581E-05	0.024964	2	0.158	0.00012695	#N/A	#N/A
17	0.00042025	0.408		4.65973E-06	0.006241	1	0.079	5.89839E-05	#N/A	#N/A
18										

	W
1	
2	60% significance
3	0.001736685
4	0.001555122
5	0.001389348
6	0.001191997
7	#N/A
8	#N/A
9	#N/A
10	#N/A
11	#N/A
12	#N/A
13	#N/A
14	#N/A
15	#N/A
16	#N/A
17	#N/A
18	#N/A

A		B	C	D	E	F	G	H	I	J	K	L
1	Half-normal plot at 20 minutes	da	do	Va	Vo	S	Yield			Contrast	absContrast	SS
2	Test No.	1	-1	-1	-1	-1	0.000494456		da	0.000420174	0.000420174	1.10341E-08
3		2	1	1	-1	-1	0.000300514		do	0.000173728	0.000173728	1.88634E-09
4		10	-1	1	-1	-1	0.00075035		Va	0.000216871	0.000216871	2.93958E-08
5		9	1	-1	-1	-1	0.000909386		Vo	-0.001120323	0.001120323	7.84452E-08
6		4	-1	1	1	-1	0.000582864		S	0.002211692	0.002211692	3.05724E-07
7		3	1	-1	1	-1	0.000317438		daVo	-0.000585399	0.000585399	2.14183E-08
8		11	-1	-1	1	-1	0.000440057		daVa	0.000207447	0.000207447	2.68964E-09
9		12	1	1	1	-1	0.000903083		daVo	9.43854E-05	9.43854E-05	5.56788E-10
10		5	-1	1	-1	-1	0.00025213		daS	0.001173276	0.001173276	8.60361E-08
11		6	1	-1	-1	-1	0.000350138		doVa	0.000989179	0.000989179	6.11547E-08
12		13	-1	-1	-1	1	0.000464558		doVo	-0.000578818	0.000578818	2.07949E-08
13		14	1	1	-1	1	0.000507819		doS	0.000257966	0.000257966	4.15914E-09
14		7	-1	-1	1	-1	0.000374997		VaVo	0.000639799	0.000639799	2.55839E-08
15		8	1	1	1	-1	0.000359603		VaS	-0.000258057	0.000258057	4.1621E-09
16		16	-1	1	1	1	0.000588488		VoS	-0.000403915	0.000403915	1.01967E-08
17		15	1	-1	1	1	0.000698892					
18												

	M	N	O	P	Q	R	S	T	U	V
1										
2	SAS SS	zi		xlzi	zi^2	Rank	zi	xi	Test statistics	
3	0.25050025	0.794		0.004538181	4.206801	15	2.051	0.002211692	95% significance	80% significance
4	0.094249	0.589		0.001907748	2.643876	14	1.826	0.001173276	0.002184949	0.001692201
5	0.050825	0.079		0.001541564	1.893376	13	1.376	0.001120323	0.001945058	0.001517145
6	0.071289	0.688		0.001178112	1.418481	12	1.191	0.00089179	0.001692201	0.001335607
7	0.028241	2.051		0.000665391	1.0816	11	1.04	0.000639799	0.00143286	0.001141101
8	0.091204	1.376		0.000532713	0.8281	10	0.91	0.000585399	#N/A	#N/A
9	0.007225	0.158		0.000457994	0.630436	9	0.794	0.000576818	#N/A	#N/A
10	0.002209	0.322		0.00028908	0.473344	8	0.688	0.000420174	#N/A	#N/A
11	0.012544	1.626		0.000237906	0.346921	7	0.589	0.000403915	#N/A	#N/A
12	0.00148225	1.04		0.000127997	0.246016	6	0.496	0.000258057	#N/A	#N/A
13	0.00099225	0.91		0.00010525	0.166464	5	0.408	0.000257966	#N/A	#N/A
14	0.01600225	0.239		6.98326E-05	0.103684	4	0.322	0.000216871	#N/A	#N/A
15	0.01809025	1.191		4.95799E-05	0.057121	3	0.239	0.000207447	#N/A	#N/A
16	0.07263025	0.496		2.74491E-05	0.024964	2	0.158	0.000173728	#N/A	#N/A
17	0.00042025	0.408		7.45645E-06	0.006241	1	0.079	9.43854E-05	#N/A	#N/A
18										

	W
1	
2	60% significance
3	0.001428376
4	0.001277255
5	0.001141101
6	0.000979013
7	#N/A
8	#N/A
9	#N/A
10	#N/A
11	#N/A
12	#N/A
13	#N/A
14	#N/A
15	#N/A
16	#N/A
17	#N/A
18	

	M	N	O	P	Q	R	S	T	U	V
1										
2	SAS SS	zi		xizi	zi ²	Rank	zi	xi	Test statistics	80% significance
3	0.25050025	0.794		0.003103976	4.208601	15	2.051	0.001513397	0.00153445	0.001188402
4	0.094249	0.589		0.001397752	2.643876	14	1.626	0.000859628	0.001365979	0.001085464
5	0.050625	0.079		0.000835608	1.893376	13	1.376	0.000607273	0.001188402	0.000937972
6	0.071289	0.688		0.000895513	1.418481	12	1.191	0.000583974	0.001006271	0.000801374
7	0.028241	2.051		0.000488953	1.0816	11	1.04	0.000468224	#N/A	#N/A
8	0.091204	1.376		0.000355949	0.8281	10	0.91	0.000391152	#N/A	#N/A
9	0.007225	0.158		0.000280245	0.630436	9	0.794	0.000365548	#N/A	#N/A
10	0.002209	0.322		0.000244141	0.473344	8	0.888	0.000354857	#N/A	#N/A
11	0.012544	1.626		0.000161946	0.346921	7	0.589	0.00027495	#N/A	#N/A
12	0.00148225	1.04		0.00012221	0.246016	6	0.496	0.000246391	#N/A	#N/A
13	0.00099225	0.91		8.52403E-05	0.186464	5	0.408	0.000208922	#N/A	#N/A
14	0.01600225	0.239		3.30132E-05	0.103684	4	0.322	0.000102526	#N/A	#N/A
15	0.01809025	1.191		1.42184E-05	0.057121	3	0.239	5.94911E-05	#N/A	#N/A
16	0.07263025	0.496		7.79281E-06	0.024964	2	0.158	4.93216E-05	#N/A	#N/A
17	0.00042025	0.408		3.6112E-06	0.006241	1	0.079	4.57114E-05	#N/A	#N/A
18										

	W
1	
2	60% significance
3	0.001001718
4	0.000896993
5	0.000801374
6	0.000687543
7	#N/A
8	#N/A
9	#N/A
10	#N/A
11	#N/A
12	#N/A
13	#N/A
14	#N/A
15	#N/A
16	#N/A
17	#N/A
18	

A		B	C	D	E	F	G	H	I	J	K	L
1	Half normal plot at 80 minutes	da	do	Va	Vo	S	Yield			Contrast	absContrast	SS
2	Test No.											
3	1	-1	-1	-1	-1	-1	0.000242706		da	-3.34627E-05	3.34627E-05	6.99847E-11
4	2	1	1	1	1	1	0.000265925		do	0.000261627	0.000261627	4.27805E-09
5	10	-1	1	1	-1	-1	0.000299483		Va	0.000567634	0.000567634	2.0138E-08
6	9	1	-1	-1	-1	1	0.000238843		Vo	-0.000484993	0.000484993	1.47011E-08
7	4	-1	1	1	1	-1	0.00036916		S	0.000353367	0.000353367	7.80425E-09
8	3	1	-1	1	-1	-1	0.000278728		dado	-5.32298E-05	5.32298E-05	1.77088E-10
9	11	-1	-1	1	-1	1	0.000331785		daVa	-1.6524E-05	1.6524E-05	1.70852E-11
10	12	1	1	1	1	1	0.000401417		daVo	8.69798E-05	8.69798E-05	4.72843E-10
11	5	-1	1	-1	-1	-1	0.000194967		daS	0.000100099	0.000100099	6.26234E-10
12	6	1	-1	-1	1	1	0.000200044		doVa	5.63128E-05	5.63128E-05	1.98194E-10
13	13	-1	-1	-1	1	1	0.000216945		doVo	-0.00023022	0.00023022	3.31259E-09
14	14	1	1	-1	1	1	0.00024082		doS	4.57663E-05	4.57663E-05	1.3091E-10
15	7	-1	-1	1	1	-1	0.000229991		VaVo	-9.66308E-05	9.66308E-05	5.83595E-10
16	8	1	1	1	1	-1	0.000227346		VaS	0.00016847	0.00016847	1.77389E-09
17	16	-1	1	1	1	1	0.000315245		VoS	0.000119351	0.000119351	8.90289E-10
18	15	1	-1	1	1	1	0.000315696					

	M	N	O	P	Q	R	S	T	U	V
1										
2	SAS SS	z _i		x _i z _i	z _i ²	Rank	z _i	x _i	Test statistics	80% significance
3	0.25050025	0.794		0.001164218	4.206601	15	2.051	0.000567634	95% significance	0.000606934
4	0.084249	0.589		0.000788598	2.643876	14	1.826	0.000484983		0.000470059
5	0.050625	0.079		0.000486232	1.893376	13	1.376	0.000353367		0.000421432
6	0.071289	0.688		0.000311598	1.418481	12	1.191	0.000261627		0.000371004
7	0.029241	2.051		0.000239429	1.0816	11	1.04	0.00023022		0.000316975
8	0.091204	1.376		0.000153308	0.8281	10	0.91	0.00016847	#N/A	#N/A
9	0.007225	0.158		9.47646E-05	0.630436	9	0.794	0.000119351	#N/A	#N/A
10	0.002209	0.322		6.88679E-05	0.473344	8	0.688	0.000100099	#N/A	#N/A
11	0.012544	1.626		5.69155E-05	0.346921	7	0.589	9.66308E-05	#N/A	#N/A
12	0.00148225	1.04		4.3142E-05	0.246016	6	0.496	8.69798E-05	#N/A	#N/A
13	0.00099225	0.91		2.29755E-05	0.166464	5	0.408	5.63126E-05	#N/A	#N/A
14	0.01600225	0.239		1.714E-05	0.103684	4	0.322	5.32298E-05	#N/A	#N/A
15	0.01809025	1.191		1.09381E-05	0.057121	3	0.239	4.57663E-05	#N/A	#N/A
16	0.07263025	0.496		5.28711E-06	0.024964	2	0.158	3.34627E-05	#N/A	#N/A
17	0.00042025	0.408		1.3054E-06	0.006241	1	0.079	1.6524E-05	#N/A	#N/A
18										

	W
1	
2	80% significance
3	0.000398218
4	0.000354795
5	0.000318975
6	0.00027195
7	#N/A
8	#N/A
9	#N/A
10	#N/A
11	#N/A
12	#N/A
13	#N/A
14	#N/A
15	#N/A
16	#N/A
17	#N/A
18	

	A	B	C	D	E	F	G	H	I
1	Half normal plot at 10 minutes								
2	Test No.	da	do	Va	Vo	S	CALCULATIONS		
3	1	-1	-1	-1	-1	-1	Yield		da
4	2	1	1	1	1	-1	=G24*1000		do
5	10	-1	1	-1	-1	1	=G25*1000		Va
6	9	1	-1	-1	-1	-1	=G33*1000		Vo
7	4	-1	1	1	1	-1	=G32*1000		S
8	3	1	-1	1	-1	-1	=G26*1000		da do
9	11	-1	-1	1	-1	1	=G34*1000		da Va
10	12	1	1	1	-1	1	=G35*1000		da Vo
11	5	-1	1	-1	1	-1	=G28*1000		da S
12	6	1	-1	1	-1	1	=G29*1000		do Va
13	13	-1	-1	-1	-1	1	=G36*1000		do Vo
14	14	1	1	-1	1	1	=G37*1000		do S
15	7	-1	-1	1	1	-1	=G30*1000		Va Vo
16	8	1	1	1	1	-1	=G31*1000		Va S
17	16	-1	1	1	1	1	=G39*1000		Vo S
18	15	1	-1	1	1	1	=G38*1000		
19									
20									
21									
22									
23									
24						1	6 27535007471016E-07		
25						2 72304756070889E-07			
26						3 07376312553943E-07			
27						7 03599706848616E-07			
28						2 61386238349557E-07			
29						4 4894669078389E-07			
30						3 71502595459434E-07			
31						3 31757612456849E-07			
32						1 05797204051967E-06			
33						8 47146895916733E-07			
34						6 77990317631678E-07			
35						1 00320349327675E-06			
36						6 52430828074283E-07			
37						5 12404221085077E-07			
38						9 42192046257798E-07			
39						6 0861569597955E-07			

1	
2	Contrast
3	=B\$3*\$G\$3-B\$4*\$G\$4+B\$5*\$G\$5+B\$6*\$G\$6+B\$7*\$G\$7+B\$8*\$G\$8+B\$9*\$G\$9+B\$10*\$G\$10+B\$11*\$G\$11+B\$12*\$G\$12+B\$13*\$G\$13+B\$14*\$G\$14+B\$15*\$G\$15
4	=C\$3*\$G\$3+C\$4*\$G\$4+C\$5*\$G\$5+C\$6*\$G\$6+C\$7*\$G\$7+C\$8*\$G\$8+C\$9*\$G\$9+C\$10*\$G\$10+C\$11*\$G\$11+C\$12*\$G\$12+C\$13*\$G\$13+C\$14*\$G\$14+C\$15*\$G\$15
5	=D\$3*\$G\$3+D\$4*\$G\$4+D\$5*\$G\$5+D\$6*\$G\$6+D\$7*\$G\$7+D\$8*\$G\$8+D\$9*\$G\$9+D\$10*\$G\$10+D\$11*\$G\$11+D\$12*\$G\$12+D\$13*\$G\$13+D\$14*\$G\$14+D\$15*\$G\$15
6	=E\$3*\$G\$3+E\$4*\$G\$4+E\$5*\$G\$5+E\$6*\$G\$6+E\$7*\$G\$7+E\$8*\$G\$8+E\$9*\$G\$9+E\$10*\$G\$10+E\$11*\$G\$11+E\$12*\$G\$12+E\$13*\$G\$13+E\$14*\$G\$14+E\$15*\$G\$15
7	=F\$3*\$G\$3+F\$4*\$G\$4+F\$5*\$G\$5+F\$6*\$G\$6+F\$7*\$G\$7+F\$8*\$G\$8+F\$9*\$G\$9+F\$10*\$G\$10+F\$11*\$G\$11+F\$12*\$G\$12+F\$13*\$G\$13+F\$14*\$G\$14+F\$15*\$G\$15
8	=B\$3*\$G\$3-B\$4*\$G\$4+B\$5*\$G\$5+B\$6*\$G\$6+B\$7*\$G\$7+B\$8*\$G\$8+B\$9*\$G\$9+B\$10*\$G\$10+B\$11*\$G\$11+B\$12*\$G\$12+B\$13*\$G\$13+B\$14*\$G\$14+B\$15*\$G\$15
9	=B\$3*\$G\$3-B\$4*\$G\$4+B\$5*\$G\$5+B\$6*\$G\$6+B\$7*\$G\$7+B\$8*\$G\$8+B\$9*\$G\$9+B\$10*\$G\$10+B\$11*\$G\$11+B\$12*\$G\$12+B\$13*\$G\$13+B\$14*\$G\$14+B\$15*\$G\$15
10	=B\$3*\$G\$3-B\$4*\$G\$4+B\$5*\$G\$5+B\$6*\$G\$6+B\$7*\$G\$7+B\$8*\$G\$8+B\$9*\$G\$9+B\$10*\$G\$10+B\$11*\$G\$11+B\$12*\$G\$12+B\$13*\$G\$13+B\$14*\$G\$14+B\$15*\$G\$15
11	=B\$3*\$G\$3-B\$4*\$G\$4+B\$5*\$G\$5+B\$6*\$G\$6+B\$7*\$G\$7+B\$8*\$G\$8+B\$9*\$G\$9+B\$10*\$G\$10+B\$11*\$G\$11+B\$12*\$G\$12+B\$13*\$G\$13+B\$14*\$G\$14+B\$15*\$G\$15
12	=C\$3*\$G\$3+C\$4*\$G\$4+C\$5*\$G\$5+C\$6*\$G\$6+C\$7*\$G\$7+C\$8*\$G\$8+C\$9*\$G\$9+C\$10*\$G\$10+C\$11*\$G\$11+C\$12*\$G\$12+C\$13*\$G\$13+C\$14*\$G\$14+C\$15*\$G\$15
13	=C\$3*\$G\$3+C\$4*\$G\$4+C\$5*\$G\$5+C\$6*\$G\$6+C\$7*\$G\$7+C\$8*\$G\$8+C\$9*\$G\$9+C\$10*\$G\$10+C\$11*\$G\$11+C\$12*\$G\$12+C\$13*\$G\$13+C\$14*\$G\$14+C\$15*\$G\$15
14	=C\$3*\$G\$3+C\$4*\$G\$4+C\$5*\$G\$5+C\$6*\$G\$6+C\$7*\$G\$7+C\$8*\$G\$8+C\$9*\$G\$9+C\$10*\$G\$10+C\$11*\$G\$11+C\$12*\$G\$12+C\$13*\$G\$13+C\$14*\$G\$14+C\$15*\$G\$15
15	=D\$3*\$G\$3+D\$4*\$G\$4+D\$5*\$G\$5+D\$6*\$G\$6+D\$7*\$G\$7+D\$8*\$G\$8+D\$9*\$G\$9+D\$10*\$G\$10+D\$11*\$G\$11+D\$12*\$G\$12+D\$13*\$G\$13+D\$14*\$G\$14+D\$15*\$G\$15
16	=D\$3*\$G\$3+D\$4*\$G\$4+D\$5*\$G\$5+D\$6*\$G\$6+D\$7*\$G\$7+D\$8*\$G\$8+D\$9*\$G\$9+D\$10*\$G\$10+D\$11*\$G\$11+D\$12*\$G\$12+D\$13*\$G\$13+D\$14*\$G\$14+D\$15*\$G\$15
17	=E\$3*\$G\$3+E\$4*\$G\$4+E\$5*\$G\$5+E\$6*\$G\$6+E\$7*\$G\$7+E\$8*\$G\$8+E\$9*\$G\$9+E\$10*\$G\$10+E\$11*\$G\$11+E\$12*\$G\$12+E\$13*\$G\$13+E\$14*\$G\$14+E\$15*\$G\$15
18	=E\$3*\$G\$3+E\$4*\$G\$4+E\$5*\$G\$5+E\$6*\$G\$6+E\$7*\$G\$7+E\$8*\$G\$8+E\$9*\$G\$9+E\$10*\$G\$10+E\$11*\$G\$11+E\$12*\$G\$12+E\$13*\$G\$13+E\$14*\$G\$14+E\$15*\$G\$15
19	
20	
21	n=15
22	n=14
23	n=13
24	n=12
25	
26	
27	
28	
29	
30	
31	
32	
33	
34	
35	
36	
37	
38	
39	

1	K	L	M	N	O	P	Q	R	S	T
2	absContrast	SS	SAS SS	zi						
3	=ABS(J3)	=K3^2/16	0.25050025	0.794						
4	=ABS(J4)	=K4^2/16	0.094249	0.589						
5	=ABS(J5)	=K5^2/16	0.050825	0.079						
6	=ABS(J6)	=K6^2/16	0.071289	0.688						
7	=ABS(J7)	=K7^2/16	0.028241	2.051						
8	=ABS(J8)	=K8^2/16	0.091204	1.376						
9	=ABS(J9)	=K9^2/16	0.007225	0.158						
10	=ABS(J10)	=K10^2/16	0.002209	0.322						
11	=ABS(J11)	=K11^2/16	0.012544	1.626						
12	=ABS(J12)	=K12^2/16	0.00148225	1.04						
13	=ABS(J13)	=K13^2/16	0.00099225	0.91						
14	=ABS(J14)	=K14^2/16	0.01600225	0.239						
15	=ABS(J15)	=K15^2/16	0.01809025	1.191						
16	=ABS(J16)	=K16^2/16	0.07263025	0.496						
17	=ABS(J17)	=K17^2/16	0.00042025	0.408						
18										
19										
20										
21	3.37	2.61	2.2	Slope =	=SUM(P25:P35)/SUM(Q25:Q35)	xi zi	zi^2	Rank	zi	xi
22	3	2.34	1.97			=T21*S21	=S21^2	15	2.051	0.00297654671874734
23	2.61	2.06	1.76			=T22*S22	=S22^2	14	1.626	0.00136689250184286
24	2.21	1.76	1.51			=T23*S23	=S23^2	13	1.376	0.0013322261398001
25						=T24*S24	=S24^2	12	1.191	0.00124275779208551
26						=T25*S25	=S25^2	11	1.04	0.00085728966841051
27						=T26*S26	=S26^2	10	0.91	0.000729108695683761
28						=T27*S27	=S27^2	9	0.794	0.000557780438167587
29						=T28*S28	=S28^2	8	0.688	0.000546527318767692
30						=T29*S29	=S29^2	7	0.589	0.000490688741528146
31						=T30*S30	=S30^2	6	0.496	0.000374447210053386
32						=T31*S31	=S31^2	5	0.408	0.000318692506978123
33						=T32*S32	=S32^2	4	0.322	0.000285111002183503
34						=T33*S33	=S33^2	3	0.239	0.000171902733682947
35						=T34*S34	=S34^2	2	0.158	0.000126949787273991
36						=T35*S35	=S35^2	1	0.079	0.0000568839329065233
37										
38										
39										

	U	V	W
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19	Test statistics		
20	95% significance	80% significance	60% significance
21	=K21*\$O\$20	=L21*\$O\$20	=M21*\$O\$20
22	=K22*\$O\$20	=L22*\$O\$20	=M22*\$O\$20
23	=K23*\$O\$20	=L23*\$O\$20	=M23*\$O\$20
24	=K24*\$O\$20	=L24*\$O\$20	=M24*\$O\$20
25	#N/A	#N/A	#N/A
26	#N/A	#N/A	#N/A
27	#N/A	#N/A	#N/A
28	#N/A	#N/A	#N/A
29	#N/A	#N/A	#N/A
30	#N/A	#N/A	#N/A
31	#N/A	#N/A	#N/A
32	#N/A	#N/A	#N/A
33	#N/A	#N/A	#N/A
34	#N/A	#N/A	#N/A
35	#N/A	#N/A	#N/A
36			
37			
38			
39			

Appendix A5.5c. ANOVA Results generated from uranium transfer data

SAS 10:15 Wednesday, April 19, 1995 1

OBS	RATE	VA	VO	DA	DO	S
1	0.62800	-1	-1	-1	-1	-1
2	0.27200	-1	-1	1	1	-1
3	0.30700	1	-1	1	-1	-1
4	0.70360	1	-1	-1	1	-1
5	0.26100	-1	1	1	-1	-1
6	0.45000	-1	1	-1	1	-1
7	0.37200	1	1	-1	-1	-1
8	0.33200	1	1	1	1	-1
9	1.05797	-1	-1	1	-1	1
10	0.84715	-1	-1	-1	1	1
11	0.67799	1	-1	-1	-1	1
12	1.00320	1	-1	1	1	1
13	0.65200	-1	1	-1	-1	1
14	0.51240	-1	1	1	1	1
15	0.94219	1	1	1	-1	1
16	0.60862	1	1	-1	1	1

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.601695	Sum	9.627124
Std Dev	0.262444	Variance	0.068877
Skewness	0.331784	Kurtosis	-1.01954
USS	6.82575	CSS	1.033155
CV	43.61747	Std Mean	0.065611
T:Mean=0	9.170637	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.937006	Prob<W	0.3115

Quantiles(Def=5)

100% Max	1.057972	99%	1.057972
75% Q3	0.775373	95%	1.057972
50% Med	0.618308	90%	1.003203
25% Q1	0.352	10%	0.272
0% Min	0.261	5%	0.261
		1%	0.261
Range	0.796972		
Q3-Q1	0.423373		
Mode	0.261		

Extremes

Lowest	Obs	Highest	Obs
0.261(	5)	0.7036(	4)
0.272(	2)	0.847147(	10)
0.307(	3)	0.942192(	15)
0.332(	8)	1.003203(	12)
0.372(	7)	1.057972(	9)

SAS 10:15 Wednesday, April 19, 1995 3
General Linear Models Procedure
Number of observations in data set = 16

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	0.97335864	0.08111322	4.07	0.1372
Error	3	0.05979609	0.01993203		
Corrected Total	15	1.03315473			
	R-Square	C.V.	Root MSE	RATE Mean	
	0.942123	23.46385	0.1411808	0.60169525	

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00395584	0.00395584	0.20	0.6861
DO	1	0.00178895	0.00178895	0.09	0.7840
VA	1	0.00442484	0.00442484	0.22	0.6697
VO	1	0.11674181	0.11674181	5.86	0.0942
S	1	0.55350773	0.55350773	27.77	0.0133
DA*DO	1	0.03311763	0.03311763	1.66	0.2878
DA*VO	1	0.00205984	0.00205984	0.10	0.7689
DA*S	1	0.18310226	0.18310226	9.19	0.0563
DO*VA	1	0.04683524	0.04683524	2.35	0.2228
DO*S	1	0.01879531	0.01879531	0.94	0.4031
VA*S	1	0.00021666	0.00021666	0.01	0.9235
VO*S	1	0.00881252	0.00881252	0.44	0.5536

Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00395584	0.00395584	0.20	0.6861
DO	1	0.00178895	0.00178895	0.09	0.7840
VA	1	0.00442484	0.00442484	0.22	0.6697
VO	1	0.11674181	0.11674181	5.86	0.0942
S	1	0.55350773	0.55350773	27.77	0.0133
DA*DO	1	0.03311763	0.03311763	1.66	0.2878
DA*VO	1	0.00205984	0.00205984	0.10	0.7689
DA*S	1	0.18310226	0.18310226	9.19	0.0563
DO*VA	1	0.04683524	0.04683524	2.35	0.2228
DO*S	1	0.01879531	0.01879531	0.94	0.4031
VA*S	1	0.00021666	0.00021666	0.01	0.9235
VO*S	1	0.00881252	0.00881252	0.44	0.5536

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.6016952500	17.05	0.0004	0.03529521
DA	-0.0157238750	-0.45	0.6861	0.03529521

General Linear Models Procedure

Dependent Variable: RATE

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
DO	-.0105740000	-0.30	0.7840	0.03529521
VA	0.0166298750	0.47	0.6697	0.03529521
VO	-.0854187500	-2.42	0.0942	0.03529521
S	0.1859952500	5.27	0.0133	0.03529521
DA*DO	-.0454956250	-1.29	0.2878	0.03529521
DA*VO	0.0113463750	0.32	0.7689	0.03529521
DA*S	0.1069761250	3.03	0.0563	0.03529521
DO*VA	0.0541036250	1.53	0.2228	0.03529521
DO*S	-.0342740000	-0.97	0.4031	0.03529521
VA*S	0.0036798750	0.10	0.9235	0.03529521
VO*S	-.0234687500	-0.66	0.5536	0.03529521

SAS 10:15 Wednesday, April 19, 1995 6

OBS	RATE	VA	VO	DA	DO	S
1	0.49400	-1	-1	-1	-1	-1
2	0.30100	-1	-1	1	1	-1
3	0.31700	1	-1	1	-1	-1
4	0.58266	1	-1	-1	1	-1
5	0.25200	-1	1	1	-1	-1
6	0.35000	-1	1	-1	1	-1
7	0.37500	1	1	-1	-1	-1
8	0.36000	1	1	1	1	-1
9	0.90939	-1	-1	1	-1	1
10	0.75035	-1	-1	-1	1	1
11	0.44006	1	-1	-1	-1	1
12	0.90308	1	-1	1	1	1
13	0.46500	-1	1	-1	-1	1
14	0.50782	-1	1	1	1	1
15	0.69989	1	1	1	-1	1
16	0.56849	1	1	-1	1	1

SAS 10:15 Wednesday, April 19, 1995 7

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.517234	Sum	8.275739
Std Dev	0.206028	Variance	0.042447
Skewness	0.767314	Kurtosis	-0.3636
USS	4.917202	CSS	0.636711
CV	39.83261	Std Mean	0.051507
T:Mean=0	10.04202	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.917142	Prob<W	0.1534

Quantiles(Def=5)

100% Max	0.909386	99%	0.909386
75% Q3	0.641278	95%	0.909386
50% Med	0.4795	90%	0.903083
25% Q1	0.355	10%	0.301
0% Min	0.252	5%	0.252
		1%	0.252
Range	0.657386		
Q3-Q1	0.286278		
Mode	0.252		

Extremes

Lowest	Obs	Highest	Obs
0.252(	5)	0.582664(	4)
0.301(	2)	0.699892(	15)
0.317(	3)	0.75035(	10)
0.35(	6)	0.903083(	12)
0.36(	8)	0.909386(	9)

SAS 10:15 Wednesday, April 19, 1995 8

General Linear Models Procedure

Number of observations in data set = 16

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	0.59179378	0.04931615	3.29	0.1777
Error	3	0.04491720	0.01497240		
Corrected Total	15	0.63671098			
	R-Square	C.V.	Root MSE		RATE Mean
	0.929454	23.65696	0.1223618		0.51723369

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00315341	0.00315341	0.21	0.6775
DO	1	0.00860576	0.00860576	0.57	0.5035
VA	1	0.00293301	0.00293301	0.20	0.6880
VO	1	0.07830777	0.07830777	5.23	0.1063
S	1	0.30592265	0.30592265	20.43	0.0202
DA*DO	1	0.02130294	0.02130294	1.42	0.3187
DA*VO	1	0.00065248	0.00065248	0.04	0.8480
DA*S	1	0.11695528	0.11695528	7.81	0.0681
DO*VA	1	0.03935294	0.03935294	2.63	0.2034
DO*S	1	0.00022306	0.00022306	0.01	0.9106
VA*S	1	0.00418282	0.00418282	0.28	0.6337
VO*S	1	0.01020166	0.01020166	0.68	0.4696

Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00315341	0.00315341	0.21	0.6775
DO	1	0.00860576	0.00860576	0.57	0.5035
VA	1	0.00293301	0.00293301	0.20	0.6880
VO	1	0.07830777	0.07830777	5.23	0.1063
S	1	0.30592265	0.30592265	20.43	0.0202
DA*DO	1	0.02130294	0.02130294	1.42	0.3187
DA*VO	1	0.00065248	0.00065248	0.04	0.8480
DA*S	1	0.11695528	0.11695528	7.81	0.0681
DO*VA	1	0.03935294	0.03935294	2.63	0.2034
DO*S	1	0.00022306	0.00022306	0.01	0.9106
VA*S	1	0.00418282	0.00418282	0.28	0.6337
VO*S	1	0.01020166	0.01020166	0.68	0.4696

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.5172336875	16.91	0.0005	0.03059044
DA	0.0140388125	0.46	0.6775	0.03059044

SAS 10:15 Wednesday, April 19, 1995 10

General Linear Models Procedure

Dependent Variable: RATE

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
DO	0.0231918125	0.76	0.5035	0.03059044
VA	0.0135393125	0.44	0.6880	0.03059044
VO	-.0699588125	-2.29	0.1063	0.03059044
S	0.1382756875	4.52	0.0202	0.03059044
DA*DO	-.0364888125	-1.19	0.3187	0.03059044
DA*VO	-.0063859375	-0.21	0.8480	0.03059044
DA*S	0.0854968125	2.79	0.0681	0.03059044
DO*VA	0.0495939375	1.62	0.2034	0.03059044
DO*S	0.0037338125	0.12	0.9106	0.03059044
VA*S	-.0161686875	-0.53	0.6337	0.03059044
VO*S	-.0252508125	-0.83	0.4696	0.03059044

SAS 10:15 Wednesday, April 19, 1995 11

OBS	RATE	VA	VO	DA	DO	S
1	0.36100	-1	-1	-1	-1	-1
2	0.30200	-1	-1	1	1	-1
3	0.31800	1	-1	1	-1	-1
4	0.50243	1	-1	-1	1	-1
5	0.23400	-1	1	1	-1	-1
6	0.29600	-1	1	-1	1	-1
7	0.28000	1	1	-1	-1	-1
8	0.29500	1	1	1	1	-1
9	0.62320	-1	-1	1	-1	1
10	0.57378	-1	-1	-1	1	1
11	0.39623	1	-1	-1	-1	1
12	0.69848	1	-1	1	1	1
13	0.35800	-1	1	-1	-1	1
14	0.41985	-1	1	1	1	1
15	0.53017	1	1	1	-1	1
16	0.50266	1	1	-1	1	1

SAS 10:15 Wednesday, April 19, 1995 12

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.418175	Sum	6.690806
Std Dev	0.13799	Variance	0.019041
Skewness	0.621993	Kurtosis	-0.66933
USS	3.083549	CSS	0.285619
CV	32.99814	Std Mean	0.034498
T:Mean=0	12.1219	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.931098	Prob<W	0.2535

Quantiles(Def=5)

100% Max	0.698484	99%	0.698484
75% Q3	0.516414	95%	0.698484
50% Med	0.378614	90%	0.623202
25% Q1	0.299	10%	0.28
0% Min	0.234	5%	0.234
		1%	0.234
Range	0.464484		
Q3-Q1	0.217414		
Mode	0.234		

Extremes

Lowest	Obs	Highest	Obs
0.234(	5)	0.502656(	16)
0.28(	7)	0.530173(	15)
0.295(	8)	0.573781(	10)
0.296(	6)	0.623202(	9)
0.302(	2)	0.698484(	12)

SAS 10:15 Wednesday, April 19, 1995 13

General Linear Models Procedure

Number of observations in data set = 16

SAS 10:15 Wednesday, April 19, 1995 14

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	0.27561226	0.02296769	6.89	0.0692
Error	3	0.01000669	0.00333556		
Corrected Total	15	0.28561895			

R-Square	C.V.	Root MSE	RATE Mean
0.964965	13.81103	0.0577543	0.41817538

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00141794	0.00141794	0.43	0.5609
DO	1	0.01498164	0.01498164	4.49	0.1243
VA	1	0.00788233	0.00788233	2.36	0.2218
VO	1	0.04616460	0.04616460	13.84	0.0338
S	1	0.14325354	0.14325354	42.95	0.0072
DA*DO	1	0.01378687	0.01378687	4.13	0.1349
DA*VO	1	0.00027124	0.00027124	0.08	0.7941
DA*S	1	0.03344089	0.03344089	10.03	0.0506
DO*VA	1	0.01315208	0.01315208	3.94	0.1413
DO*S	1	0.00044887	0.00044887	0.13	0.7381
VA*S	1	0.00015452	0.00015452	0.05	0.8434
VO*S	1	0.00065774	0.00065774	0.20	0.6871

Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00141794	0.00141794	0.43	0.5609
DO	1	0.01498164	0.01498164	4.49	0.1243
VA	1	0.00788233	0.00788233	2.36	0.2218
VO	1	0.04616460	0.04616460	13.84	0.0338
S	1	0.14325354	0.14325354	42.95	0.0072
DA*DO	1	0.01378687	0.01378687	4.13	0.1349
DA*VO	1	0.00027124	0.00027124	0.08	0.7941
DA*S	1	0.03344089	0.03344089	10.03	0.0506
DO*VA	1	0.01315208	0.01315208	3.94	0.1413
DO*S	1	0.00044887	0.00044887	0.13	0.7381
VA*S	1	0.00015452	0.00015452	0.05	0.8434
VO*S	1	0.00065774	0.00065774	0.20	0.6871

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.4181753750	28.96	0.0001	0.01443858
DA	0.0094138750	0.65	0.5609	0.01443858

SAS 10:15 Wednesday, April 19, 1995 15

General Linear Models Procedure

Dependent Variable: RATE

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
DO	0.0305998750	2.12	0.1243	0.01443858
VA	0.0221956250	1.54	0.2218	0.01443858
VO	-.0537148750	-3.72	0.0338	0.01443858
S	0.0946221250	6.55	0.0072	0.01443858
DA*DO	-.0293543750	-2.03	0.1349	0.01443858
DA*VO	-.0041173750	-0.29	0.7941	0.01443858
DA*S	0.0457171250	3.17	0.0506	0.01443858
DO*VA	0.0286706250	1.99	0.1413	0.01443858
DO*S	0.0052966250	0.37	0.7381	0.01443858
VA*S	-.0031076250	-0.22	0.8434	0.01443858
VO*S	-.0064116250	-0.44	0.6871	0.01443858

SAS 10:15 Wednesday, April 19, 1995 16

OBS	RATE	VA	VO	DA	DO	S
1	0.24300	-1	-1	-1	-1	-1
2	0.26600	-1	-1	1	1	-1
3	0.27700	1	-1	1	-1	-1
4	0.36916	1	-1	-1	1	-1
5	0.19500	-1	1	1	-1	-1
6	0.20000	-1	1	-1	1	-1
7	0.23000	1	1	-1	-1	-1
8	0.22700	1	1	1	1	-1
9	0.23884	-1	-1	1	-1	1
10	0.29948	-1	-1	-1	1	1
11	0.33178	1	-1	-1	-1	1
12	0.40142	1	-1	1	1	1
13	0.21700	-1	1	-1	-1	1
14	0.24082	-1	1	1	1	1
15	0.31570	1	1	1	-1	1
16	0.31524	1	1	-1	1	1

SAS 10:15 Wednesday, April 19, 1995 17

UNIVARIATE PROCEDURE

Variable=RATE

Moments

N	16	Sum Wgts	16
Mean	0.272966	Sum	4.367449
Std Dev	0.060654	Variance	0.003679
Skewness	0.707151	Kurtosis	-0.29987
USS	1.247347	CSS	0.055184
CV	22.22037	Std Mean	0.015163
T:Mean=0	18.0015	Prob> T	0.0001
Sgn Rank	68	Prob> S	0.0001
Num ^= 0	16		
W:Normal	0.935968	Prob<W	0.3005

Quantiles(Def=5)

100% Max	0.401417	99%	0.401417
75% Q3	0.315471	95%	0.401417
50% Med	0.2545	90%	0.36916
25% Q1	0.2285	10%	0.2
0% Min	0.195	5%	0.195
		1%	0.195
Range	0.206417		
Q3-Q1	0.08697		
Mode	0.195		

Extremes

Lowest	Obs	Highest	Obs
0.195(	5)	0.315245(	16)
0.2(	6)	0.315696(	15)
0.217(	13)	0.331785(	11)
0.227(	8)	0.36916(	4)
0.23(	7)	0.401417(	12)

SAS 10:15 Wednesday, April 19, 1995 18

General Linear Models Procedure

Number of observations in data set = 16

SAS 10:15 Wednesday, April 19, 1995 19

General Linear Models Procedure

Dependent Variable: RATE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	0.05156731	0.00429728	3.57	0.1615
Error	3	0.00361621	0.00120540		
Corrected Total	15	0.05518352			
	R-Square	C.V.	Root MSE		RATE Mean
	0.934469	12.71916	0.0347189		0.27296556

Source	DF	Type I SS	Mean Square	F Value	Pr > F
DA	1	0.00012043	0.00012043	0.10	0.7727
DO	1	0.00458332	0.00458332	3.80	0.1463
VA	1	0.02010419	0.02010419	16.68	0.0265
VO	1	0.01475782	0.01475782	12.24	0.0395
S	1	0.00779376	0.00779376	6.47	0.0845
DA*DO	1	0.00017826	0.00017826	0.15	0.7262
DA*VO	1	0.00036518	0.00036518	0.30	0.6204
DO*VA	1	0.00076208	0.00076208	0.63	0.4846
DO*S	1	0.00013157	0.00013157	0.11	0.7628
VA*S	1	0.00008318	0.00008318	0.07	0.8098
VO*S	1	0.00178162	0.00178162	1.48	0.3110
	1	0.00090590	0.00090590	0.75	0.4498
Source	DF	Type III SS	Mean Square	F Value	Pr > F
DA	1	0.00012043	0.00012043	0.10	0.7727
DO	1	0.00458332	0.00458332	3.80	0.1463
VA	1	0.02010419	0.02010419	16.68	0.0265
VO	1	0.01475782	0.01475782	12.24	0.0395
S	1	0.00779376	0.00779376	6.47	0.0845
DA*DO	1	0.00017826	0.00017826	0.15	0.7262
DA*VO	1	0.00036518	0.00036518	0.30	0.6204
DO*VA	1	0.00076208	0.00076208	0.63	0.4846
DO*S	1	0.00013157	0.00013157	0.11	0.7628
VA*S	1	0.00008318	0.00008318	0.07	0.8098
VO*S	1	0.00178162	0.00178162	1.48	0.3110
	1	0.00090590	0.00090590	0.75	0.4498

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
INTERCEPT	0.2729655625	31.45	0.0001	0.00867973
DA	-.0027435625	-0.32	0.7727	0.00867973

SAS 10:15 Wednesday, April 19, 1995 20

General Linear Models Procedure

Dependent Variable: RATE

Parameter	Estimate	T for H0: Parameter=0	Pr > T	Std Error of Estimate
DO	0.0169250625	1.95	0.1463	0.00867973
VA	0.0354473125	4.08	0.0265	0.00867973
VO	-.0303704375	-3.50	0.0395	0.00867973
S	0.0220705625	2.54	0.0845	0.00867973
DA*DO	-.0033378125	-0.38	0.7262	0.00867973
DA*VO	0.0047774375	0.55	0.6204	0.00867973
DA*S	0.0069014375	0.80	0.4846	0.00867973
DO*VA	0.0028675625	0.33	0.7628	0.00867973
DO*S	0.0022800625	0.26	0.8098	0.00867973
VA*S	0.0105523125	1.22	0.3110	0.00867973
VO*S	0.0075245625	0.87	0.4498	0.00867973

Appendix A5.7a. Determination of reaction rate constants from test data.

L			M		N		O		P	
1	10 min		20 min		40 min		80 min		10 min	
2	dCo/dt		dCo/dt		dCo/dt		dCo/dt		krs	
3	mol/Ls		mol/Ls		mol/Ls		mol/Ls		cm/s	
4	6.27535007471018E-07		4.94455730366798E-07		3.61415834882472E-07		2.42706479280298E-07		0.000874246557982216	
5	2.72304758070889E-07		3.00514054778882E-07		3.02200660458523E-07		2.65825410480079E-07		0.000398715930033573	
6	3.07376312553943E-07		3.17438477822177E-07		3.17893693466195E-07		2.76727803593982E-07		0.00044776833118499	
7	7.03599708848618E-07		0.000005826635788713		5.02425517288583E-07		3.6916020023849E-07		0.00107730975149681	
8	2.61386238349557E-07		2.5212983207805E-07		2.336524043866578E-07		1.94967173576915E-07		0.000497018873808577	
9	4.4994669078389E-07		3.50138418358375E-07		2.96147134638568E-07		2.0004401281445E-07		0.000890483451347448	
10	3.71502595459434E-07		3.7498675742634E-07		2.80047557949407E-07		2.29990534163144E-07		0.000710405006321513	
11	3.31757612458849E-07		3.59603462855915E-07		2.95338422147726E-07		2.27346445493847E-07		0.000630401893350491	
12	1.05797204051987E-06		9.09385781975387E-07		6.23202425859411E-07		2.3884277432962E-07		0.00129892748661859	
13	8.47146899916733E-07		7.50350142438863E-07		5.73780942356899E-07		2.99482911775142E-07		0.000997048394063856	
14	6.77980317631679E-07		4.4005725433588E-07		3.96229188937194E-07		3.31784885992608E-07		0.000753409518781202	
15	1.00320348327675E-06		9.03082647116752E-07		6.98484224329051E-07		4.01417208606284E-07		0.0011659767604827	
16	6.52430928074283E-07		4.64558120439173E-07		3.57936720255617E-07		2.16945238154217E-07		0.000985652849582406	
17	5.12404221085077E-07		5.0781871723846E-07		4.19855025293294E-07		2.4082025090177E-07		0.000748915998812408	
18	9.42192046257798E-07		6.98891687477142E-07		5.30172981720663E-07		3.15896090586409E-07		0.00145245537987361	
19	6.0861569597955E-07		5.68488192539681E-07		5.02656290293739E-07		3.15245318139348E-07		0.000881746728329768	
20										
21										
22										
										kr=dCo/dt*Vo/S/[Ca]

	Q		R		S	
	1 20 min	40 min	80 min			
2	krs	krs	krs			
3	cm/s	cm/s	cm/s			
4	0.000821811739761375	0.000868910407467865	0.000523418494859516			
5	0.000464393800003306	0.000526547025840223	0.000622157951330841			
6	0.000481677681476317	0.000528023828814574	0.000552969410106466			
7	0.000952652936359169	0.000957405698389552	0.000957898433310357			
8	0.000505100370741243	0.000522502484153409	0.000554072505273706			
9	0.000735082590895532	0.00071698956319018	0.000581426847439871			
10	0.000765162274681904	0.000615165135346809	0.000614159327781214			
11	0.000729635439501082	0.00065754227529342	0.000602647768628299			
12	0.00136533917769443	0.00145028456780717	0.00152851213719833			
13	0.00102305928060055	0.00107801892282847	0.00113156504478689			
14	0.000502584100983996	0.000505601388436241	0.000549625425731743			
15	0.00120126519681029	0.00122165247649579	0.00118566136654376			
16	0.000755317402337815	0.000895753781695847	0.000501696497155463			
17	0.000847177408214591	0.000833006344165275	0.00105029859373894			
18	0.001195081988953	0.00115750137645359	0.00110242509349495			
19	0.000912701644359709	0.0010437658905673	0.00103755204459399			
20		avg	0.00083658226297609			
21						
22						

T	
1	10 min
2	k/s
3	cm/s
4	=L4*\$C4/\$F4/(((\$G4*\$B4/1000-H4*\$C4/1000)/1000/238/\$B4*1000)
5	=L5*\$C5/\$F5/(((\$G5*\$B5/1000-H5*\$C5/1000)/1000/238/\$B5*1000)
6	=L6*\$C6/\$F6/(((\$G6*\$B6/1000-H6*\$C6/1000)/1000/238/\$B6*1000)
7	=L7*\$C7/\$F7/(((\$G7*\$B7/1000-H7*\$C7/1000)/1000/238/\$B7*1000)
8	=L8*\$C8/\$F8/(((\$G8*\$B8/1000-H8*\$C8/1000)/1000/238/\$B8*1000)
9	=L9*\$C9/\$F9/(((\$G9*\$B9/1000-H9*\$C9/1000)/1000/238/\$B9*1000)
10	=L10*\$C10/\$F10/(((\$G10*\$B10/1000-H10*\$C10/1000)/1000/238/\$B10*1000)
11	=L11*\$C11/\$F11/(((\$G11*\$B11/1000-H11*\$C11/1000)/1000/238/\$B11*1000)
12	=L12*\$C12/\$F12/(((\$G12*\$B12/1000-H12*\$C12/1000)/1000/238/\$B12*1000)
13	=L13*\$C13/\$F13/(((\$G13*\$B13/1000-H13*\$C13/1000)/1000/238/\$B13*1000)
14	=L14*\$C14/\$F14/(((\$G14*\$B14/1000-H14*\$C14/1000)/1000/238/\$B14*1000)
15	=L15*\$C15/\$F15/(((\$G15*\$B15/1000-H15*\$C15/1000)/1000/238/\$B15*1000)
16	=L16*\$C16/\$F16/(((\$G16*\$B16/1000-H16*\$C16/1000)/1000/238/\$B16*1000)
17	=L17*\$C17/\$F17/(((\$G17*\$B17/1000-H17*\$C17/1000)/1000/238/\$B17*1000)
18	=L18*\$C18/\$F18/(((\$G18*\$B18/1000-H18*\$C18/1000)/1000/238/\$B18*1000)
19	=L19*\$C19/\$F19/(((\$G19*\$B19/1000-H19*\$C19/1000)/1000/238/\$B19*1000)
20	
21	
22	

		U	
1	20 min		
2	krs		
3	cm/s		
4	=M4*\$C4/\$F4/(((\$G4*\$B4/1000-I4*\$C4/1000)/1000/238/\$B4*1000)		
5	=M5*\$C5/\$F5/(((\$G5*\$B5/1000-I5*\$C5/1000)/1000/238/\$B5*1000)		
6	=M6*\$C6/\$F6/(((\$G6*\$B6/1000-I6*\$C6/1000)/1000/238/\$B6*1000)		
7	=M7*\$C7/\$F7/(((\$G7*\$B7/1000-I7*\$C7/1000)/1000/238/\$B7*1000)		
8	=M8*\$C8/\$F8/(((\$G8*\$B8/1000-I8*\$C8/1000)/1000/238/\$B8*1000)		
9	=M9*\$C9/\$F9/(((\$G9*\$B9/1000-I9*\$C9/1000)/1000/238/\$B9*1000)		
10	=M10*\$C10/\$F10/(((\$G10*\$B10/1000-I10*\$C10/1000)/1000/238/\$B10*1000)		
11	=M11*\$C11/\$F11/(((\$G11*\$B11/1000-I11*\$C11/1000)/1000/238/\$B11*1000)		
12	=M12*\$C12/\$F12/(((\$G12*\$B12/1000-I12*\$C12/1000)/1000/238/\$B12*1000)		
13	=M13*\$C13/\$F13/(((\$G13*\$B13/1000-I13*\$C13/1000)/1000/238/\$B13*1000)		
14	=M14*\$C14/\$F14/(((\$G14*\$B14/1000-I14*\$C14/1000)/1000/238/\$B14*1000)		
15	=M15*\$C15/\$F15/(((\$G15*\$B15/1000-I15*\$C15/1000)/1000/238/\$B15*1000)		
16	=M16*\$C16/\$F16/(((\$G16*\$B16/1000-I16*\$C16/1000)/1000/238/\$B16*1000)		
17	=M17*\$C17/\$F17/(((\$G17*\$B17/1000-I17*\$C17/1000)/1000/238/\$B17*1000)		
18	=M18*\$C18/\$F18/(((\$G18*\$B18/1000-I18*\$C18/1000)/1000/238/\$B18*1000)		
19	=M19*\$C19/\$F19/(((\$G19*\$B19/1000-I19*\$C19/1000)/1000/238/\$B19*1000)		
20			
21			
22			

		V
1	40 min	
2	krs	
3	cm/s	
4		=N4*\$C4/\$F4/(((\$G4*\$B4/1000-J4*\$C4/1000)/1000/238/\$B4*1000)
5		=N5*\$C5/\$F5/(((\$G5*\$B5/1000-J5*\$C5/1000)/1000/238/\$B5*1000)
6		=N6*\$C6/\$F6/(((\$G6*\$B6/1000-J6*\$C6/1000)/1000/238/\$B6*1000)
7		=N7*\$C7/\$F7/(((\$G7*\$B7/1000-J7*\$C7/1000)/1000/238/\$B7*1000)
8		=N8*\$C8/\$F8/(((\$G8*\$B8/1000-J8*\$C8/1000)/1000/238/\$B8*1000)
9		=N9*\$C9/\$F9/(((\$G9*\$B9/1000-J9*\$C9/1000)/1000/238/\$B9*1000)
10		=N10*\$C10/\$F10/(((\$G10*\$B10/1000-J10*\$C10/1000)/1000/238/\$B10*1000)
11		=N11*\$C11/\$F11/(((\$G11*\$B11/1000-J11*\$C11/1000)/1000/238/\$B11*1000)
12		=N12*\$C12/\$F12/(((\$G12*\$B12/1000-J12*\$C12/1000)/1000/238/\$B12*1000)
13		=N13*\$C13/\$F13/(((\$G13*\$B13/1000-J13*\$C13/1000)/1000/238/\$B13*1000)
14		=N14*\$C14/\$F14/(((\$G14*\$B14/1000-J14*\$C14/1000)/1000/238/\$B14*1000)
15		=N15*\$C15/\$F15/(((\$G15*\$B15/1000-J15*\$C15/1000)/1000/238/\$B15*1000)
16		=N16*\$C16/\$F16/(((\$G16*\$B16/1000-J16*\$C16/1000)/1000/238/\$B16*1000)
17		=N17*\$C17/\$F17/(((\$G17*\$B17/1000-J17*\$C17/1000)/1000/238/\$B17*1000)
18		=N18*\$C18/\$F18/(((\$G18*\$B18/1000-J18*\$C18/1000)/1000/238/\$B18*1000)
19		=N19*\$C19/\$F19/(((\$G19*\$B19/1000-J19*\$C19/1000)/1000/238/\$B19*1000)
20	avg	
21		
22		

		W
1	80 min	
2	krs	
3	cm/s	
4	=O4*\$C4/\$F4/(((\$G4*\$B4/1000-K4*\$C4/1000)/1000/238/\$B4*1000)	
5	=O5*\$C5/\$F5/(((\$G5*\$B5/1000-K5*\$C5/1000)/1000/238/\$B5*1000)	
6	=O6*\$C6/\$F6/(((\$G6*\$B6/1000-K6*\$C6/1000)/1000/238/\$B6*1000)	
7	=O7*\$C7/\$F7/(((\$G7*\$B7/1000-K7*\$C7/1000)/1000/238/\$B7*1000)	
8	=O8*\$C8/\$F8/(((\$G8*\$B8/1000-K8*\$C8/1000)/1000/238/\$B8*1000)	
9	=O9*\$C9/\$F9/(((\$G9*\$B9/1000-K9*\$C9/1000)/1000/238/\$B9*1000)	
10	=O10*\$C10/\$F10/(((\$G10*\$B10/1000-K10*\$C10/1000)/1000/238/\$B10*1000)	
11	=O11*\$C11/\$F11/(((\$G11*\$B11/1000-K11*\$C11/1000)/1000/238/\$B11*1000)	
12	=O12*\$C12/\$F12/(((\$G12*\$B12/1000-K12*\$C12/1000)/1000/238/\$B12*1000)	
13	=O13*\$C13/\$F13/(((\$G13*\$B13/1000-K13*\$C13/1000)/1000/238/\$B13*1000)	
14	=O14*\$C14/\$F14/(((\$G14*\$B14/1000-K14*\$C14/1000)/1000/238/\$B14*1000)	
15	=O15*\$C15/\$F15/(((\$G15*\$B15/1000-K15*\$C15/1000)/1000/238/\$B15*1000)	
16	=O16*\$C16/\$F16/(((\$G16*\$B16/1000-K16*\$C16/1000)/1000/238/\$B16*1000)	
17	=O17*\$C17/\$F17/(((\$G17*\$B17/1000-K17*\$C17/1000)/1000/238/\$B17*1000)	
18	=O18*\$C18/\$F18/(((\$G18*\$B18/1000-K18*\$C18/1000)/1000/238/\$B18*1000)	
19	=O19*\$C19/\$F19/(((\$G19*\$B19/1000-K19*\$C19/1000)/1000/238/\$B19*1000)	
20	=AVERAGE(T4:W19)	
21		
22		

Appendix A5.7b. Determination of reaction rate constants by regression of rate data

A		B		C		D		E		F		G		H		I	
Uranium results								ORGANIC		SAMPLES							
Test No.		ml	Org. Vol	ml	Aq. Vol	cm2	Interface	Time	minutes	conc.	mg/L	[Ca]S/Vo	dCo/dt				
1		1	350	350	350	59.242		10		94.3		0.000644123	6.27535E-07				Regression dCo/dt
2		2	350	350	350	59.242		10		38.7		0.000682954	2.72305E-07				5.38035E-07
3		3	350	350	350	59.242		10		44.7		0.000686463	3.07378E-07				5.7047E-07
4		4	350	350	350	59.242		10		105		0.000653108	7.036E-07				5.73401E-07
5		5	450	450	450	59.242		10		38.3		0.000525908	2.61386E-07				5.45539E-07
6		6	450	450	450	59.242		10		67.3		0.000505284	4.49847E-07				4.3929E-07
7		7	450	450	450	59.242		10		54.6		0.000522845	3.71503E-07				4.22062E-07
8		8	450	450	450	59.242		10		48.6		0.000526264	3.31758E-07				4.36814E-07
9		9	350	350	350	81.352		10		166		0.000814497	1.05797E-06				4.39587E-07
10		10	350	350	350	81.352		10		130		0.000849655	8.47147E-07				6.80347E-07
11		11	350	350	350	81.352		10		101		0.000898986	6.7799E-07				7.09714E-07
12		12	350	350	350	81.352		10		153		0.000860398	1.0032E-06				7.51681E-07
13		13	450	450	450	81.352		10		100		0.000681928	6.52431E-07				7.18688E-07
14		14	450	450	450	81.352		10		77.2		0.000684195	5.12404E-07				5.52906E-07
15		15	450	450	450	81.352		10		146		0.000648689	9.42192E-07				5.71506E-07
16		16	450	450	450	81.352		10		91.3		0.000690239	6.08616E-07				5.41848E-07
17		17	350	350	350	59.242		20		154		0.000601665	4.94456E-07				5.76554E-07
18		18	350	350	350	59.242		20		90.1		0.00064711	3.00514E-07				5.0257E-07
19		19	350	350	350	59.242		20		94.3		0.000659027	3.17438E-07				5.4053E-07
20		20	350	350	350	59.242		20		180		0.000611622	5.82664E-07				5.50483E-07
21		21	350	350	350	59.242		20		75.9		0.000499167	2.5213E-07				5.10866E-07
22		22	350	350	350	59.242		20		108		0.000476338	3.50138E-07				4.16953E-07
23		23	350	350	350	59.242		20		114		0.000490088	3.74997E-07				3.97884E-07
24		24	350	350	350	59.242		20		109		0.000492854	3.59603E-07				4.09369E-07
25		25	350	350	350	59.242		20		318		0.000666051	9.09386E-07				4.11679E-07
26		26	350	350	350	59.242		20		249		0.000733438	7.5035E-07				5.56351E-07
27		27	350	350	350	59.242		20		133		0.000875589	4.40057E-07				6.12638E-07
28		28	350	350	350	59.242		20		296		0.000751776	9.03083E-07				7.31377E-07
29		29	350	350	350	59.242		20		148		0.00061505	4.64558E-07				6.27957E-07
30		30	350	350	350	59.242		20		164		0.000598424	5.07819E-07				5.1375E-07
31		31	350	350	350	59.242		20									5.00698E-07
32		32	350	350	350	59.242		20									
33		33	350	350	350	59.242		20									

	A	B	C	D	E	F	G	H	I
34	15	450	450	81.352	20	229	0.000585843	6.99892E-07	4.89186E-07
35	16	450	450	81.352	20	180	0.000622863	5.68488E-07	5.20276E-07
36	1	350	350	59.242	40	238	0.000541928	3.61416E-07	4.52689E-07
37	2	350	350	59.242	40	193	0.000573929	3.02201E-07	4.79401E-07
38	3	350	350	59.242	40	198	0.000601665	3.17694E-07	5.0257E-07
39	4	350	350	59.242	40	337	0.000524778	5.02426E-07	4.38346E-07
40	5	450	450	59.242	40	149	0.00044718	2.33652E-07	3.73528E-07
41	6	450	450	59.242	40	197	0.000413042	2.96147E-07	3.45013E-07
42	7	450	450	59.242	40	177	0.00045524	2.80048E-07	3.8028E-07
43	8	450	450	59.242	40	188	0.000449155	2.85338E-07	3.75178E-07
44	9	350	350	81.352	40	560	0.00042871	6.23202E-07	3.58938E-07
45	10	350	350	81.352	40	455	0.000532255	5.73781E-07	4.44591E-07
46	11	350	450	81.352	40	254	0.000783679	3.96229E-07	6.54605E-07
47	12	350	450	81.352	40	533	0.000571754	6.98484E-07	4.77584E-07
48	13	450	350	81.352	40	251	0.000514459	3.57937E-07	4.29728E-07
49	14	450	350	81.352	40	317	0.000450002	4.19855E-07	3.75888E-07
50	15	450	450	81.352	40	397	0.000458032	5.30173E-07	3.82593E-07
51	16	450	450	81.352	40	366	0.00048158	5.02656E-07	4.02262E-07
52	1	350	350	59.242	80	348	0.000463695	2.42706E-07	3.87323E-07
53	2	350	350	59.242	80	399	0.000427424	2.6925E-07	3.57026E-07
54	3	350	450	59.242	80	381	0.00050044	2.76728E-07	4.18016E-07
55	4	350	450	59.242	80	589	0.000385385	3.9916E-07	3.21911E-07
56	5	450	350	59.242	80	283	0.00035188	1.94967E-07	2.93925E-07
57	6	450	350	59.242	80	294	0.000344057	2.0004E-07	2.8739E-07
58	7	450	450	59.242	80	323	0.00037448	2.29891E-07	3.12802E-07
59	8	450	450	59.242	80	318	0.000377248	2.27348E-07	3.15113E-07
60	9	350	350	81.352	80	840	0.000156258	2.38843E-07	1.30522E-07
61	10	350	350	81.352	80	729	0.000284663	2.99483E-07	2.21072E-07
62	11	350	450	81.352	80	491	0.000603856	3.31785E-07	5.04233E-07
63	12	350	450	81.352	80	840	0.00033856	4.01417E-07	2.82798E-07
64	13	450	350	81.352	80	335	0.000432423	2.16945E-07	3.61202E-07
65	14	450	350	81.352	80	543	0.000229287	2.4082E-07	1.91523E-07
66	15	450	450	81.352	80	623	0.000286365	3.15696E-07	2.392E-07

	A	B	C	D	E	F	G	H	I
67	16	450	450	81.352	80	600	0.000303836	3.15245E-07	2.53783E-07
68									

	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	Regression Statistics								
4	Multiple R	0.652964785							
5	R Square	0.42636301							
6	Adjusted R Square	0.410489994							
7	Standard Error	1.64401E-07							
8	Observations	64							
9									
10	ANOVA								
11		df	SS	MS	F	Significance F			
12	Regression	1	1.26558E-12	1.26558E-12	46.82555361	4.01816E-09			
13	Residual	63	1.70274E-12	2.70276E-14					
14	Total	64	2.96832E-12						
15									
16		Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%		
17	Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A		
18	X Variable 1	0.000835297	3.62242E-05	23.05906866	2.05324E-32	0.000762909	0.000907686	Lower 95.0%	Upper 95.0%
19									
20									
21									
22	RESIDUAL OUTPUT								
23									
24	Observation	Predicted Y	Residuals						
25	1	5.38035E-07	8.95005E-08						
26	2	5.7047E-07	-2.98165E-07						
27	3	5.73401E-07	-2.66024E-07						
28	4	5.45539E-07	1.5806E-07						
29	5	4.3929E-07	-1.77903E-07						
30	6	4.22062E-07	2.78847E-08						
31	7	4.36814E-07	-6.53118E-08						
32	8	4.39587E-07	-1.07829E-07						
33	9	6.80347E-07	3.77625E-07						
34	10	7.09714E-07	1.37433E-07						
35	11	7.51681E-07	-7.36905E-08						

	A	B	C	D	E	F	G	H	I
36	12	7.18688E-07	2.84516E-07						
37	13	5.52906E-07	9.95245E-08						
38	14	5.71508E-07	-5.91016E-08						
39	15	5.41848E-07	4.00344E-07						
40	16	5.76554E-07	3.20612E-08						
41	17	5.0257E-07	-8.11378E-09						
42	18	5.4053E-07	-2.40015E-07						
43	19	5.50483E-07	-2.33045E-07						
44	20	5.10886E-07	7.17773E-08						
45	21	4.16953E-07	-1.64824E-07						
46	22	3.97884E-07	-4.77456E-08						
47	23	4.09369E-07	-3.43723E-08						
48	24	4.11679E-07	-5.20758E-08						
49	25	5.56351E-07	3.53035E-07						
50	26	6.12638E-07	1.37712E-07						
51	27	7.31377E-07	-2.9132E-07						
52	28	6.27957E-07	2.75126E-07						
53	29	5.1375E-07	-4.91916E-08						
54	30	5.00698E-07	7.12125E-09						
55	31	4.89186E-07	2.10705E-07						
56	32	5.20276E-07	4.82123E-08						
57	33	4.52669E-07	-9.12532E-08						
58	34	4.79401E-07	-1.77201E-07						
59	35	5.0257E-07	-1.84876E-07						
60	36	4.38346E-07	6.40798E-08						
61	37	3.73528E-07	-1.39875E-07						
62	38	3.45013E-07	-4.88661E-08						
63	39	3.8026E-07	-1.00213E-07						
64	40	3.75178E-07	-7.98395E-08						
65	41	3.58936E-07	2.64266E-07						
66	42	4.44591E-07	1.2919E-07						
67	43	6.54605E-07	-2.58376E-07						
68	44	4.77584E-07	2.209E-07						
69	45	4.29726E-07	-7.17894E-08						
70	46	3.75886E-07	4.39693E-08						

	A	B	C	D	E	F	G	H	I
71		47 3.82593E-07	1.4758E-07						
72		48 4.02262E-07	1.00394E-07						
73		49 3.87323E-07	-1.44617E-07						
74		50 3.57026E-07	-9.11009E-08						
75		51 4.18016E-07	-1.41288E-07						
76		52 3.21911E-07	4.72491E-08						
77		53 2.93925E-07	-9.89574E-08						
78		54 2.8739E-07	-8.7346E-08						
79		55 3.12802E-07	-8.28118E-08						
80		56 3.15113E-07	-8.77661E-08						
81		57 1.30522E-07	1.08321E-07						
82		58 2.21072E-07	7.8411E-08						
83		59 5.04233E-07	-1.72448E-07						
84		60 2.82798E-07	1.18819E-07						
85		61 3.61202E-07	-1.44257E-07						
86		62 1.91523E-07	4.92971E-08						
87		63 2.392E-07	7.84961E-08						
88		64 2.53793E-07	6.14522E-08						

VITA

Joseph Franklin Birdwell is a native East Tennessean, having been born in Kingsport in 1957 and living in the Knoxville area since 1972 except for a ten-month residence in western North Carolina. He is a 1975 graduate of Farragut High School in Knox County, Tennessee, and received bachelors and masters degrees in chemical engineering from the University of Tennessee in 1979 and 1986 respectively.

After receiving his baccalaureate, the author was employed briefly by E. I. DuPont de Nemours at Brevard, North Carolina. Upon deciding to enter graduate school he returned to the Knoxville area, accepting employment at the Oak Ridge National Laboratory as a process design engineer. At present, he continues to be employed by Lockheed Martin Energy Systems at the Oak Ridge National Laboratory as a development staff member in the Robotics and Process Systems Division.