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**Interphase Transfer Kinetics of Uranium
Using the Drop Method, Lewis Cell, and
Kenics Mixer**

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OAK RIDGE NATIONAL LABORATORY
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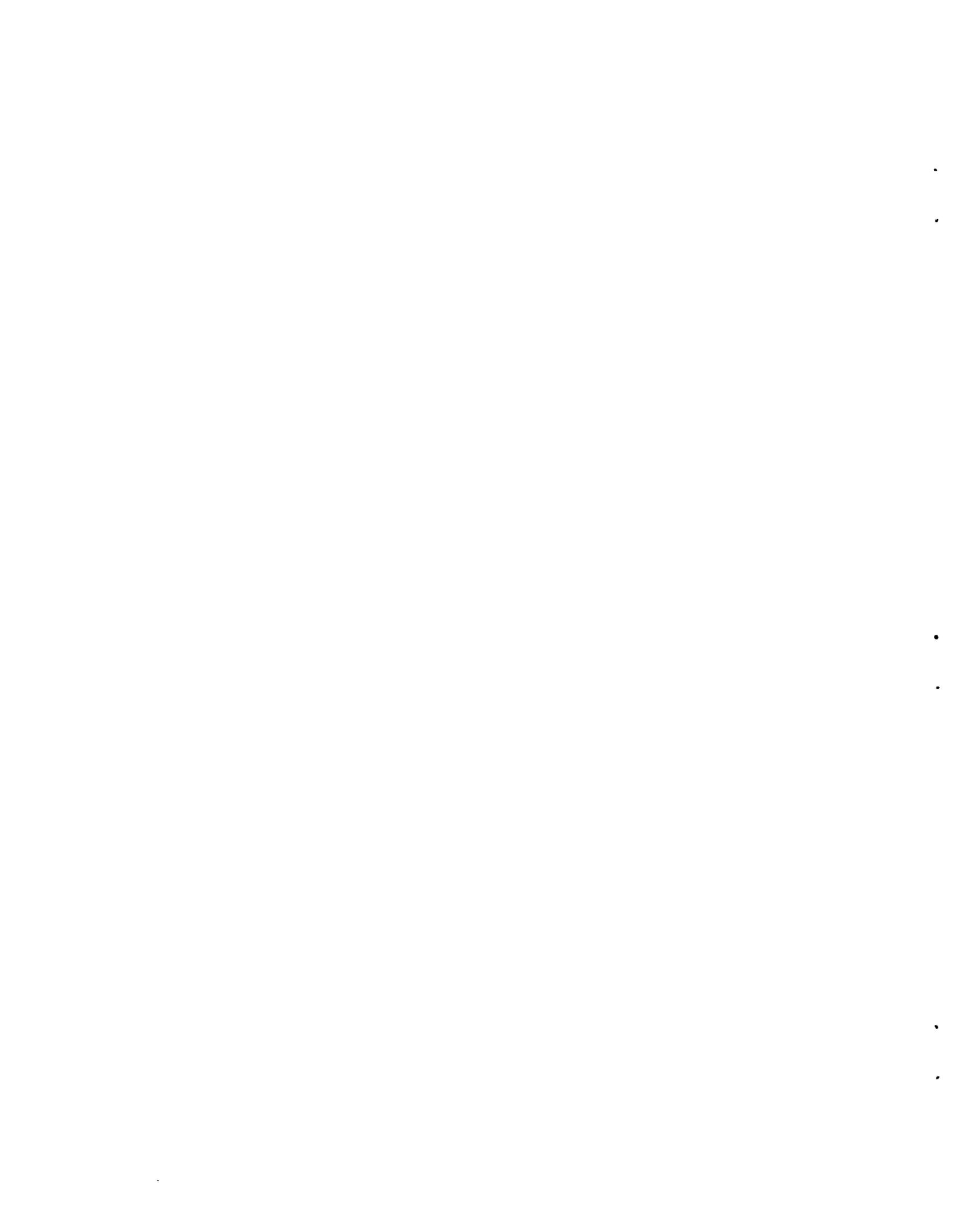
INTERPHASE TRANSFER KINETICS OF URANIUM USING THE
DROP METHOD, LEWIS CELL, AND KENICS MIXER

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ABSTRACT

The rate constants for the interphase transfer of uranium between 3.5 M HNO₃ and tributyl phosphate (TBP)--normal hydrocarbon diluent solutions have been measured using the single drop method, Lewis cell method, and a Kenics mixer--centrifugal separator. Rate constants obtained by all methods were the same within experimental error. The variables studied that affect the rate constants include the TBP concentration, the acidity and total neutral nitrate concentrations of the aqueous phase, and temperature. Results of these tests indicate that the rate controlling mechanism is chemical reaction at the interface.

INTRODUCTION

Rate constants for the interphase transfer of uranium between nitric acid and tributyl phosphate (TBP)--normal hydrocarbon solutions have been reported by Burger (1959), Keisch (1959), Knoch and Lindner (1960), Baumgartner and Finsterwalder (1970), Farbu et al. (1974), and Moszkowicz and Kikindai (1975). The latter three authors, using the drop method, and Burger (1959), using the Lewis cell, obtained pseudo-first-order rate constants for the transfer of uranium from nitric acid to 0.73 M TBP ranging from about 6×10^{-3} to 20×10^{-3} cm/sec. Knoch and Lindner (1960), using uranium exchange in a stirred cell, obtained much smaller values in the range of 10^{-5} to 10^{-7} cm/sec. The existing literature data give variable rate constants but do not give values for the rate constants as a function of TBP concentration and temperature for the aqueous to organic (A to O) and the organic to aqueous (O to A) transfer directions. We have tested these transfers between 3.5 M HNO₃ and 0.5 to 30 vol % TBP in a normal hydrocarbon diluent (NHD) and have determined the activation energies of the A to O and O to A reactions. All known contacting devices with a defined interfacial area have been examined (i.e., the rising and falling drop apparatus, Lewis cells, and the Kenics mixer--centrifugal separator).

The data obtained in earlier reported studies, which used either drop or Lewis cell methods for the A to O transfer of uranium from nitric acid to TBP-NHD, are summarized in Table 1. General conclusions are that: (1) the transfer rate is controlled by the rate of reaction at the interface; (2) the reaction is approximately first-order with respect to uranium; (3) the reaction is of variable order with respect to TBP; (4) the effect of nitric acid is slight; and (5) the effect of temperature is small.

EXPERIMENTAL PROCEDURE

Reagents

A purified, crystalline uranyl nitrate hexahydrate was used for all uranium solutions. The organic phase was obtained by diluting TBP (Ashland Chemical Company) with a mixed long-chain normal hydrocarbon, which was primarily dodecane, tridecane, and tetradecane (supplied by Eastman Kodak Company). In all cases, the TBP solutions were washed several times with a 10% Na_2CO_3 solution followed by a water wash to remove any acidic degradation products such as mono- and dibutyl phosphoric acids.

Apparatus: Drop Method

Equipment used for the rising and falling drop experiments is shown in Figure 1; all materials that contact the phases are glass, Teflon, or stainless steel. The columns are standard lengths of Pyrex pipe connected by flanges with Teflon gaskets. A syringe pump feeds either an aqueous (falling drop) or organic (rising drop) phase through Teflon tubing to a stainless steel needle that forms a stream of individual drops. During elevated temperature tests, the flowing stream was preheated in a jacketed coil and the column was heated with heating tape ($\pm 3^\circ\text{C}$ control). In the falling drop apparatus, the aqueous phase is collected at the bottom of the column and exits through a needle valve; the outflow rate is regulated so that it is identical to the dropping rate. In the rising drop apparatus a simple overflow system allows the organic phase to exit from the column.

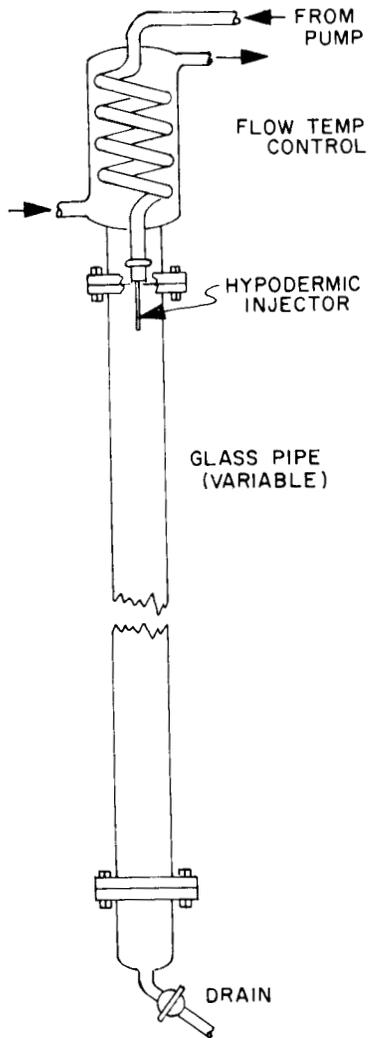
Table 1. Comparison of literature values of the pseudo-first-order rate constants for uranium transfer from nitric acid to TBP-NHD at about 25°C

k' (cm/sec)	HNO ₃ (M) ³	TBP	Method	Reference
5.8 x 10 ⁻³ , 9.7 x 10 ⁻³ ,	0	0.73	Stirred cell	Burger (1959)
9.9 x 10 ⁻³	0	1.1	Stirred cell	Burger (1959)
4.5 x 10 ⁻³	0	1.1	Stirred cell	Burger (1959)
2 x 10 ⁻⁷ to 200 x 10 ⁻⁷	0	0.36-1.1	Stirred cell (uranium exchange)	Keisch (1959)
6.88 x 10 ⁻³	0.1	0.73	Drop	Knoch and Lindner (1960)
5.81 x 10 ⁻³	0.5	0.73	Drop	Knoch and Lindner (1960)
5.97 x 10 ⁻³	2.0	0.73	Drop	Knoch and Lindner (1960)
11.5 x 10 ⁻³ to 20 x 10 ⁻³	3.0	0.73	Drop	Baumgartner and Finsterwalder (1970)
3.8 x 10 ⁻³	0.01 ^a	0.4	Drop	Farbu et al. (1974)
6.4 x 10 ⁻³	b	0.73	Drop	Moszkowicz and Kikindai (1975)

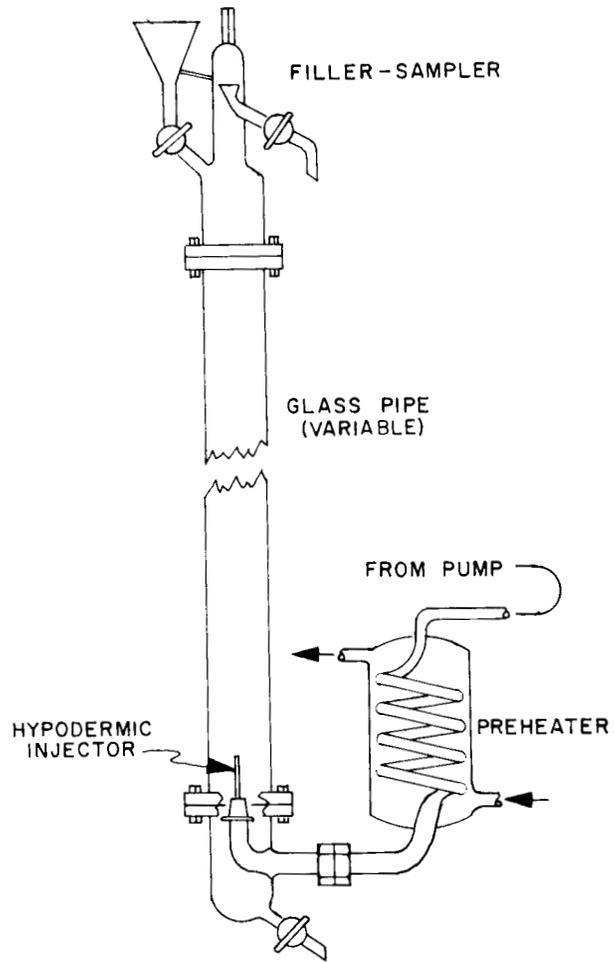
^aIncludes 0.99 M NaNO₃.

^bAcid concentration not given.

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FALLING DROP ARRANGEMENT



RISING DROP ARRANGEMENT

Fig. 1. Falling and rising drop equipment

Apparatus: Lewis Cell

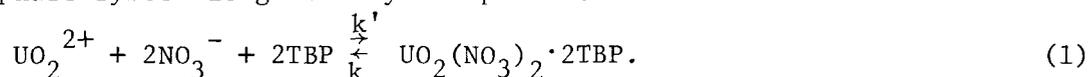
The Lewis cell is shown in Figure 2. The two phases are individually mixed by two paddles revolving at 100 rpm, at which speed the interface is not appreciably disturbed. A stainless steel insert is used to improve the mixing, to take aqueous samples (O to A transfer tests), and to add a concentrated aqueous stock solution to the lower phase at time zero (A to O transfer tests). A pipette or hypodermic needle is inserted through a hollow leg to perform the latter two functions.

Apparatus: Kenics Mixer--Centrifugal Separator

The experimental contactor, shown in Figure 3, consists of a Kenics motionless mixer (Kenics Corporation, Danvers, Mass.) and a high-speed centrifuge (Metalleaktraktion AB, Sweden). During operation, the aqueous and organic feeds are delivered from pressurized tanks through flexible lines A and B to the Kenics mixer, C. After mixing and phase contact, the streams pass into the centrifugal separator, D. The separator is driven by the motor, E, and can be controlled at speeds between 5000 and 25,000 rpm. The separated streams leave the separator, pass through rotameters, and are collected at the exits of lines F and G. In the tests of this unit, the centrifuge speed was 12,500 rpm, the organic-to-aqueous ratio was varied from about 1 to 9.5, and the total flow was varied from 250 to 630 ml/min.

Mathematical Equations

The overall chemical reaction representing extraction of uranium in a two-phase system is generally accepted as:



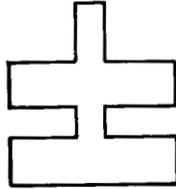
If simple first-order kinetics are assumed, differential equations describing the overall net mass transfer for the single drop technique (to or from the drops) are:

$$dc = \left(\frac{k'ac' - kac}{v} \right) dt, \text{ for organic drops,} \quad (2)$$

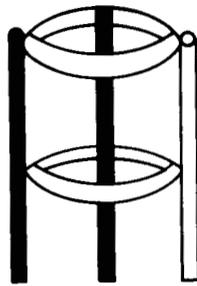
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STIRRER



BAFFLE



HOLLOW LEG FOR
SOLUTION ADDITION
AND SAMPLING

JACKETED
CELL

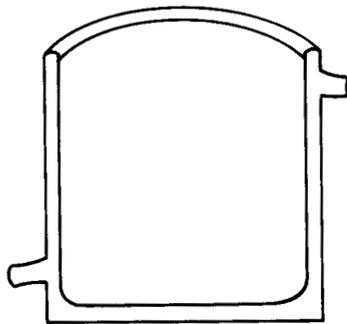


Fig. 2. Lewis cell.

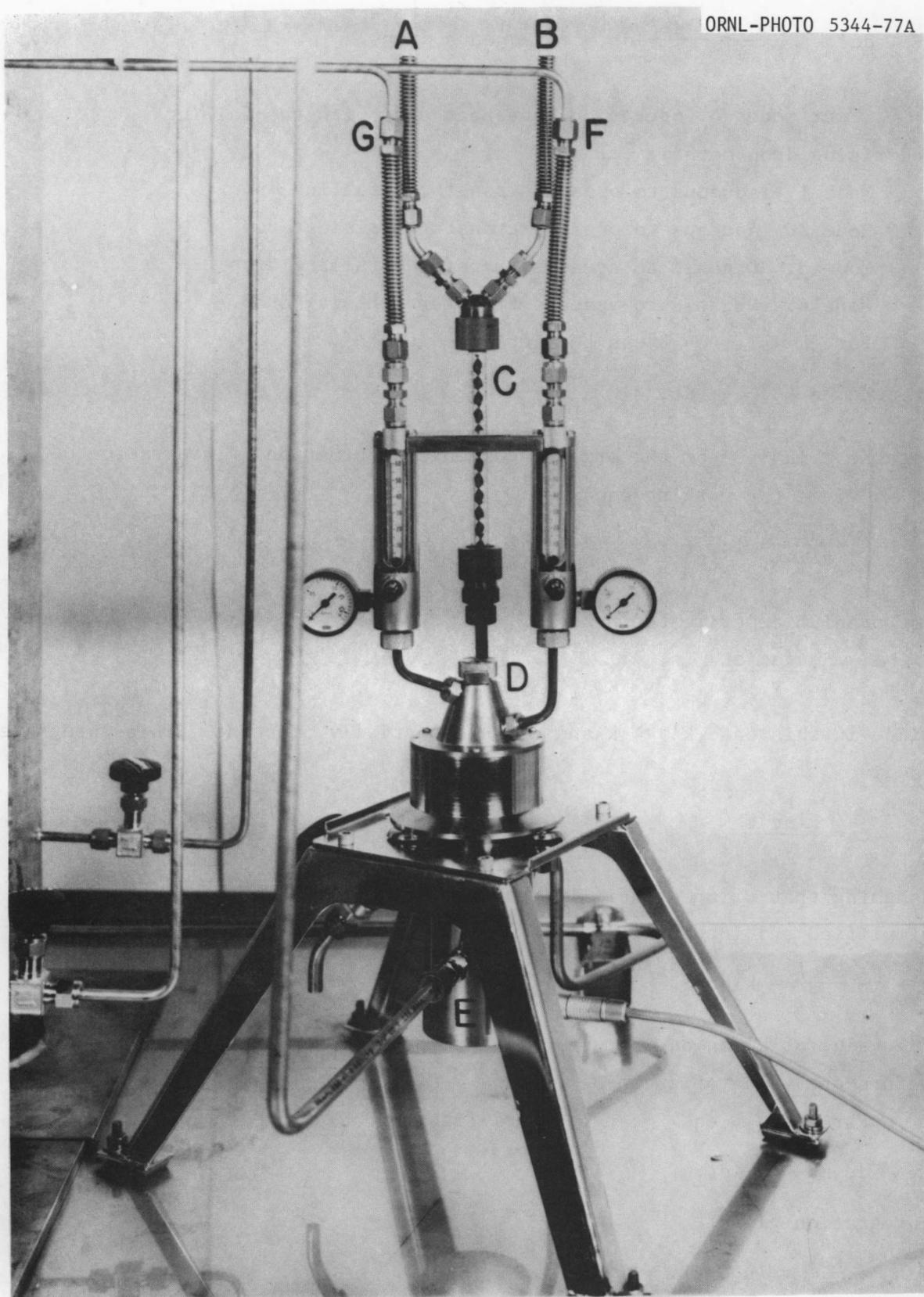


Fig. 3. Kenics mixer--centrifugal separator.

$$dc' = \left(\frac{kac - k'ac'}{v'} \right) dt, \text{ for aqueous drops.} \quad (3)$$

Four modes of operation have been used with the falling and rising drop method:

Mode 1. Aqueous to organic transfer - falling drop

Mode 2. Aqueous to organic transfer - rising drop

Mode 3. Organic to aqueous transfer - falling drop

Mode 4. Organic to aqueous transfer - rising drop.

For Mode 1, eq 3 can be simplified to:

$$dc' = - \frac{k'ac'}{v'} dt, \quad (4)$$

because c is ≈ 0 for the organic column concentration. Integration of eq 4 gives the working equation:

$$- \frac{k'at}{v'} = \ln \frac{c'}{c'_0}. \quad (5)$$

For uranium experiments in Mode 2, eq 2 can be simplified to:

$$dc = \frac{k'ac'dt}{v},$$

since in this case $k' \gg k$ and c' is essentially constant. This integrates to give

$$c = \frac{k'ac't}{v}. \quad (7)$$

Assuming that c is essentially constant for Mode 3, eq 3 cannot be simplified and integration gives

$$- \frac{k'c'}{c} = k \left(e^{-k'at/v'} - 1 \right). \quad (8)$$

The value of k' in eq 8 must be determined from an A to 0 transfer test before the value of k can be found.

For Mode 4, eq 2 can be simplified (because $c' \approx 0$) to

$$dc = - \frac{kac}{v} dt. \quad (9)$$

Integration gives

$$- \frac{kac}{v} = \ln c/c_0. \quad (10)$$

The Lewis cell data consist of samples of only the initially barren phase; concentrations in the other phase were determined by material balance. For the Lewis cell, eq 2 can be applied and developed to give a working equation by using the material balance equation

$$I = cv + c'v', \quad (11)$$

and assuming that

$$D = k'/k. \quad (12)$$

Substituting eqs 11 and 12 into eq 2 results in an equation that can be integrated between limits to give

$$k' = \ln \left[\frac{I/v' - (v/v' + 1/D)c_o}{I/v' - (v/v' + 1/D)c_t} \right] / \left(\frac{v}{v'} + \frac{1}{D} \right) \frac{a}{v} \Delta t, \quad (13)$$

from which k' can be calculated.

For the reverse extraction rate constant (O to A) a similar expression is obtained:

$$k = \ln \left[\frac{I/v - (v'/v + D)c'_o}{I/v - (v'/v + D)c'_t} \right] / \left(\frac{v'}{v} + D \right) \frac{a}{v'} \Delta t. \quad (14)$$

Procedures and Data Handling: Drop Method

The major complication of the drop method for determining interphase transfer rates is the need to correct for "end" effects. These end effects consist of the transfer that occurs while the drop is forming on the needle and during its time in the collecting pool before leaving the column. The two reported methods of correcting for end effects are (1) to use several lengths of column, thereby changing the travel time of the drop while maintaining the same end effect; or (2) to increase the flow rate of the drop phase over a range which allows extrapolation to infinite flow and zero end-effect time. Because Farbu et al. (1974) showed the latter technique to be erroneous due to turbulence created at higher flows, we have chosen to use four column lengths ranging from about 9 to 60 cm. This method requires great care to maintain constant end effects for the several tests with different lengths of column; the drop flow rate and the pool volumes must be as constant as possible. The phase contact time is assumed

to be the interval between the time the drops break free and when they coalesce; a stopwatch was used to make several measurements for each test. The drop volume was measured by counting the number of drops per unit volume of feed phase, and the surface was calculated by assuming that the drops were spherical.

After a test, data for each column length are plotted by rearranging the integrated rate equations so that the slope is the value of k or k' . This line is displaced by the end effects, but the slope is not affected. This statement can be justified because the collecting pool has a small volume, and the residence time for an element of volume in the pool is constant. The transfer that occurs in the pool for a first-order transfer only adds proportionately to the total transfer, because the constant interfacial areas and residence times in the pool were carefully maintained. Thus, for a first-order transfer, the rate constant can still be determined from the standard semilog plots. Typical results by the drop technique are shown in Figure 4 for an O to A extraction at 40°C using falling drops (Mode 3). The value for k , 1.21×10^{-4} cm/sec, is the slope of the line obtained as a least-squares fit to the points. Similar lines were obtained for the other extraction modes by plotting the appropriate functions from the solutions of the rate equations.

A major limitation of the drop method results from the limited, practical height of the column, which, in turn, limits the drop transit times to a few seconds. Only a small quantity of material can be transferred out of a drop and, for cases where the drop is the loaded phase, this leads to rate calculations based on a small difference of large numbers. This is the case for the A to O transfer from aqueous drops and for the O to A transfer from organic drops. We have found that if the rate constant is less than about 10^{-3} cm/sec for these two cases, the data are very uncertain.

Procedure and Data Handling: Lewis Cell

The major problem encountered with Lewis cells is the poor mixing of the individual phases relative to the mixing obtained in the drop phase of the single-drop method and in the Kenics mixer. This leads to a more-or-less rapid shift from chemical control to diffusion control if

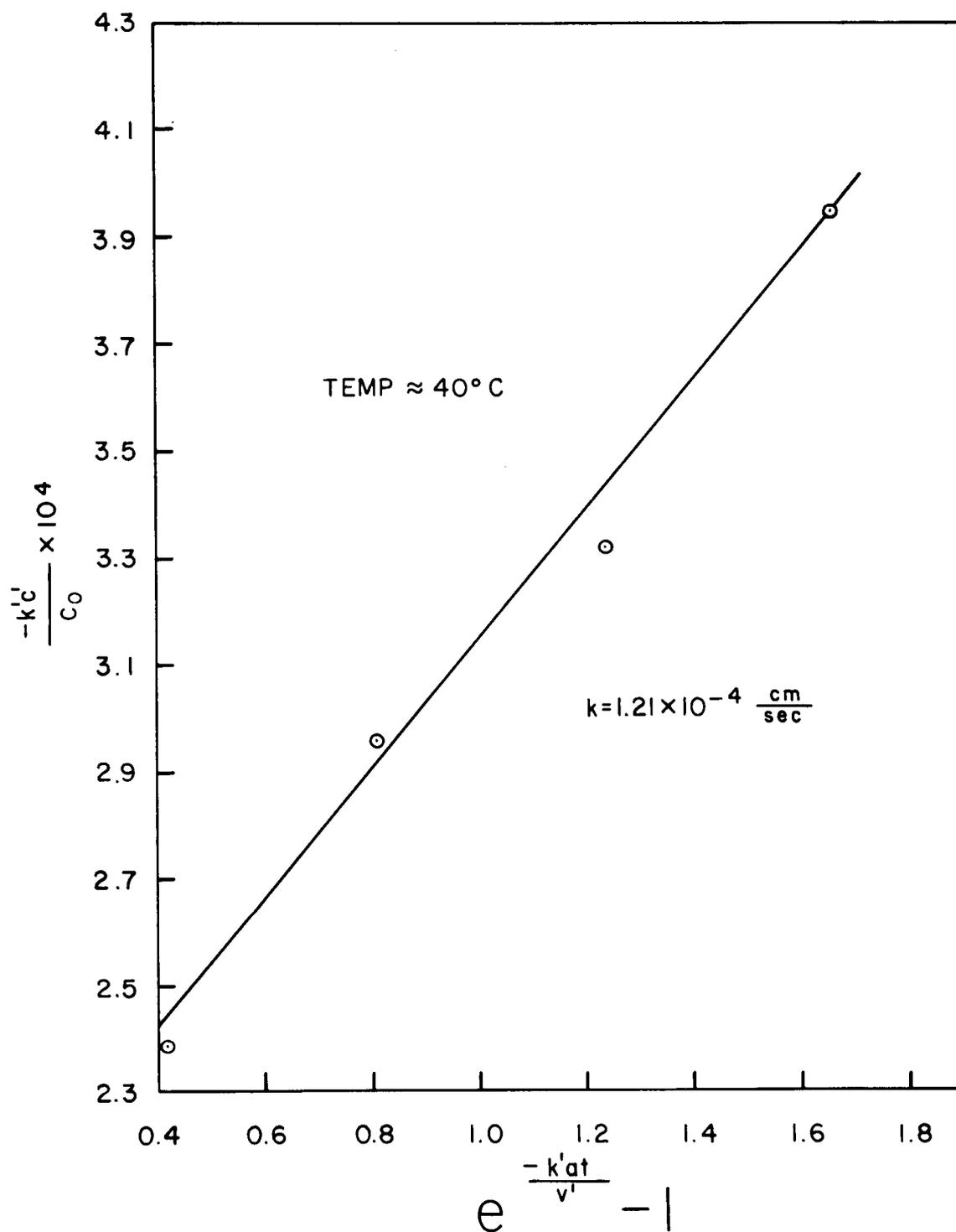


Fig. 4. Typical results of a rising drop experiment: organic to aqueous extraction of uranium from 30% TBP--NHD into 3.5 M HNO_3 .

the chemical rate constant is large, as is the case for uranium transfer. A variety of experimental techniques were examined with the Lewis cell to improve the reproducibility and accuracy of the data. It was determined that the best procedure was to introduce pre-equilibrated, barren phases into the cell; after the phases were allowed to settle, they were slowly stirred. A concentrated solution of the ion to be studied was introduced into the appropriate phase, and samples of the other phase were taken as a function of time. Rate constants were calculated using the equations presented earlier.

Although these rate constants generally decreased with time, initially when little or no uranium had transferred, the rate was not diffusion controlled, because no (or very little) diffusion gradient exists at initial contact. Hence, an extrapolation back to initial time (the time of injection of the concentrated ion solution) yields the rate constant for the chemical reaction. This procedure was verified by the agreement of the rate constants obtained in all the experimental methods (Lewis cell, drop, and Kenics mixer). The extrapolation method, illustrated in Figure 5 for duplicate 0 to A tests of uranium transfer, gives a straight-line plot as k vs time with an intercept k value of $(1.64 \pm 0.2) \times 10^{-4}$ (95% confidence limits) based on the duplicate runs. No uranium is present in the barren phases at this initial time, and the reverse transfer of uranium is negligible. The exact mathematical equations for the Lewis cell contain the quantity D , but the rate constant determined by extrapolation is independent of the value of D and does not require that $k'/k = D$.

Procedures and Data Handling: Kenics Mixer--Centrifugal Separator

In the Kenics mixer, the organic and aqueous streams are subdivided and mixed by an array of motionless mixer elements. Chen (1972) has developed a set of correlations which makes it possible to estimate the interfacial area created at known conditions of flow rate, interfacial tension, and phase density. In all tests using this system, the initial aqueous uranium concentration was 10 g/liter; under these conditions, the free TBP in the organic phase remains nearly constant at 1.1 M. Equation 2 can be integrated for this condition to yield:

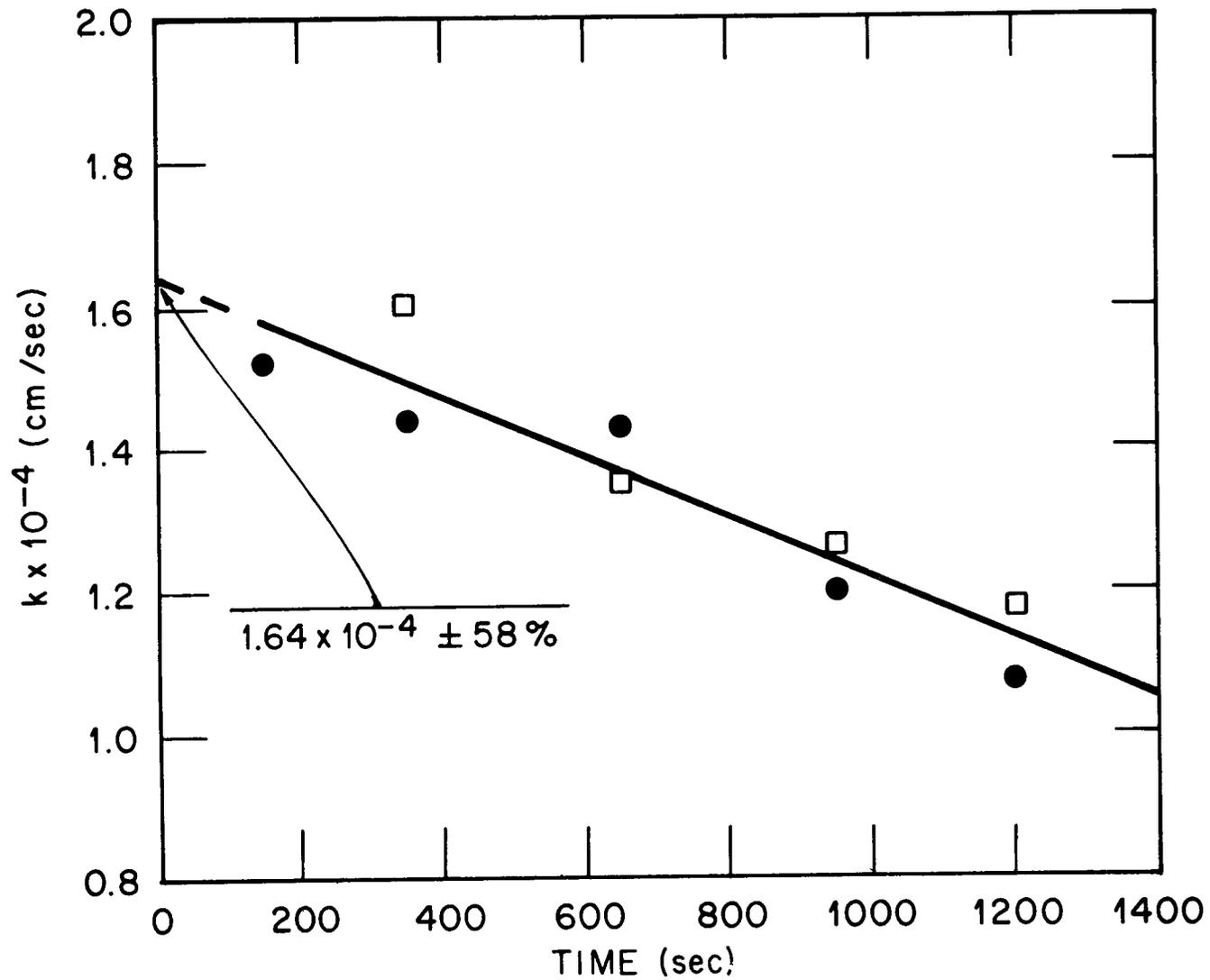


Fig. 5. Typical results of a Lewis-cell experiment: uranium extraction from 3.5 M HNO_3 into 30% TBP--NHD.

$$k' = \frac{\ln \left(-\frac{vc}{v'c'_o} - \frac{c}{Dc'_o} + 1 \right)}{\left(-\frac{a}{v'} - \frac{a}{Dv} \right)t} \quad (15)$$

Since (c/c') for uranium never exceeded 14% of the D, good approximate values of k' can be obtained from the simplified equation:

$$k' = -\frac{v'}{atD} \ln \left(1 - \frac{vc}{v'c'_o} \right) \quad (16)$$

Values from eq 16 were about 3% lower than those using eq 15.

RESULTS

The major fraction of the experimental data was obtained in drop and Lewis cell tests. The Kenics mixer--centrifugal separator was used in more limited tests to confirm the same values of the rate constant.

Effect of Uranium Concentration

It was necessary to demonstrate that the uranium extraction is first order over the experimental range of uranium concentrations and to determine whether the Marangoni effect, described by Sternling and Seriven (1959), exists in this system. Although the mechanics of this phenomenon are quite complicated, the effects result from interfacial tension differences causing turbulence, which effectively increases the interfacial area by an unknown amount; this increases the rate of transfer and leads to the calculation of erroneously high transfer rate constants. McDowell (1978) indicated this effect can lead to rate constant "increases" by factors of ≥ 2 . The data for the effect of uranium on the rate constant for the A to O transfer are given in Table 2. At concentration factors >100 , the rate constant remains the same. Hence, the extraction is first order with respect to uranium, and no Marangoni effect was observed. The mass transfer rates in the O to A direction are much smaller than those in the A to O direction, and no systematic examination of the Marangoni effect was made; a few determinations at different uranium concentrations indicated that the O to A transfer was also first order.

Table 2. Kinetic constants as a function of initial uranium concentration in extractions from 3.5 M HNO₃^a into 30% TBP--NHD

Initial uranium concentration (g/liter)	System	Kinetic constant, k (cm/sec)
2	Falling drop	6.9 x 10 ⁻³
5	Lewis cell	6.4 x 10 ⁻³
10 ^b	Rising and falling drop	8.5 x 10 ⁻³
10 ^c	Kenics mixer	7.1 x 10 ⁻³
50 ^d	Rising drop and Lewis cell	5.0 x 10 ⁻³
238 ^e	Lewis cell	5.3 x 10 ⁻³
	Average	7.3 x 10 ⁻³ ± 2.5 x 10 ⁻³

^aKenics mixer runs contacted acid-free 30% TBP--NDD with 3.5 M HNO₃ solutions; final aqueous solutions were approximately 2 M HNO₃.

^bAverage of nine determinations.

^cAverage of ten determinations.

^dAverage of two determinations.

^eAverage of three determinations.

Effect of TBP Concentration

Data for the drop and the Lewis-cell tests are plotted as a function of free TBP concentration in Figure 6. The free TBP was calculated for the drop tests as the initial concentration of TBP less that complexed with uranium by eq 1. For A to O extractions in the Lewis cell tests, the free TBP was assumed to be equal to the initial TBP, because extrapolation of the curve to the "zero" point should nearly eliminate any loading effects. The source of the variability of the results is not understood but may be due to small amounts of surface active agents (in addition to TBP). The ratio of the rate constants, k'/k , at different TBP concentrations is shown as curve A in Figure 7, and the equilibrium extraction coefficient is shown by curve B. These curves are identical within the experimental error, which is as expected if the rate determining step is the chemical reaction.

Effect of Nitric Acid and Nitrate

Neither nitric acid nor nitrate affected the A to O transfer of uranium in nitrate or nitric acid solutions up to 4 M. Figure 8 shows the effects on the O to A transfer of uranium. Nitrate added as NaNO_3 has approximately a power of -2 effect on the O to A rate constant; nitrate added as HNO_3 has the effect of approximately a power of -1. The lower effect of HNO_3 is probably the result of its ability to form complexes with TBP, which competes with the formation of uranyl complexes.

Effect of Temperature

Plots of $\ln k$ and $\ln k'$ vs $1/RT$ (30, 40, and 60°C) are shown with the least-squares lines in Figures 9 and 10 respectively. Slopes of these lines show activation energies of -3.2 kcal/mole for the A to O transfer and -6.9 kcal/mole for the O to A transfer. The difference of these values gives ΔH as -3.7 kcal/mole. The ΔH can be independently determined from equilibrium constants for the uranium reaction by

$$\ln D = \ln \frac{[C_{u,o}]}{[C_{u,A}][\text{TBP}]^2} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}. \quad (17)$$

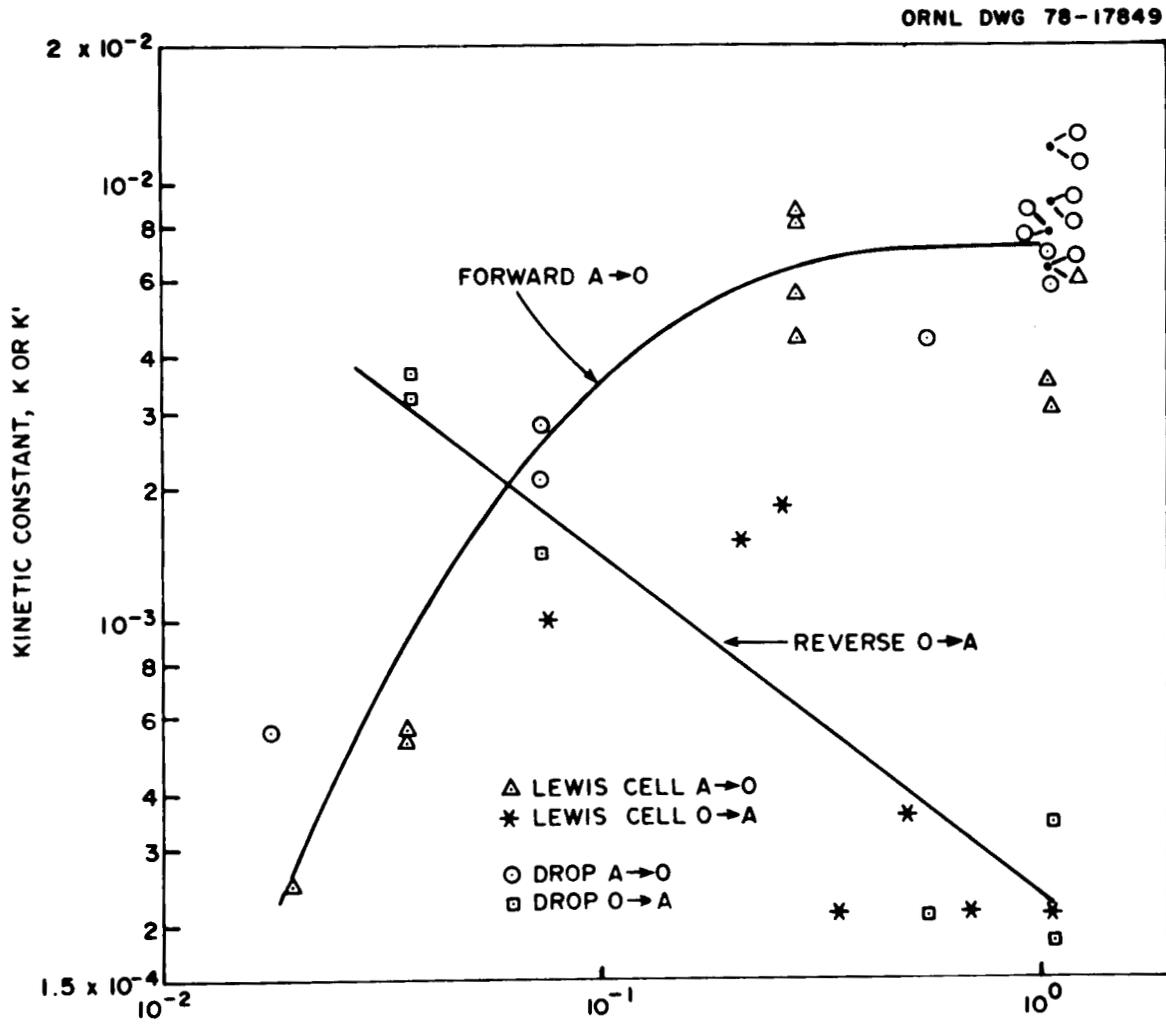


Fig. 6. Uranium forward and reverse extraction rate constants as a function of free TBP concentration.

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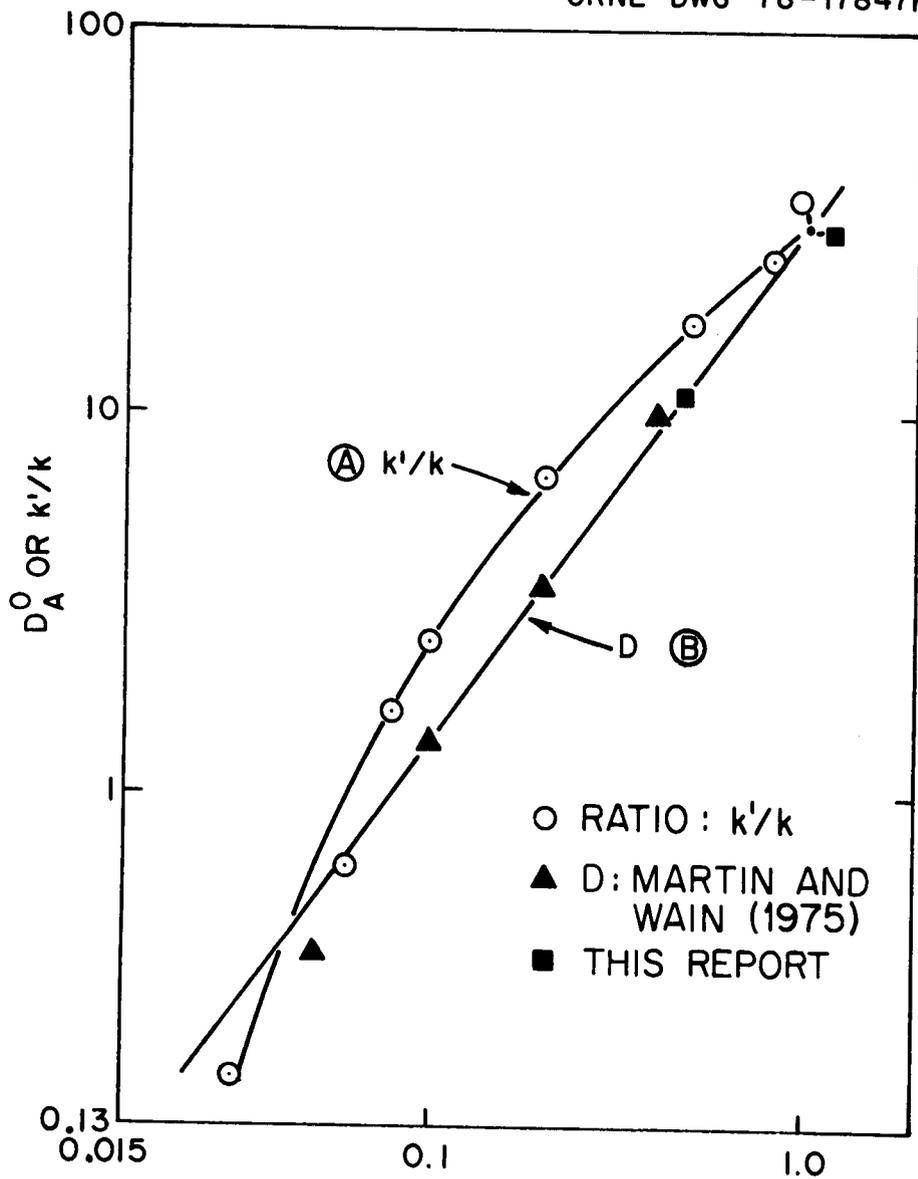


Fig. 7. (A) Kinetic constant ratios and (B) equilibrium distribution coefficients as a function of free TBP concentrations.

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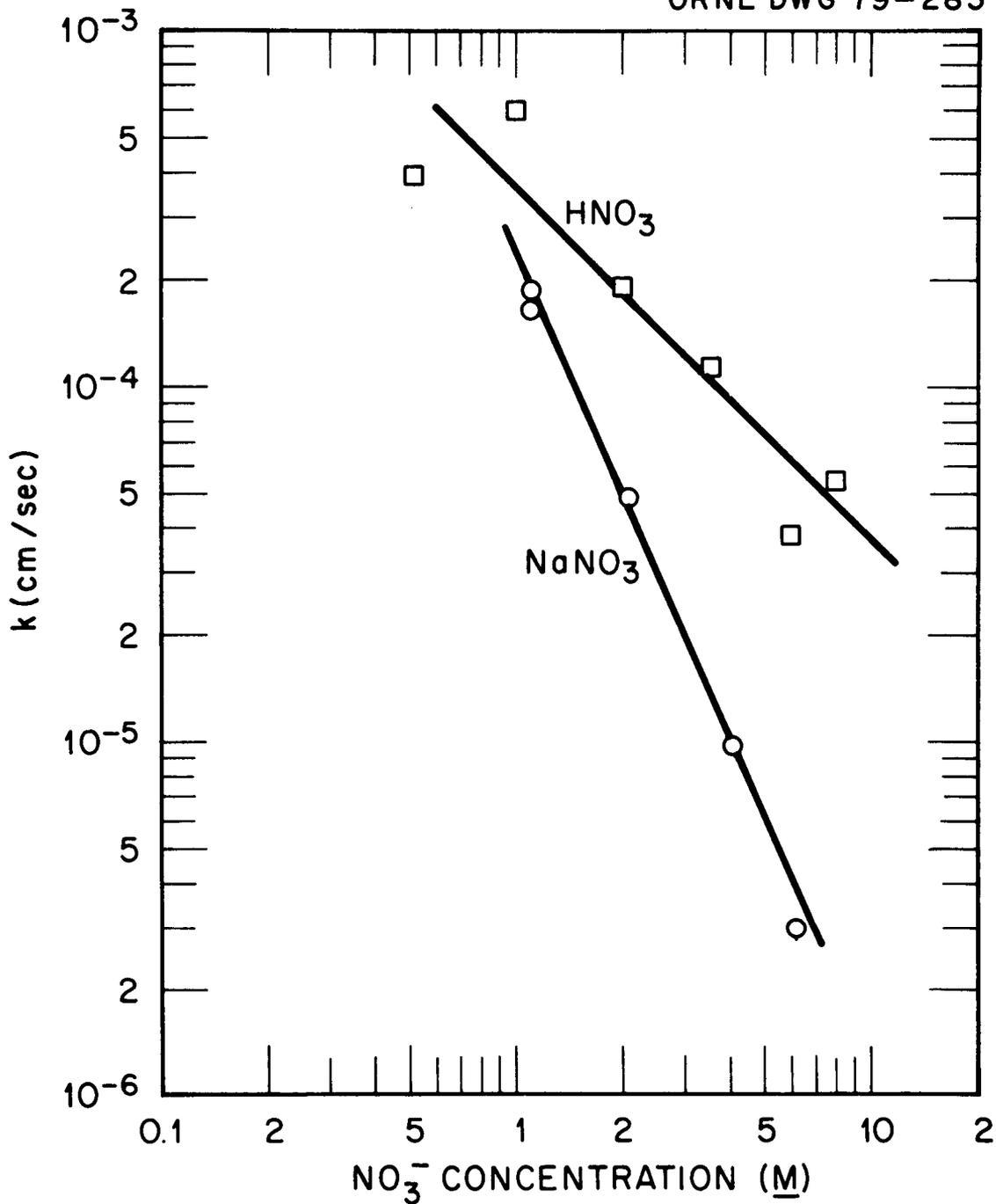


Fig. 8. Extraction rate constants as a function of HNO_3 and neutral nitrate.

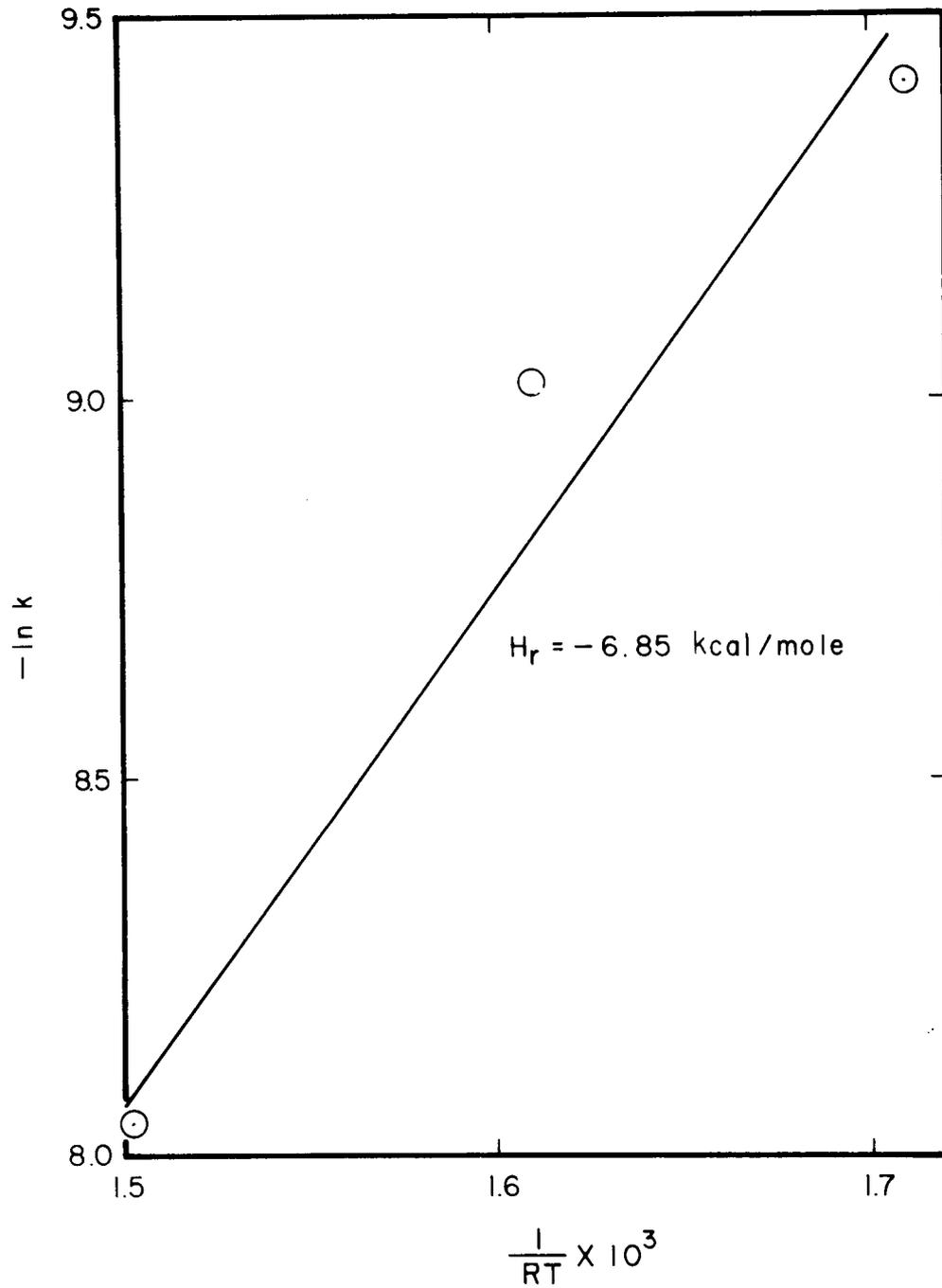


Fig. 9. Activation energy plot for reverse extraction (O to A) of uranium (3.5 M HNO₃, 30% TBP--NHD).

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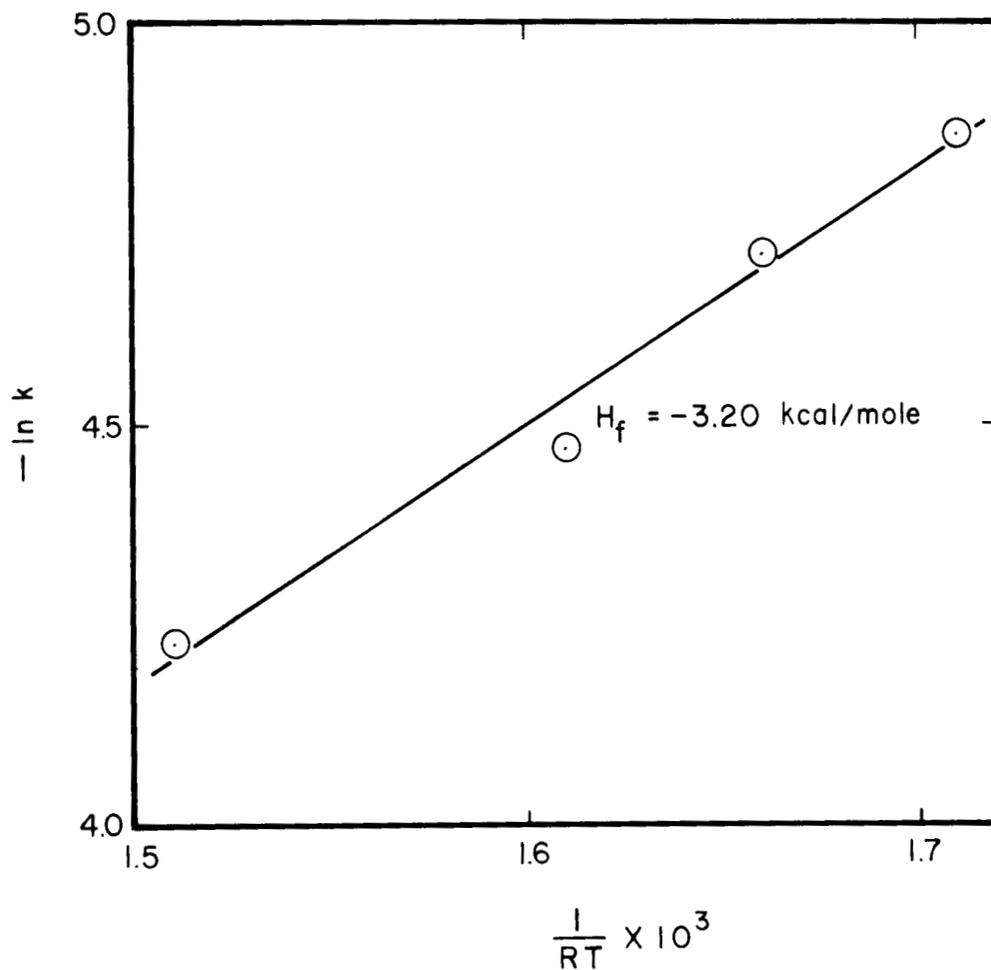


Fig.10. Activation energy plot for forward extraction (A to O) of uranium (3.5 M HNO₃, 30% TBP--NHD).

Using data compiled by Petrich and Kolarik (1977) for nitric acid concentrations between 3.05 and 3.8 M HNO₃ (44 determinations), and discarding six obviously bad points (i.e., more than a factor of 2 away from the average of all data for the temperature), we obtained a value of -3.8 kcal/mole for the ΔH . The ΔH with pure TBP is -3.6 kcal/mole, as published by Healy (1956). The value determined from the difference of the activation energies is in excellent agreement with these two values.

Kenics Mixer--Centrifugal Separator Tests

Table 3 lists the rate constants for the A to O transfer of uranium determined by using the Kenics mixer--centrifugal separator. The aqueous phase in all tests was 3.5 M HNO₃, initially containing 10 g of uranium per liter, and the organic phase was non-acidified 30% TBP--NHD. The average value found using the Kenics mixer, 7.1×10^{-3} cm/sec, is in excellent agreement with the average of all drop and Lewis cell tests under similar conditions, 7.2×10^{-3} cm/sec. This is particularly significant because the drops in the Kenics mixer are about 0.3 mm in diameter as compared to the approximately 3-mm drops in the falling and rising drop tests. Diffusion control in such small drops is unlikely; that all systems give the same rate constants is strong evidence against any type of diffusion control mechanism.

CONCLUSIONS

All three systems used to measure rate constants for uranium transfer give the same values for cases which have been examined. This is encouraging and is an indication that rate constants can be measured in such simple types of apparatus as Lewis cells and the drop apparatus, instead of in more complex types of apparatus.

The transfer of uranium from nitric acid to TBP--NHD is controlled by the chemical reaction at the interface. This conclusion is based on the following:

1. The forward rate constant divided by the reverse rate constant is equal, within experimental error, to the equilibrium constant over the range of TBP concentrations. In complete diffusion control, the forward and reverse rate constants are expected to be equal.

Table 3. Results of Kenics mixer tests using 3.5 M HNO₃ containing 10 g of uranium per liter and 30% TBP--NHD at approximately 25°C; calculated using eq 15

Aqueous flow rate (ml/min)	Organic flow rate (ml/min)	Area to volume ratio ^a (cm ⁻¹)	k' (cm/sec)
49	200	14.2	7.5 x 10 ⁻³
109	333	30.2	7.2 x 10 ⁻³
158	467	47.8	8.4 x 10 ⁻³
81	375	22.3	11.5 x 10 ⁻³
216	250	63.4	2.9 x 10 ⁻³
51	225	16.0	5.2 x 10 ⁻³
73	375	21.9	7.6 x 10 ⁻³
104	525	33.2	9.0 x 10 ⁻³
44	417	13.9	6.6 x 10 ⁻³
191	250	60.3	6.4 x 10 ⁻³
	Average		7.1 x 10 ⁻³ ± 2.3 x 10 ⁻³

^aBy Kenics correlation of Chen (1972).

2. The difference between the activation energies of the forward and reverse reactions is equal to the heat of reaction of uranium with TBP. This situation should not be true for diffusion control unless it occurs by chance.
3. The rate constants for uranium (A to O) were the same for the 3- and the 0.3-mm drops in the Kenics mixer; however, the latter case should have evidenced a higher diffusion rate.

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NOMENCLATURE

k	Reverse rate constant (organic to aqueous)
k'	Forward rate constant (aqueous to organic)
c	Concentration of drop, organic phase after time t
c'	Concentration of drop, aqueous phase at time t
v	Volume of drop, organic phase
v'	Volume of drop, aqueous phase
a	Interfacial area (total surface of drops) between drops and column phase
t	Interphase contact time
c_o	Initial concentration in organic phase at $t = 0$
c'_o	Initial concentration in aqueous phase at $t = 0$
I	Total inventory of uranium
D	Aqueous to organic equilibrium distribution coefficient
Δt	Time change corresponding to concentration changes $c_t - c_o$ or $c'_t - c'_o$
ΔH	Heat of reaction, $T_2 - T_1$
$[c_{u,o}]$	Molar concentration of uranium in organic phase equilibrium
$[c_{u,A}]$	Molar concentration of uranium in aqueous phase at equilibrium
[TBP]	Free TBP concentration ($[TBP_{initial}] - 2[c_{u,o}]$)

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