Title

Prediction of Concentration Gradients in Multicomponent Mass Transfer

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PREDICTION OF CONCENTRATION GRADIENTS IN MULTICOMPONENT MASS TRANSFER

DISCLAIMER

Errata

p. 6 Line 2, line 12. For HT, read H_T.

p. 17 Eq. (7). Insert exponent: $4\ m_{ul}\ \gamma_{ul}^{3}$.

Line following Eq. (9), change: aqueous to: organic.

p. 18 Eq. (11) should read:

$$m_{ul}(m_{ul} + \frac{m_{hl}}{2})^2\ \gamma_{ul}^{3}\ a_w^{4} = K'_e\ m_{ug}\ \gamma_{ug}\ .$$

Eq. (12) should read:

$$a_{ul} = m_{ul}(m_{ul} + \frac{m_{hl}}{2})^2\ \gamma_{ul}^{3}\ a_w^{4} / K'_e\ .$$

p. 51 8th line below Eq. (62), insert prime: K'_e.

p. 52 Fig. (12). In left-hand legend, read: $c_{ul}\ \gamma_{ul}\ a_w^{4/3}$.

p. 54 Eq. (67), change: K''_2 to: K''_e.

Next two lines following Eq. (67), insert subscript 1: $(\gamma_{ul})_c$; $(\gamma_{ul})_m$.

Eq. (68), insert subscript 1: a_{ul}.

p. 55 Insert at end of first paragraph:

Eq. (68) gives a misleading result, because it should have been modeled after Eq. (12) as corrected. Further, the correlation for organic-phase concentrations is empirical, and the particular algebraic form arrived at is fortuitous.

p. 57 Fig. (14). In the title and in the left-hand legend, read: Organic-phase concentration function.

p. 76 First complete paragraph. Replace by:

Considerable difference is observed between the two pseudoequilibrium curves. Since the "thermodynamic" method has not been applied properly, the values obtained from the empirical equations are to be preferred. In fact, until activity-coefficient calculations for the organic phase can be correlated by a Duhem-Margules approach, the "thermodynamic" method is also in part empirical.

Two primary conclusions may be drawn from our analysis:

(1) For systems in which no activities have been determined, the phase equilibria can (and must) be used as a basis for estimating the activities and the pseudoequilibrium concentrations.

(2) Even for such systems, a simpler and more accurate fit will probably result from use of mass-action relations as a guide to activity behavior in the aqueous phase.

p. 80 Footnote to last paragraph:

The values obtained are indicative of the method, but are not quantitatively correct because of the previously-mentioned error in the thermodynamic treatment.

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PREDICTION OF CONCENTRATION GRADIENTS IN MULTICOMPONENT MASS TRANSFER

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PREDICTION OF CONCENTRATION GRADIENTS IN MULTICOMPONENT MASS TRANSFER

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ABSTRACT

Equilibrium data on the four-component system pentaether (dibutoxy-tetraethylene glycol)-uranyl nitrate-nitric acid-water are presented. From these data, equations and graphical correlations have been developed which express the activities or effective activities of nitric acid and uranyl nitrate in the organic and aqueous phases as functions of their molar concentrations.

When these activity relations are utilized, a general method is outlined for calculating the number and height of transfer units in continuous countercurrent extraction columns. The method may be applied to systems consisting of two immiscible phases and two or more transferring components, both present in sufficient concentration to affect the equilibrium, and to systems with one diffusing component that deviate appreciably from ideal-solution behavior.

The extraction characteristics of the four-component system have been tested in a continuous countercurrent pulse column, one inch in diameter and five feet high. When uranyl nitrate is extracted into pentaether from aqueous acid solutions, uranium recovery is limited by the column height to 85 percent; however, when uranyl nitrate is re-extracted from pentaether into nitric acid, uranium recovery approaches 99.9 percent. A numerical interpretation is given for these results.

I. STATEMENT OF THE PROBLEM

The main purpose of this investigation has been to develop calculation methods for liquid-liquid extraction applicable to systems containing two or more transferring components, each present in sufficient concentration to affect the equilibrium. Up to this time, the available calculation methods have been limited to systems containing only one transferring component. Where additional transferring components are present, it has been necessary to assume that their presence has essentially no effect on the equilibrium distribution of the main transferring component. When several transferring components affect the equilibrium, the driving force for mass transfer of a particular component becomes a function of the nonequilibrium distribution which exists for the other diffusing components.

The major problem in developing a calculation method is the establishment of the "pseudoequilibrium" curve or line (on the distribution diagram) for the transferring component on which the calculations are to be based. For the distribution diagram, the abscissa and ordinate give respectively the concentrations of the diffusing component in the aqueous and in the organic phases. The pseudoequilibrium line for a tower is defined as the locus of points on the diagram whose distance from the operating line expresses the true effective driving force for transfer of the pertinent component, considering the nonequilibrium distribution of all transferring components. This distance between curves is measured vertically if the resistance is entirely in the aqueous "film," or horizontally, if entirely in the organic film. To establish the pseudoequilibrium line, we must know the activity difference across the film for the component on which calculations are to be based. For

each diffusing component there will be a different composition diagram, hence the HT (height of a "transfer unit") for each diffusing component may be determined.

Two alternate methods of calculating activities from equilibrium data are utilized, which express the activity coefficient for a particular component as a function of the concentration variables in the system. These methods are used to calculate the activities of a particular component in each phase. Since the relation between activity and concentrations is known, the pseudoequilibrium line may be established. The number of transfer units for a specified separation may then be calculated by use of equations analogous to Colburn's original equations for the HT, but modified to account for the presence of other components.

II. INTRODUCTION

In the past few years considerable effort has been expended by this and other laboratories to develop solvent-extraction processes for the separation and recovery of heavy metals.[5,10] In particular, excellent extraction and selectivity have been obtained with pentaether for purification of uranium solutions.[5,8] The high viscosity of this solvent serves to retard mass transfer between phases, so that accurate design of the countercurrent extraction equipment becomes quite important.

Although liquid-liquid extraction operations have been extensively used in industry for a number of years, calculation methods for tower design are still limited to systems containing only one transferring component, or to systems containing several transferring components where it can be assumed that the concentrations of one have no effect on the equilibrium concentrations of the others. This approximation is sometimes valid, but does not apply in the pentaether system. Therefore a detailed thermodynamic analysis of the problem has been necessary in order to develop a satisfactory method for calculating multicomponent transfer problems.

In order to demonstrate the complexity of calculation methods for multicomponent transfer systems the theories of liquid-liquid equilibria and mass transfer in extraction towers, and their use in design, are briefly reviewed.

Liquid-Liquid Equilibria

The Phase Rule. In the study of heterogeneous equilibria, Gibbs' phase rule[2] is of basic importance. It may be simply stated:

$$F = C - P + 2 \qquad (1)$$

where F is the number of degrees of freedom, or the number of independent

variables (limited to temperature, pressure, and composition) which must be fixed to define completely a system at equilibrium; C is the number of components, or the lowest number of independent variables required to express the composition of each phase; and P is the number of phases. For four components, at constant temperature, three mole-fractions of the eight measurable values x_A, x_B, x_C, x_D (aqueous), y_A, y_B, y_C, and y_D (organic) will define an equilibrium state completely.

Liquid-liquid extraction processes are naturally limited to systems of two relatively immiscible liquids, between which additional components may distribute.

The Activity. At moderate pressures the activity of a component can be measured by the ratio of the partial pressure of the component to the vapor pressure of the pure material at the same temperature. As applied to heterogeneous systems, the activity of any component in one phase indicates its potential for mass transfer to the coexisting phase. Thus if the activity of a component distributed between coexisting phases is not the same in each phase, mass transfer will tend to occur. At equilibrium, the activity of any component is the same in all phases.

The Activity Coefficient. The activity coefficient is defined as the ratio of activity to concentration. It is not yet possible, except for very dilute solutions, to predict the activity coefficient behavior of electrolytes. For weak electrolytes, the Arrhenius theory of dissociation is applicable in aqueous solutions only up to about 0.01 M. For strong electrolytes, where dissociation is complete, the interionic attraction theory of Debye and Huckel[4] has proved satisfactory in aqueous solution where the square root of the ionic strength is less than 0.1. The limits in nonaqueous solutions are lower. In more concentrated

solutions, the problems of interionic attraction, dissociation, and chemical complexing become so involved that no theory has yet been developed that can satisfactorily explain the experimental results. Because of this, empirical methods have been developed to describe the apparent activity coefficient behavior which may be used when experimental activity data are lacking.

Mass Transfer in Extraction Towers

When material is being transferred between two fluid streams moving countercurrently to each other, as in a liquid extraction tower, it is usually assumed that transfer occurs so rapidly at the interface that equilibrium exists between the two adjacent phases. This theory, postulated by Whitman[12] in 1923, further assumes the existence of two films, one on each side of the interface. Concentration gradients exist within the films which represent the driving force for mass transfer between the interface and the bulk streams.

In interpreting continuous countercurrent extraction operations, it is ordinarily very difficult to determine the interfacial concentrations and thus to obtain the driving forces through the separate films. To overcome this problem, the entire potential for transfer is calculated as if it lay within one film, and is referred to as an overall driving force.

Three general design methods are available for calculating continuous countercurrent extraction towers. The simplest adapts the McCabe-Thiele graphical procedure commonly used to calculate the number of theoretical plates in distillation towers. This method is fundamentally unsound for use in extraction-tower calculations, since it applies a procedure involving stepwise changes in concentration to

an operation where the concentration actually changes differentially with height. Practically, experimental information is so often lacking for application of the preferred methods that the McCabe-Thiele procedure is used extensively.

A second and more reliable method of extraction-tower design involves the use of overall mass-transfer coefficients, in which the coefficient is assumed to remain constant, and all the resistance to transfer is calculated as if it were in one phase. The mass-transfer equation is written for any typical differential section of the tower, and is integrated over the desired concentration limits to determine the height of tower required.

The third method is closely related to the second, but is based on the concept of a "transfer unit" at constant height. Colburn[1] noted in his study of mass transfer that, by grouping the terms involved in the mass-transfer equation, and giving concentrations in mole-fraction units, one can express the height of a column simply:

$$\mathcal{L} = N_{OG} H_{OG} \tag{2}$$

where $\mathcal{L}$ is the height of the tower, N_{OG} is a dimensionless group and represents the number of transfer units based on all resistance to transfer being in the G or organic phase, and H_{OG} is referred to as the height of an overall transfer unit (HTU) based on the organic phase.

For simplified cases of this type, the N_{OG} may be expressed by the equation

$$N_{OG} = \int \frac{dy}{y^* - y} \tag{3}$$

where y* and y are the mole fractions of diffusing material in the organic phase at the interface and in the bulk stream respectively.

The H_{OG} may be defined for this case by the equation

$$H_{OG} = \frac{M_{fG}}{K_G a \, (1-y)_m \, S \, C_{gm}} \quad , \tag{4}$$

where M_{fG} is the mass flow rate of the organic phase, $K_G a$ is an overall mass-transfer film coefficient, $(1-y)_m$ is the logarithmic mean of (1-y) and (1-y*), S is the cross-sectional area of the tower, and C_{gm} is the logarithmic mean concentration of the diffusing material between interface and bulk stream in the organic phase.

In extraction tower design the use of HTU's rather than overall mass transfer coefficients is preferred, as they are much less sensitive to composition changes and remain reasonably constant over a tower. Like transfer coefficients, they do vary appreciably with flow rates. Although several methods of predicting HTU values based on dimensional analysis have been proposed,[11] the results cannot yet be relied upon. Where it is necessary to design liquid-extraction towers for large-scale operations, it is best to determine experimental HTU values in pilot-plant columns.

III. MULTICOMPONENT MASS-TRANSFER THEORY

Equilibrium Considerations

Stover[10] investigated the system pentaether-uranyl nitrate-nitric acid-water over a broad concentration range at 25°C, and found the maximum quantity of pentaether in the aqueous phase to be 0.31 mole percent. For simplification, it is henceforth assumed that pentaether is immiscible in the aqueous phase. Stover also reported the solubility of water in pentaether to be 41.6 mole percent or 4 percent by weight. The solubility increased to a maximum of approximately 16 percent by weight as uranium and acid were added to the system; Stover showed the major portion of the solubility increase could be attributed to complex formation. Although the exact nature of the complexes has not been determined, it will be assumed that the compositions of the two phases may be completely expressed in terms of the following species.

Organic Phase	Aqueous Phase
$PE \cdot \ell H_2O$	H_2O
$HNO_3 \cdot mH_2O$	$HNO_3 \cdot mH_2O$
$UO_2(NO_3)_2 \cdot nH_2O$	$UO_2(NO_3)_2 \cdot nH_2O$

where ℓ, m, and n are constants to be determined.

Application of the phase rule to the system at equilibrium reveals that (in addition to the assumed zero pentaether concentration in the aqueous phase and the assumed zero water in the organic phase) two composition variables must be specified for either phase in order to fix its composition. Uranium nitrate and nitric acid concentrations were chosen arbitrarily as the variables to be specified, since they are the main transferring components of interest. We will not concern ourselves here with the actual species, since this knowledge is not

necessary for solution of the problem.

Pseudoequilibrium. Figure 1 illustrates the concentration gradients of uranium and acid at some particular cross-section in an extraction tower, assuming all resistance to transfer to be in the G (organic) film. The main-stream aqueous concentrations, which are equal to aqueous interfacial concentrations for this case, are designated $C_{u\ell}$ and $C_{h\ell}$ for the uranium and acid respectively. The organic interfacial concentrations are designated as c_{ugi} and c_{hgi}, and the main-stream organic concentrations c_{ug} and c_{hg}.

If changes in concentration of acid had no effect on the activity of uranium, the driving force for its mass transfer through the organic film could be expressed as $(c_{ug} - c_{ugi})$. To allow for the fact that C_{hg} is not in equilibrium with $c_{h\ell}$, we may define a pseudoequilibrium concentration of uranium at the interface c'_{ug}, such that $(c_{ug} - c'_{ug})$ represents the true driving force for mass transfer of uranium through the organic film, considering the nonequilibrium distribution of acid within the film. This gradient is shown by a dashed line in Figure 1 because of its imaginary nature.

Since it has been shown that two composition variables are required to fix the composition of an individual phase, the activity of any component in that phase should also be a function of these variables. It can be assumed that a method is available for calculating the uranium activity in the aqueous phase, $a_{u\ell}$, from $c_{u\ell}$ and $c_{h\ell}$, the aqueous uranium and acid concentrations. Since all the resistance to transfer was assumed to be in the organic film, the uranium activity thus calculated for the aqueous phase is also the interfacial equilibrium activity. Knowing the uranium equilibrium activity and c_{hg}, one can then

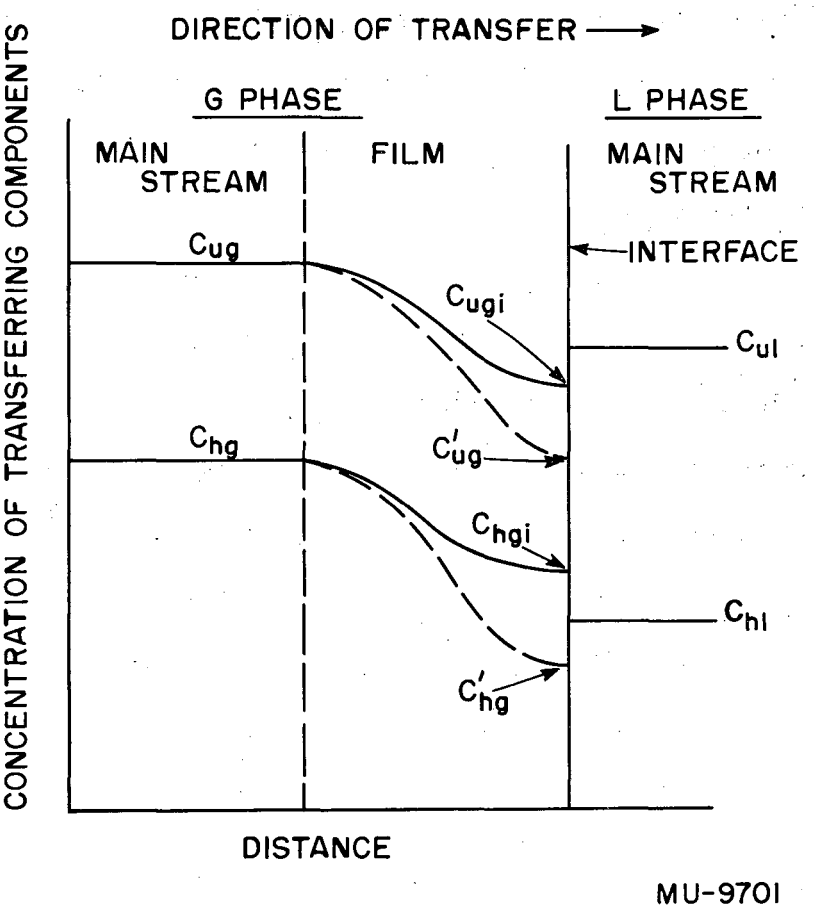


Fig. 1. Concentration gradients in multicomponent mass transfer with all resistance in one film.

calculate c'_{ug} if the functional relationship between the uranium activity and the main composition variables c_{ug} and c_{hg} is known for the organic phase. The difference $(c_{ug} - c'_{ug})$ then represents the true thermodynamic driving force for mass transfer of uranium through the organic film expressed as a concentration gradient.

One value for c'_{ug} can be obtained for each point within a tower. By sampling the tower at several points and determining the uranium and acid concentrations in each phase, we can calculate values of c'_{ug} if the previously described activity relationships are known. Plotting c'_{ug} versus the aqueous uranium concentration, $c_{u\ell}$, for the several calculated points establishes the pseudoequilibrium line for the tower. This, with the operating line, may be used to calculate the number of overall uranium transfer units based on the organic film, $(N_{OG})_u$, using modified forms of Colburn's equations. If the aqueous film offers the major resistance to mass transfer, values of $c'_{u\ell}$ could be determined similarly to permit calculation of $(N_{OL})_u$. Further, if the relation between acid activity, a_h, and the concentration variables is known, the acid pseudoequilibrium may be similarly established which, with the acid operating line, will permit calculating the number of acid transfer units.

As contrasted to a three-component system consisting of two immiscible solvents and one transferring component, where only one equilibrium line exists for any set temperature and pressure, an entire family of true equilibrium lines may be determined for four-component systems. For any particular tower operating at constant temperature the pseudoequilibrium line will be a function of the feed concentrations and flow rates. Thus different pseudoequilibrium lines can result from

differences in feed concentrations and flow rates.

The main problem in establishing the pseudoequilibrium line is to develop equations or graphical correlations that will express the activity of the component, on which calculations are to be based, in terms of measurable concentration variables. Although experimental determination of the activity behavior of transferring components in such complex systems as the one under discussion would be a long and tedious procedure, it is sometimes possible to extrapolate experimental data obtained from simpler systems from a knowledge of relative ionic strengths. Fortunately this is the case for uranyl nitrate, and such an extrapolation method is described later. An alternative approach was also developed which allows "apparent" activity behavior to be predicted from equilibrium distribution data, and is proposed for use where experimental activity data are lacking. Activities calculated by this method are intended primarily as an engineering aid, and are on a convenient scale of relative values independent of the usual infinite-dilution reference state.

Activity Coefficients: Thermodynamic Method. Glueckauf, McKay, and Mathieson[3] have extensively studied the partition of uranyl nitrate between water and organic solvents. Since the concentration of pentaether in the aqueous phase may be considered negligible in the three-component system pentaether-uranyl nitrate-water, they assumed that the following equilibrium exists:

$$UO_2(NO_3)_2 \cdot hH_2O = UO_2^{++} + 2NO_3^- + hH_2O \qquad (5)$$

which implies the equilibrium constant

$$K_e = \frac{\left[UO_2^{++}\right]\left[NO_3^-\right]^2 \left[H_2O\right]^h}{\left[UO_2(NO_3)_2 \cdot hH_2O\right]} \qquad (6)$$

where the square brackets denote thermodynamic activities.

By definition $\gamma_{u\ell}$, the mean molal activity coefficient for uranyl nitrate in the aqueous phase, is given by

$$[UO_2^{++}][NO_3^-]^2 = 4\, m^3_{u\ell}\, \gamma^3_{u\ell} \quad , \tag{7}$$

where m_u is the aqueous uranyl nitrate molality.

Similarly for the organic phase,

$$[UO_2(NO_3)_2 \cdot hH_2O] = m_{ug}\ \gamma_{ug} \quad , \tag{8}$$

where m_{ug} and γ_{ug} are the uranyl nitrate molality and activity coefficient respectively.

The infinitely dilute solution is taken as the reference state, so $\gamma_{ug} \longrightarrow 1$ as $m_{ug} \longrightarrow 0$; thus

$$m^3_{u\ell}\, \gamma^3_{u\ell}\ a_w^h = K'_e\ m_{ug}\ \gamma_{ug} \tag{9}$$

where a_w is the activity of water and $K'_e = K_e/4$.

Although the degree of hydration of aqueous uranyl nitrate may vary from h = 3 to h = 6, an average value of h = 4 was found most satisfactory by Glueckauf and associates.[3]

Robinson and co-workers[8] have determined γ_u and a_w for the system uranyl nitrate-water, using an integration method outlined by Harned and Owen.[4] These results are reported by Glueckauf and associates and may be assumed to apply to the aqueous phase of the three-component system pentaether-uranyl nitrate-water, since pentaether is essentially insoluble in that phase. When these values are utilized, the organic activity coefficients and K_e may be readily determined from equilibrium data. The calculations are shown in the subsequent section.

In order to extrapolate these data to the four-component system under consideration, it was again assumed that the aqueous pentaether solubility was negligible and that the aqueous activities were a function of total ionic strength, μ_ℓ, which is given by

$$\mu_\ell = \sum \frac{1}{2}\ mZ^2 = 3m_{u\ell} + m_{h\ell} \tag{10}$$

Hence for the four-component system, Eq. (9) may be expressed

$$(m_m + \frac{m_h \ell}{3})^3 \gamma_{u\ell}^3 a_w^4 = K'_e m_{ug} \gamma_{ug} . \qquad (11)$$

Thus, by applying the activity data of Robinson to aqueous solutions of equivalent ionic strength, and by knowing the equilibrium distribution, one may calculate organic activity coefficients for the four-component system. These calculations and their graphical correlation are given in Section V.

For our purpose, it will be convenient to describe the aqueous uranyl nitrate activity as

$$a_u = \frac{(m_u \ell + \frac{m_h \ell}{3})(\gamma_{u\ell} a_w^{4/3})^3}{K''_e} . \qquad (12)$$

Hence at equilibrium

$$a_{u\ell} = a_{ug} . \qquad (13)$$

Activity Coefficients: Empirical Method. As previously mentioned, the equations developed in this section are offered for use only when thermodynamic activity data are unavailable.

The uranium activities, a_u, for the respective phases may be defined by the equations

$$a_{ug} = c_{ug} \gamma_{ug} \qquad (14)$$

$$a_{u\ell} = c_{u\ell} \gamma_{u\ell} \qquad (15)$$

where γ is the activity coefficient, and c_u the uranyl nitrate molar concentrations.

Since the composition of each phase is set by two composition variables, the uranium activity coefficients for the respective phases

may be expressed

$$\gamma_{ug} = \gamma^{\circ}_{ug} + f(c_{hf} c_{ug}), \tag{16}$$

$$\gamma_{u\ell} = \gamma^{\circ}_{u\ell} + f(c_{h\ell} c_{u\ell}), \tag{17}$$

where γ°_{ug} and $\gamma^{\circ}_{u\ell}$ are the uranium activity coefficients in the organic and aqueous solutions, respectively, extrapolated to apparent zero concentration.

The uranium equilibrium distribution coefficient, E_u, is defined by the equation

$$E_u = \frac{c_{ug}}{c_{u\ell}} = \frac{\gamma_{u\ell}}{\gamma_{ug}} \tag{18}$$

An empirical power series equation may now be written to express the uranium activity coefficients in terms of concentration variables:

$$\gamma_{ug} = \gamma^{\circ}_{ug} + Ac_{ug} + Bc^2_{ug} + Cc^3_{ug} + Dc_{hg} + Ec^2_{hg} + Fc^3_{hg} + Gc_{ug}\, c_{hg} + Hc^2_{ug}\, c_{hg} + Ic_{ug}\, c^2_{hg}, \tag{19}$$

$$\gamma_{u\ell} = \gamma^{\circ}_{u\ell} + A'c_{u\ell} + B'c^2_{u\ell} + C'c^3_{u\ell} + D'c_{h\ell} + E'c^2_{h\ell} + F'c^3_{h\ell} + G'c_{u\ell}\, c_{h\ell} + H'c^2_{u\ell} c_{h\ell} + I'c_{u\ell}\, c_{h\ell} \tag{20}$$

where A,B,C,...I and A',B',C'...I' are constants to be determined for the organic and aqueous phases respectively.

Under equilibrium conditions, the activities of the coexisting phases are equal, and we have

$$c_{ug}\left[\gamma^{\circ} + Ac_{ug} + Bc^2_{ug} + \ldots . Ic_{ug}\, c^2_{hg}\right] = c_u\left[\gamma^{\circ}_{u\ell} + A'c_{u\ell} + B'c^2_{u\ell} + \ldots . I'c_{u\ell} c^2_{h\ell}\right]. \tag{21}$$

Similarly we may derive the acid equilibrium equation,

$$c_{hg}\left[\gamma^{o}_{hg} + Ac_{hg} + Bc^{2}_{hg} + \cdots\ I\, c_{hg}\, c^{2}_{ug}\right] = c_{h\ell}\left[\gamma^{o}_{h\ell} + A'c_{h\ell} + B'c^{2}_{h\ell} + \cdots\ I'\, c_{h\ell}c^{2}_{ug}\right] \qquad (22)$$

The constants of Eq. (21) will of course be different from those of Eq. (22). To evaluate the constants, equilibrium data are substituted into the equations and the constants are determined algebraically.

Calculation of Pseudoequilibrium Curve. The activity equations and graphical correlations may now be applied to extraction tower calculations, and pseudoequilibrium values may be determined. By sampling the tower at several points and determining the uranium and acid concentrations of each phase, activities and activity coefficients may be calculated for each phase. If it is assumed that the organic phase is controlling, the calculated bulk aqueous-phase activities will also represent the aqueous interfacial activities and hence the organic interfacial activities. From knowledge of the bulk organic phase activity coefficients the pseudo-equilibrium concentrations are given by a modified form of the defining activity equations:

$$c'_{ug} = \frac{a_{ugi}}{\gamma_{ug}} \qquad (23)$$

$$c'_{hg} = \frac{a_{hgi}}{\gamma_{hg}} \qquad (24)$$

Similarly when the aqueous phase is controlling,

$$c'_{u\ell} = \frac{a_{u\ell i}}{\gamma_{u\ell}} \qquad (25)$$

$$c'_{h\ell} = \frac{a_{h\ell i}}{\gamma_{h\ell}} \qquad (26)$$

Development of Transfer-Unit Equations for Ternary Systems

In order to calculate transfer units for any transferring species of a multicomponent mass-transfer system, Eqs. (3) and (4) must be modified to account for the additional components, and the calculations must be based on the pseudoequilibrium-line concept.

For the system pentaether-nitric acid-water-uranyl nitrate, it was assumed that the compositions of the two phases could be expressed in terms of the following species: H_2O — P.E. · ℓ H_2O — HNO_3 · mH_2O — UNH · nH_2O, where ℓ , m, and n are constants.

The total volume of organic solution, V_g, containing n_{PE}, n_u, and n_h moles of pentaether, uranium, and nitric acid respectively, may be expressed in terms of the partial molal volumes, v, of the several components if the partial molal volumes are assumed to be constant:

$$V_g = n_{pg} \bar{v}_p + n_{ug} \bar{v}_u + n_{hg} \bar{v}_h \quad , \tag{27}$$

and since

$$n_{pg} = c_{pg} V_g; \quad n_{ug} = c_{ug} V_g ; \text{ and } n_{hg} = c_{hg} V_g \quad , \tag{28-30}$$

the total volume fraction is expressed

$$1 = c_{pg} \bar{v}_p + c_{ug} \bar{v}_u + c_{hg} \bar{v}_h \cdot \tag{31}$$

The molar concentration of pentaether in the organic phase may then be expressed

$$c_{pg} = \frac{1}{\bar{v}_p} (1 - c_{ug} \bar{v}_u - c_{hg} \bar{v}_h), \tag{32}$$

where

$$\frac{1}{\bar{v}_p} = c_p^o \tag{33}$$

and c_p^o is the molar concentration of pure pentaether under standard conditions.

Since pentaether has been assumed to be immiscible in the aqueous phase, the pentaether flow is constant throughout the tower and may be expressed

$$v_g \times c_{pg} = K_f. \tag{34}$$

Combining Eqs. (32), (33), and (34), we have

$$v_g \times c_p^o \ (1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h) = K_f. \tag{35}$$

The flow of organic phase may be expressed by material balance:

$$v_g = \frac{\left[v_{go} \ (1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_o\right]}{1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h}, \tag{36}$$

where subscript zero refers to known conditions at one end of the tower.

Multiplying Eq. (36) by c_{ug} and differentiating, we obtain

$$d(v_g \ c_{ug}) = \frac{(v_g)_o \ (1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_o \ (1 - c_{hg}\bar{v}_h) \ d \ c_{ug}}{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)^2} \tag{37}$$

Combining Eqs. (36) and (37), we have

$$d(v_g \ c_{ug}) = \frac{v_g \ (1 - c_{hg}\bar{v}_h) \ d \ c_{ug}}{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)} \tag{38}$$

For a differential section of column, the mass transfer of uranium may be expressed by

$$d \ (v_g \ c_{ug}) = (K'_G a)_u \ S \ (c'_{ug} - c_{ug}) \ dH, \tag{39}$$

where $(c'_{ug} - c_{ug})$ is the difference between the pseudoequilibrium and operating concentrations at any particular point in the tower and represents the thermodynamic driving force for mass transfer when the resistance to diffusion is entirely within the organic film. Here $(K'_G)_u$ is the overall uranium mass-transfer coefficient.

Combining Eqs. (38) and (39), we may express the differential height of tower under consideration,

$$d\,h = \frac{v_g (1 - c_{hg}\bar{v}_h)\, d\, c_{ug}}{(K'_G a)_u\, S\, (1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)(c'_{ug} - c_{ug})}, \qquad (40)$$

and integrating over the height of the tower we obtain

$$h = \frac{v_g(1 - c_{hg}\bar{v}_h)_m}{(K'_G a)_u\, S(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_m} \int_0^H \frac{(1 - c_{hg}\bar{v}_h)}{(1 - c_{hg}\bar{v}_h)_m} \cdot \frac{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_m}{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)} \cdot \frac{d\, c_{ug}}{(c'_{ug} - c_{ug})},$$

where the subscripts m refer to log mean values.

Since H is defined by

$$h = (H_{OG})\,(N_{OG}) \qquad (42)$$

and

$$h = (H_{OL})\,(N_{OL}), \qquad (43)$$

the H_{OG} and N_{OG} for uranium may be expressed

$$(H_{OG})_u = \frac{v_g\,(1 - c_{hg}\bar{v}_h)_m}{(K'_G a)_u\, S(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_m}, \qquad (44)$$

$$(N_{OG})_u = \int_0^H \frac{(1 - c_{hg}\bar{v}_h)}{(1 - c_{hg}\bar{v}_h)_m} \cdot \frac{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_m}{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)} \cdot \frac{d\, c_{ug}}{(c'_{ug} - c_{ug})} \qquad (45)$$

When the major resistance to mass transfer is centered in the aqueous film, the equations for the $(H_{OL})_u$ and $(N_{OL})_u$ may be similarly derived and are expressed

$$(H_{OL})_u = \frac{v_\ell \, (1 - c_{h\ell} \, \bar{v}_h)_m}{(K'_L a)_u \; S \; (1 - c_{u\ell} \bar{v}_u - c_{h\ell} \, \bar{v}_h)_m} \quad , \qquad (46)$$

$$(N_{OL})_u = \int_{c_1}^{c_2} \frac{(1 - c_{h\ell} \bar{v}_h)}{(1 - c_{h\ell} \bar{v}_h)_m} \cdot \frac{(1 - c_{u\ell} \bar{v}_u - c_{h\ell} \bar{v}_h)_m}{(1 - c_{u\ell} \bar{v}_u - c_{h\ell} \bar{v}_h)} \cdot \frac{d \, c_{u\ell}}{(c_{u\ell} - c'_{u\ell})} \qquad (47)$$

For dilute solutions, the equations may be simply expressed

$$(H_{OG})_u = \frac{v_g}{(K'_G a)_u \; S} \qquad (48)$$

$$(N_{OG})_u = \int_{c_1}^{c_2} \frac{d \, c_{ug}}{(c'_{ug} - c_{ug})} \qquad (49)$$

$$(H_{OL})_u = \frac{v_\ell}{(K'_L a)_u \; S} \qquad (50)$$

$$(N_{OL})_u = \int_{c_1}^{c_2} \frac{d \, c_{u\ell}}{(c_{u\ell} - c'_{u\ell})} \qquad (51)$$

Similarly, equations may be derived for the acid HTU's and NTU's:

$$(H_{OG})_h = \frac{v_g \, (1 - c_{ug} \, \bar{v}_u)_m}{(K'_G a)_h \; S \; (1 - c_{ug} \, \bar{v}_u - c_{hg} \, \bar{v}_h)_m} \qquad (52)$$

$$(N_{OG})_h = \int_{c_1}^{c_2} \frac{(1-c_{ug}\bar{v}_u)}{(1-c_{ug}\bar{v}_u)_m} \cdot \frac{(1-c_{ug}\bar{v}_u-c_{hg}\bar{v}_h)_m}{(1-c_{ug}\bar{v}_u-c_{hg}\bar{v}_h)} \cdot \frac{d\,c_{hg}}{(c'_{hg}-c_{hg})} \quad , \quad (53)$$

$$(H_{OL})_h = \frac{v_\ell\,(1-c_{u\ell}\,\bar{v}_u)_m}{(K'_L a)_h\, S(1-c_{u\ell}\,\bar{v}_u - c_{h\ell}\,\bar{v}_h)_m} \quad , \quad (54)$$

$$(N_{OL})_h = \int_{c_1}^{c_2} \frac{(1-c_{u\ell}\bar{v}_u)}{(1-c_{u\ell}\bar{v}_u)_m} \cdot \frac{(1-c_{u\ell}\bar{v}_u-c_{h\ell}\bar{v}_h)_m}{(1-c_{u\ell}\bar{v}_u-c_{h\ell}\bar{v}_h)} \cdot \frac{d\,c_{h\ell}}{(c_{h\ell}-c'_{h\ell})} \quad , \quad (55)$$

and for dilute solutions, equations analogous to Eq. (48) to (51) will apply.

Equations Based on Mean Film Values

In considering mass transfer through a film, it may be desirable to base the thermodynamic driving force on mean film values. Thus the thermodynamic driving force through the G-phase film may more properly be expressed

$$\frac{a_{gi} - a_g}{\gamma_{gm}}$$

rather than $(c'_g - c_g)$, where γ_{gm} is the log mean activity coefficient of the transferring component in the g phase. Dimensions of concentration rather than activity are retained in the expression, since it appears certain that the mass-transfer coefficients will be more completely independent of the concentration values.

Substituting this new driving-force expression in Eq. (39) and expressing the mass-transfer coefficient as K''_G for this case, we have:

$$d(v_g\, c_{ug}) = (K''_G a)_u\, S\, \left(\frac{a_{ugi} - a_{ug}}{\gamma_{ugm}}\right)\, d\,H \qquad (56)$$

Since by definition $c'_{ug} = \frac{a_{ui}}{\gamma_{ug}}$, we have

$$d(v_g\, c_{ug}) = \frac{(K''_G a)_u}{\gamma_{ugm}}\, S\, (c'_{ug} - c_{ug})\, \gamma_{ug}\, dH\,. \qquad (57)$$

Comparing Eq. (39) and (57) we have

$$(K'_G a)_u = (K''_G a)_u\, \frac{\gamma_{ug}}{\gamma_{ugm}} \qquad (58)$$

It is evident from Eq. (58) that, if γ_{ug}/γ_{ugm} varies significantly throughout the tower and $(K''_G a)_u$ is reasonably constant, $(K'_G a)_u$ will not be constant.

The simplified equations for this case are

$$(N_{OG})_u = \int_{\mathcal{C}_1}^{\mathcal{C}_2} \frac{\gamma_{ugm}\, d\, c_{ug}}{(a_{ugi} - a_{ug})} \quad , \tag{59}$$

$$(N_{OL})_u = \int_{\mathcal{C}_1}^{\mathcal{C}_2} \frac{\gamma_{ulm}\, d\, c_{ul}}{(a_{ul} - a_{ui})} \quad . \tag{60}$$

The equations will remain as previously derived, except that K"a will be preferred over K'a.

IV. EXPERIMENTAL

Equilibrium Experiments

A series of equilibrium experiments was conducted in order to expand the range of data available for the system pentaether-uranyl nitrate-nitric acid-water. In each experiment 5 ml of pure pentaether was added to 5 ml of uranyl nitrate-nitric acid solution of known uranium and acid concentration. The mixture was placed in a glass-stoppered test tube, sealed, and agitated on a shaking rack immersed in a constant-temperature bath at 25°C for at least two hours. Stover[10] has demonstrated that the system attains equilibrium within this time. After sufficient agitation, the test tube was removed from the rack, centrifuged as quickly as possible, and the phases separated. Each phase was analyzed for uranium and nitric acid content. The aqueous-phase uranium analysis was conducted gravimetrically, while the organic-phase uranium was determined spectrophotometrically by means of the ascorbic acid technique.[6] Acid analysis was accomplished in both phases by complexing the uranium with $K_2C_2O_4$ and then titrating with 0.1 N NaOH.[6] The results of these experiments are given in Table I. The data are represented graphically in Figs. 2 through 5 and compared with the data of Stover.

Pulse Column Experiments

Simulated column data obtained from batch counterflow experiments have demonstrated excellent extraction and selectivity obtainable when pentaether is used as a uranium solvent.[5] Because the high viscosity of pentaether-uranyl nitrate and aqueous-uranyl nitrate solutions, good mixing and phase dispersion is necessary to obtain rapid mass-transfer between phases.

Rubin[8a] used the three-component system pentaether-uranyl nitrate-water and demonstrated with a 0.5-inch diameter pulse column that overall

Table I

Equilibrium Concentrations 25°C - System P.E. - $UO_2(NO_3)_2$ - HNO_3 - H_2O

Initial Aqueous Molarity		Final Aqueous Molarity		Final Organic Molarity	
$UO_2(NO_3)_2$	HNO_3	$UO_2(NO_3)_2$	HNO_3	$UO_2(NO_3)_2$	HNO_3
0.210	0.197	0.201	0.084	0.035	0.085
0.220	0.522	0.190	0.344	0.064	0.187
0.220	1.032	0.166	0.712	0.090	0.372
0.220	2.010	0.112	1.224	0.113	0.788
0.223	3.121	0.089	1.893	0.133	1.293
0.519	0.197	0.416	0.141	0.175	-
0.522	0.522	0.400	0.306	0.215	.224
0.520	1.032	0.343	0.664	0.249	.346
0.518	2.010	0.299	1.232	0.297	.692
0.526	3.121	0.230	1.910	0.318	1.090
1.06	0.197	0.632	0.145	0.486	0.0775
1.05	0.522	0.610	0.360	0.510	0.203
1.07	1.032	0.566	0.666	0.544	0.408
1.07	2.010	0.527	1.216	0.586	0.770
1.07	3.121	0.462	2.015	0.611	1.24
2.02	0.197	1.142	0.160	1.04	0.053
2.01	0.522	1.142	0.285	1.06	0.182
2.01	1.032	1.092	0.598	1.08	0.407
2.0*	2.01	1.040	1.272	1.11	0.782
2.0*	3.12	0.978	2.205	1.15	1.14
3.0*	0.197	1.765	0.094	1.55	0.064
3.0*	0.522	1.775	0.293	1.56	0.183
3.0*	1.032	1.775	0.656	1.57	0.370
3.0*	2.010	1.672	1.42	1.60	0.753

*These solutions were saturated in uranium at the acid concentration indicated.

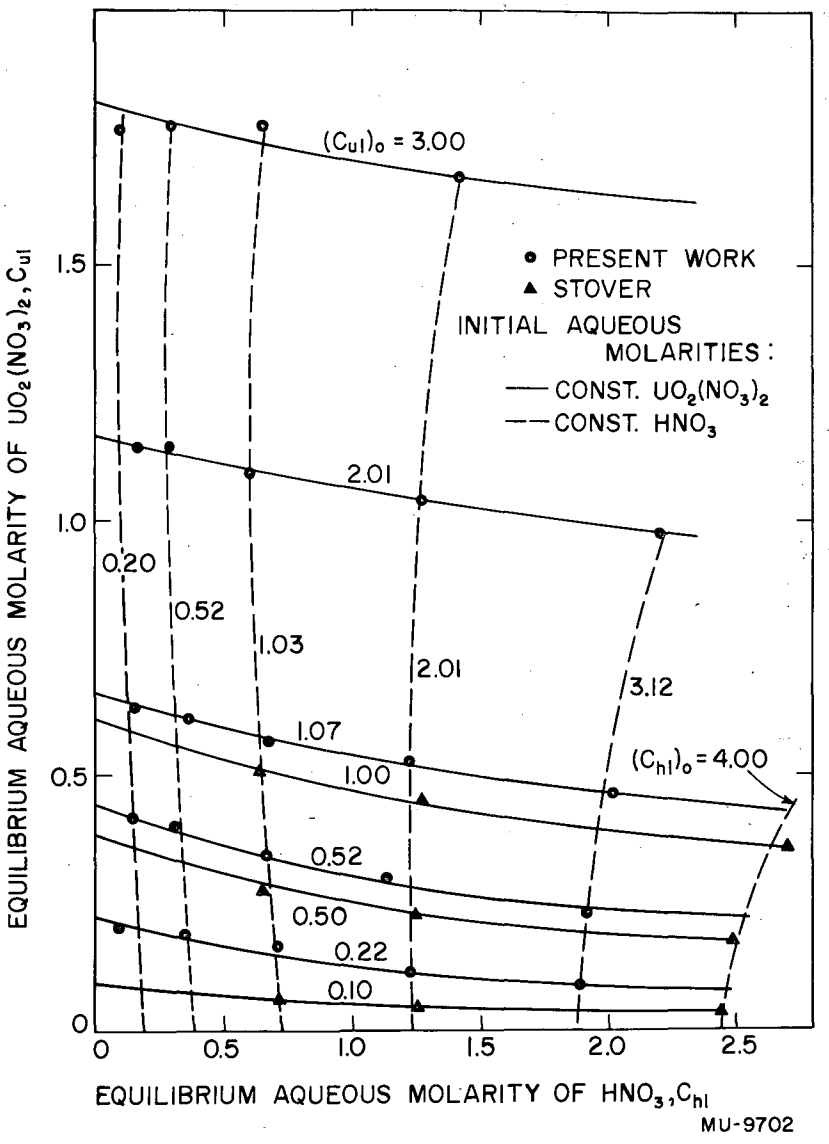


Fig. 2. Equilibrium data for P. E. -HNO_3-H_2O-$UO_2(NO_3)_2$ at 25° C.

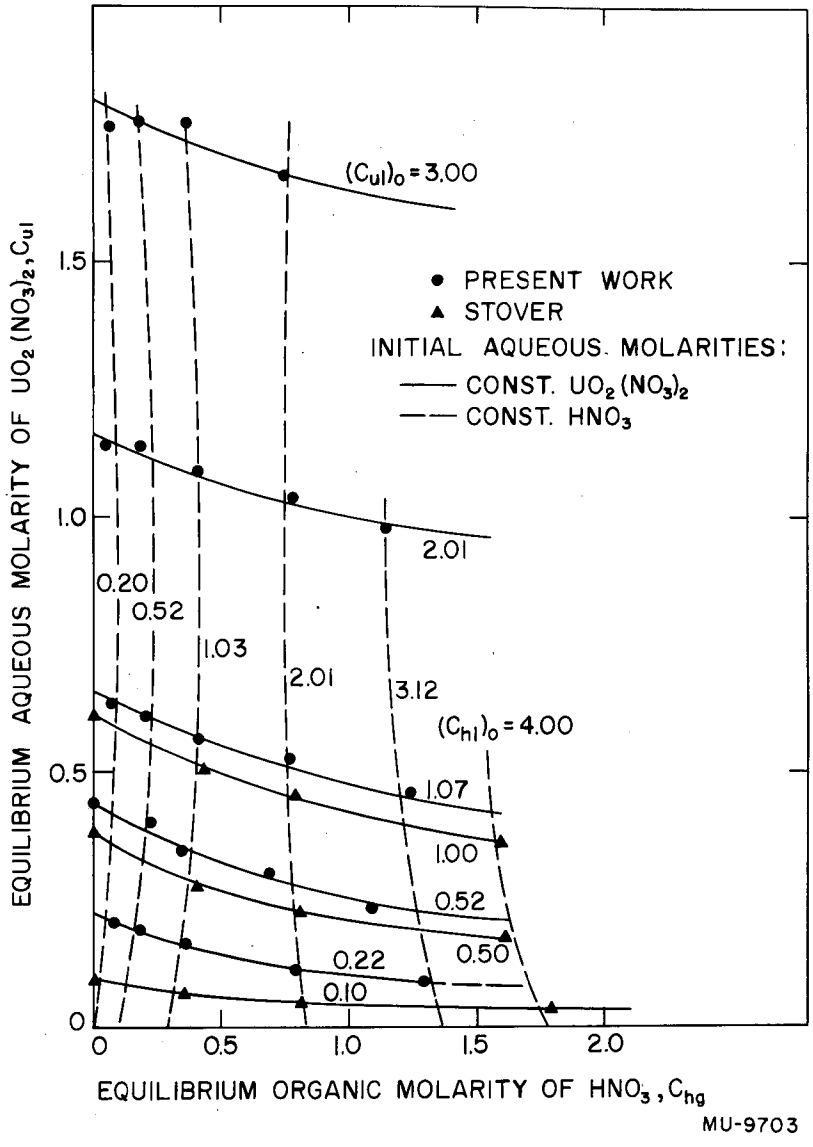


Fig. 3. Equilibrium data for P. E. -HNO_3-H_2O-$UO_2(NO_3)_2$ at 25° C.

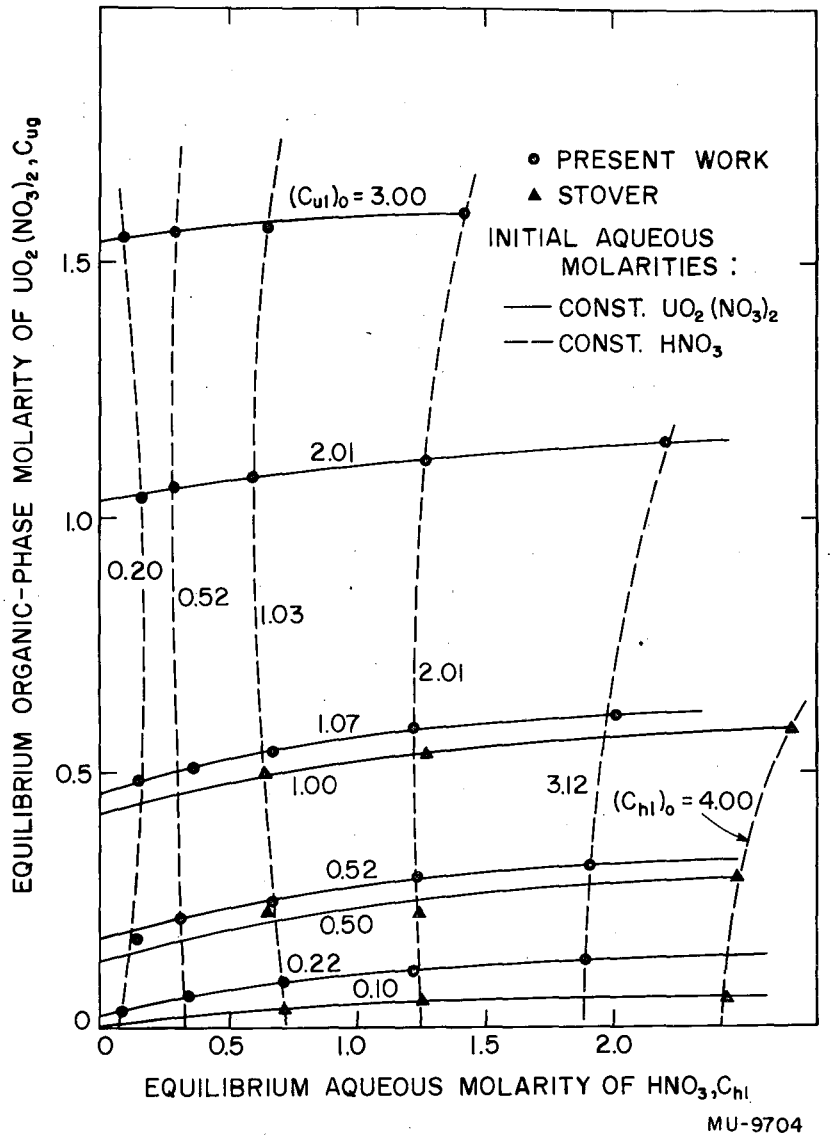


Fig. 4. Equilibrium data for P. E. -HNO_3-H_2O-$UO_2(NO_3)_2$ at 25° C.

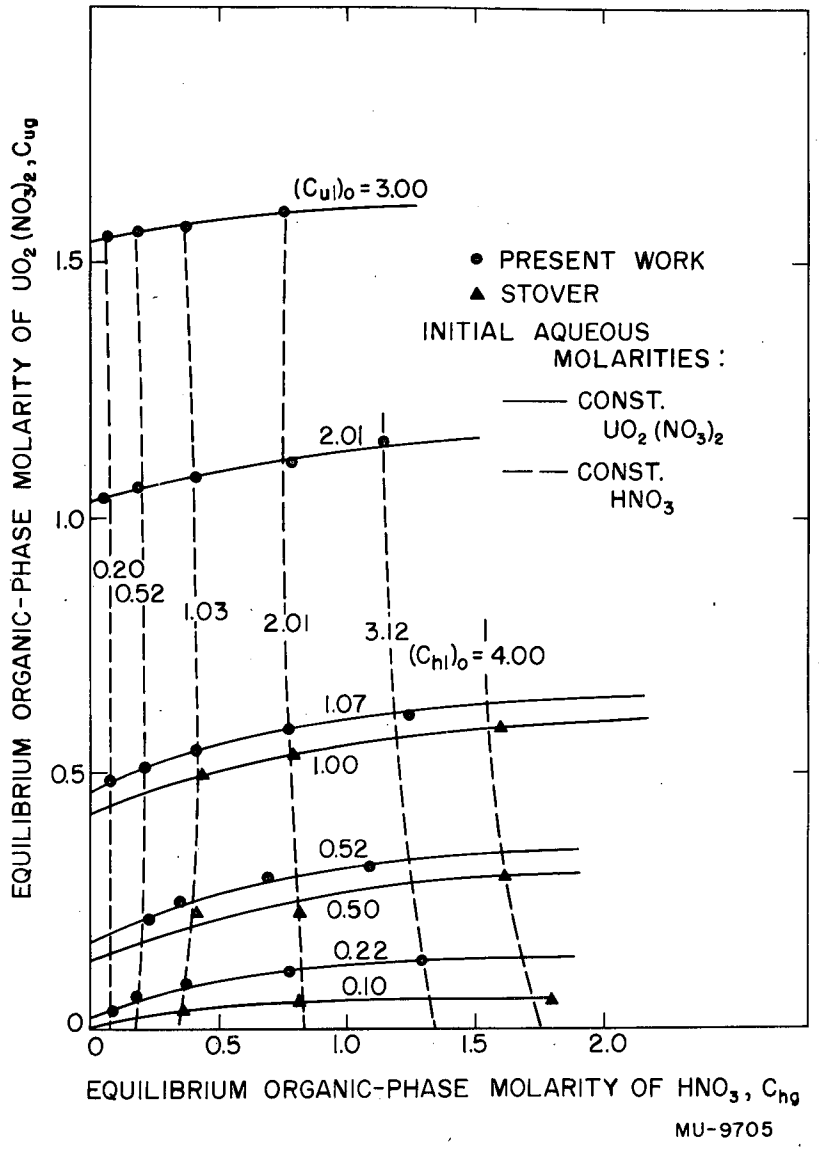


Fig. 5. Equilibrium data for P.E. -HNO_3-H_2O-$UO_2(NO_3)_2$ at 25° C.

HTU's as low as 6-inches, based on the organic film, could be obtained at flow rates up to 300 gal/hr/ft^2.

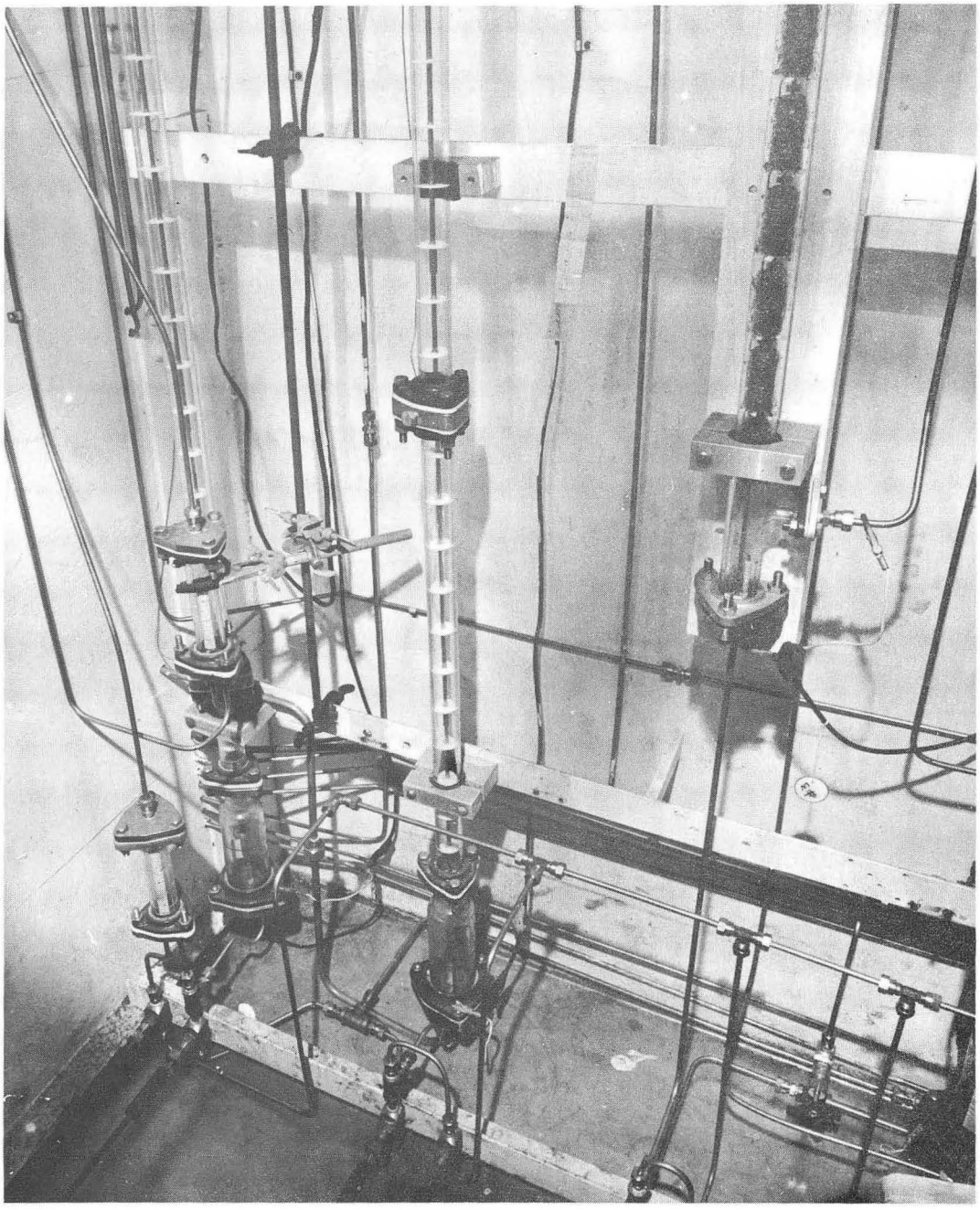
Equipment Description. To demonstrate the four-component system pentaether-uranyl nitrate-nitric acid-water in continuous countercurrent apparatus, a 1-inch diameter pulse column was designed and constructed (Fig. 7). Lehman subsequently used this diameter pulse column which is extensively described, with accessory facilities, in another report.[7] In brief, Lehman's column consisted of several flanged sections of 1-inch diameter commercial pyrex pipe vertically bracketed to cast-iron wall supports. To allow for adequate phase separation, sections expanding to 2-inches in diameter and 1-foot in length were attached to both ends. Stainless steel base- and headplates, equipped with the necessary feed and overflow lines, were flanged to the top and bottom of the column. All feed and overflow lines were of 0.25-inch stainless steel tubing. Feed and overflow reservoirs were converted stainless steel oxygen tanks. Column feed rates were controlled with small bellows-type diaphragm pumps equipped with an adjustable displacement mechanism. To impart pulse action to the column a 6-inch bellows-type diaphragm pump of adjustable frequency and displacement was installed in the "cold" feed line. To obtain adequate mixing and phase dispersion from the pulsed feed, 1-inch diameter Teflon or stainless steel perforated plates were placed on a stainless steel center rod within the column and evenly spaced with stainless steel spacers which slipped on the center rod between the plates. The interface was maintained at a constant level in the column by a bare-tipped, glass-shielded, platinum wire probe, which, operating on the conductivity difference of the two phases, indirectly controlled a stainless steel air-operated needle valve in

the bottom take-off line. Calibrated glass reservoirs equipped with remote-control solenoid valves were installed in the overflow lines to measure the overflow rates. Photographs of the column, feed-pump rack and feed tanks, and the pulse pump are shown in Figures 6, 6a and 6b.

Simple Extraction. Three extraction experiments were conducted in which the column was operated with conventional top and bottom feed streams and overflows. In each experiment uranium was extracted from an aqueous uranyl nitrate solution into an organic pentaether phase. The top aqueous feed was approximately 1.5 M in uranyl nitrate and 0.1 M in nitric acid, and the bottom pulsed pentaether feed was approximately 1.9 M in nitric acid. The column had a 5-foot effective extraction section and contained approximately 60 perforated plates spaced 1-inch apart. In Run No. 1N stainless steel plates containing 55 perforations 0.062-inch in diameter were used, while in runs No. 2N and 3N Teflon plates containing 60 perforations 0.040-inch in diameter were used.

Since the column was pulsed from the bottom in these runs, the top overflow was taken off through a side arm in the upper settling section to which was flanged an end plate containing the connecting line to the overflow reservoir. The column was operated with the organic phase continuous, the interface being maintained in the lower settling section by inserting the glass-shielded platinum-tipped electronic probe through the bottom baseplate so the bare platinum tip was approximately 6-inches from the bottom of the column. Figure 7 illustrates the column setup for these runs.

To assure that steady-state conditions were attained before termination of any experiment, samples of the overflow streams were taken every half hour, and the specific gravities of the samples were



ZN-1284

Fig. 6. General view - 1" pulse column.

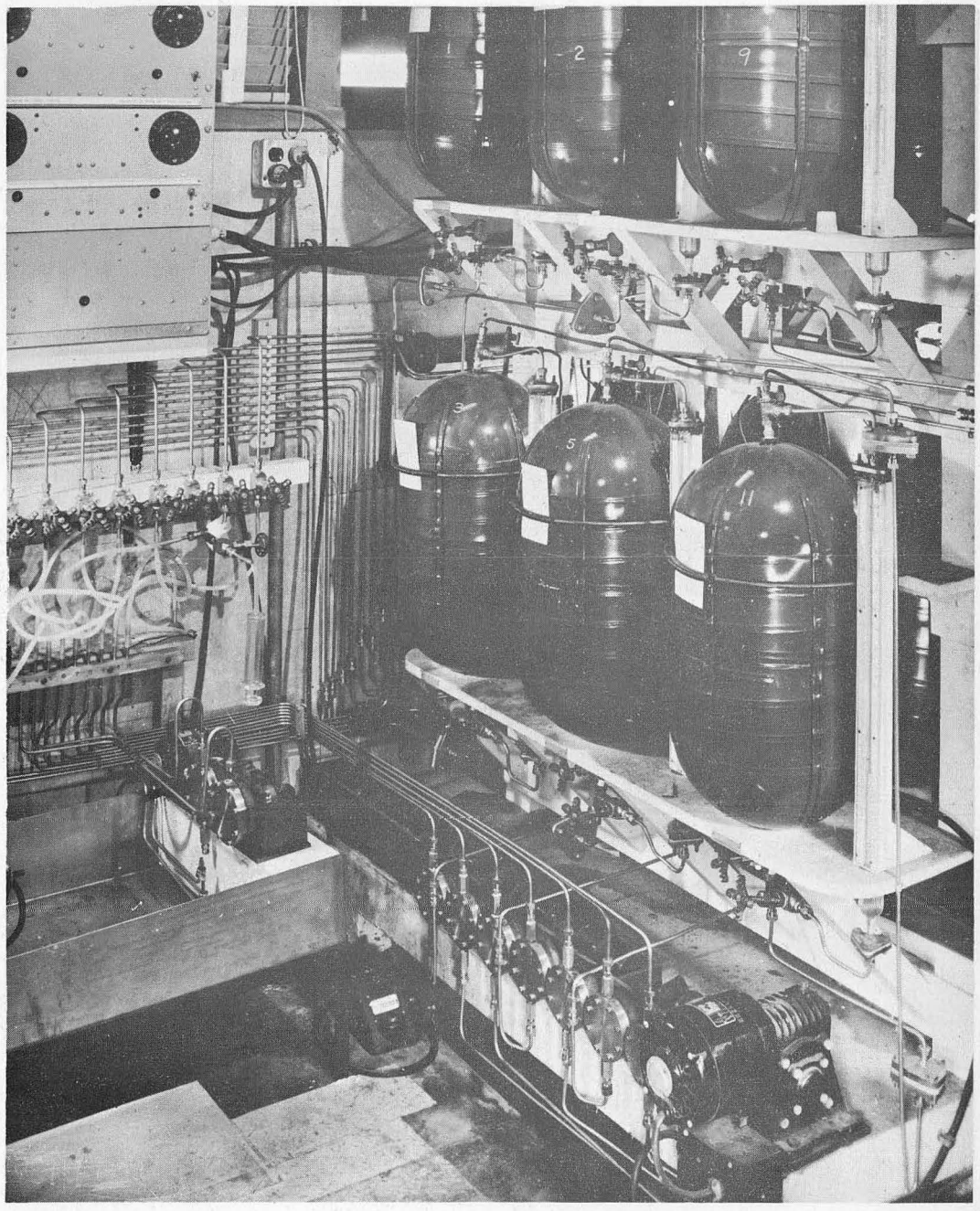


Fig. 6A. Feed tanks and pumps. ZN-1285

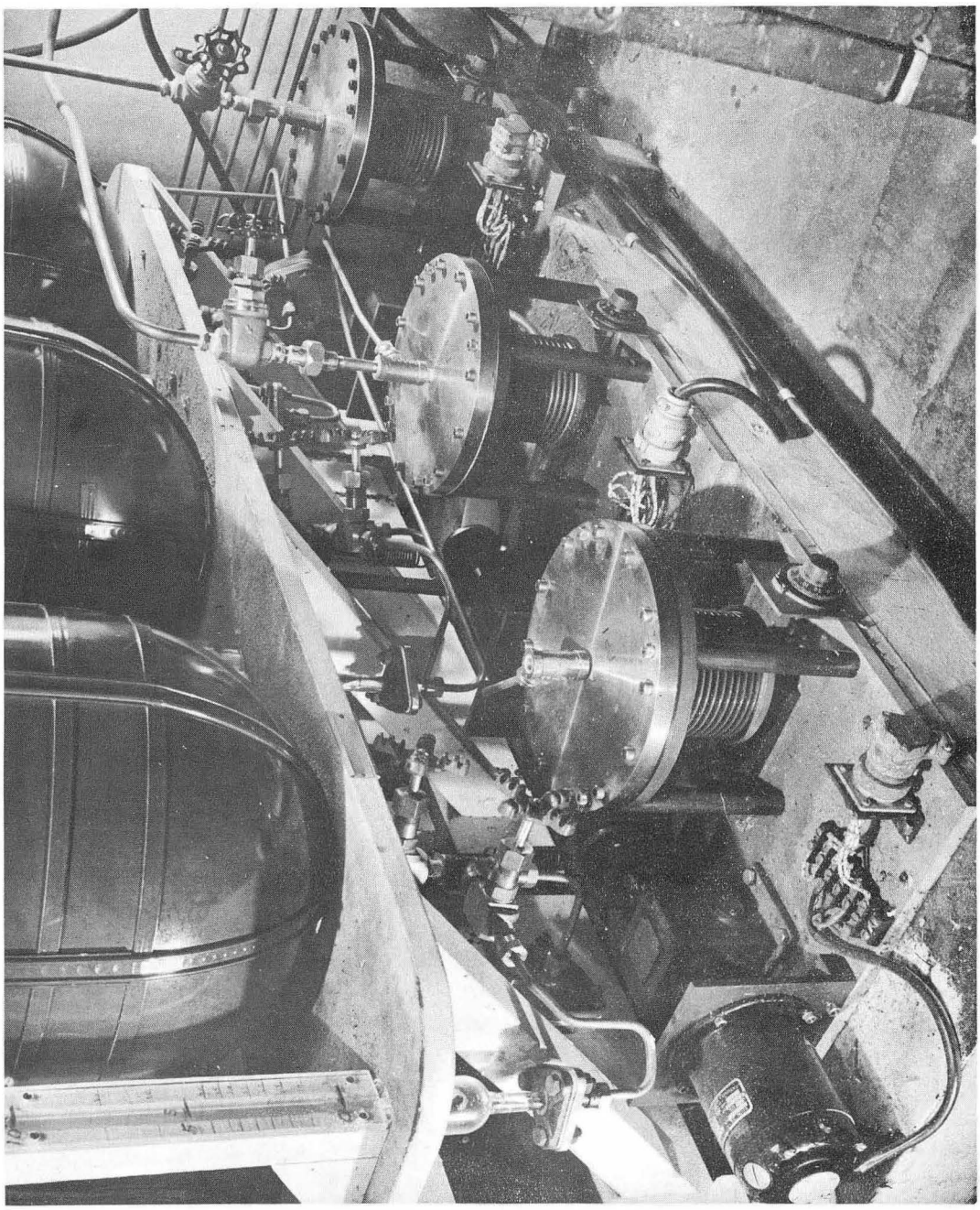


Fig. 6B. Bellows - type pulse pumps.

ZN-1283

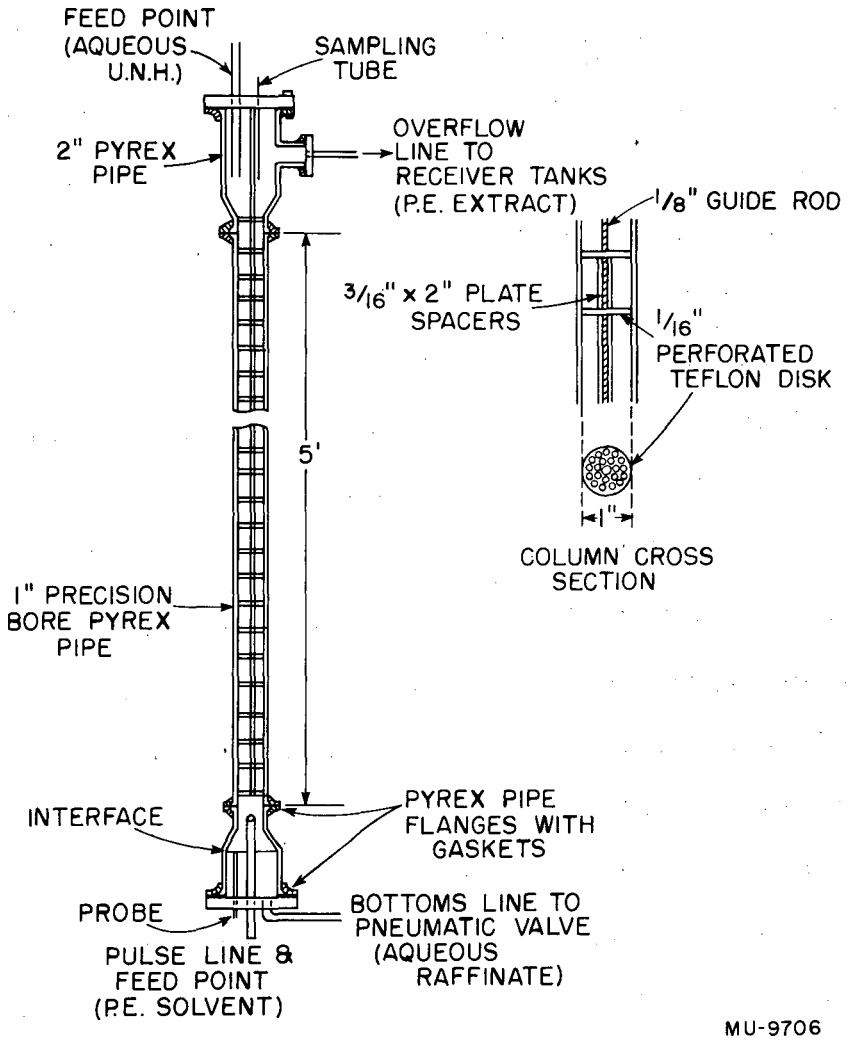


Fig. 7. Bottom-pulsed column for simple extraction.

determined with a Westphal balance. A plot of specific gravity versus time was made for each overflow stream. When the curve drawn through the points for each stream became horizontal it was assumed the column had attained the steady-state condition. Final overflow samples were then taken and the run was terminated. The exact conditions and results of each run are given in Table II.

Center-Feed Extraction. Excellent uranium recovery had been obtained with a center-feed flow scheme in simulated-column batch experiments by Hicks, Mayer, and Crandall.[5] In the study reported here, in order to determine the operating characteristics of the pulse column under similar flow conditions, the column was modified to utilize center feeding, and four experiments were conducted using the same flow ratios as in the previous work. Aqueous solution, approximately 2.0 M in uranyl nitrate and 0.1 N in nitric acid, was introduced as the center feed; organic pentaether solution, approximately 2.0 N in nitric acid, was the bottom feed; and distilled water was fed into the top of the column as scrub. The effective length of the lower extractant section was 62 inches, and that of the upper scrub section was 31.5 inches. In the first two experiments Teflon plates as mentioned above were used throughout, spaced 1 inch apart; in the latter two experiments, the Teflon plates in the scrub section were replaced with stainless steel plates at the same plate spacing. The ratio of the three feeds-- water scrub, center-fed uranyl nitrate-nitric acid solution, and bottom-fed pentaether-nitric acid extractant-- was maintained at 1:2:4 in all runs.

In each experiment the column was operated with the aqueous phase continuous; the interface was maintained at the top of the column, and the tip of the platinum-electrode probe, inserted through the column

headplate, was approximately 6 inches below the organic overflow arm. Sampling tubes were inserted at the center-feed and scrub-feed plates and at the middle of the extraction section. As in the end-fed extraction experiments, the organic overflow was taken off through the side arm of the upper settling section. To define the mass-transfer conditions in the scrub section more precisely, the scrub feed was introduced into the column at the junction of the stripping section and the upper settling section, rather than directly into the settling section. The column setup for these runs is illustrated in Fig. 8.

Re-extraction. Since efficient solvent recovery is an important economic feature of any solvent-extraction process, several column experiments were conducted in which uranium was re-extracted from an organic pentaether phase into an aqueous stream. In these experiments the pulsed aqueous feed was introduced into the column through the top headplate. The uranium-rich organic feed was introduced approximately 1 foot from the bottom of the column at the junction of the lower settling section and the main extraction section. The overflow streams were taken off through the top headplate and bottom baseplate. In order that the pulse action from the top aqueous feed be successfully transmitted to all sections of the column, it was necessary to operate the column completely full of liquid with no air space or vent in the upper settling section. Further, to absorb the pulse shock, small reservoirs containing air locks were placed in the bottom organic feed and aqueous overflow lines quite near the column. To prevent undue loss of pulse through the top overflow, the overflow line was coiled to give additional flow resistance. In all re-extraction experiments the aqueous phase was continuous, the interface being maintained in the

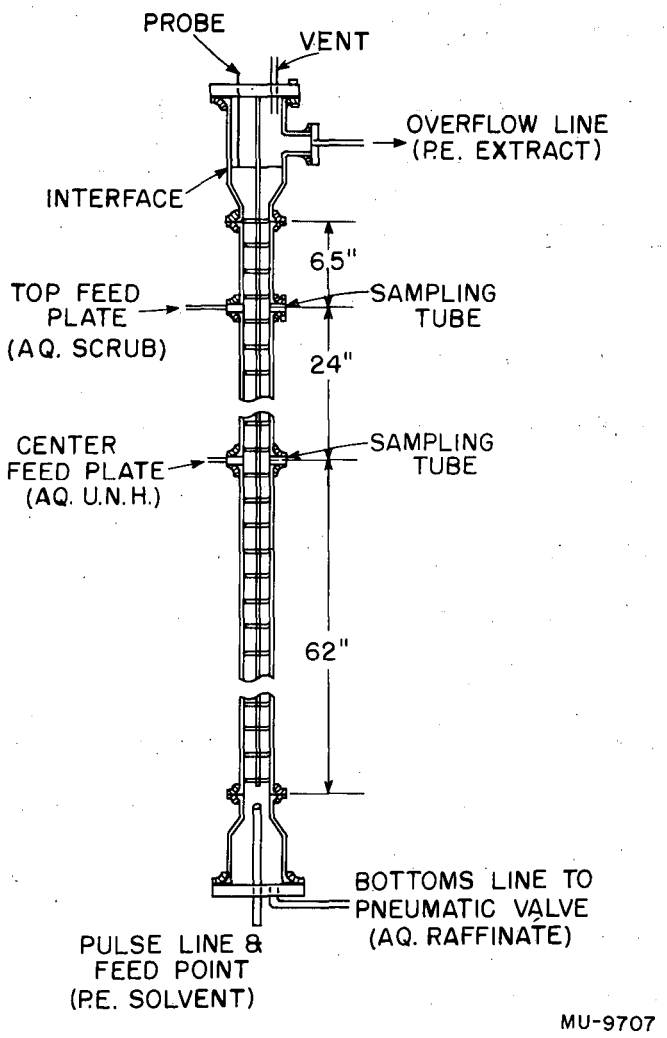


Fig. 8. Center-fed column.

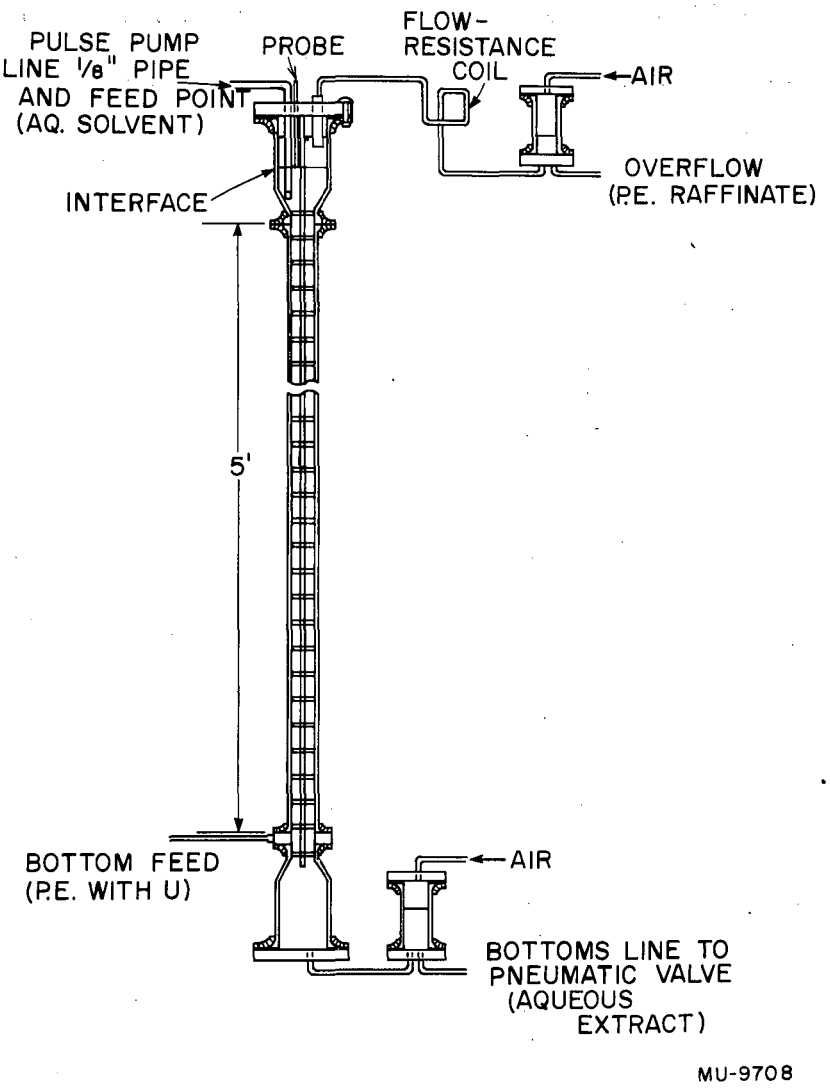


Fig. 9. Top pulsed column for re-extraction.

upper settling section by insertion of the bare platinum-tipped electronic probe through the headplate and adjustment of the bare tip to the proper level.

In these experiments, perforated Teflon plates containing 0.040-inch diameter holes were spaced 1 inch apart in the 5-foot-long effective extraction section of the column. The column setup for these runs is illustrated in Fig. 9. Data and results for these runs are presented in Table II.

Table II-a

PULSE COLUMN EXPERIMENTS

Simple Extraction

Run No.	Cont. Phase	Aqueous Feed Gal Hr/ft^2	UO_2^{++} M	HNO_3 M	Pentaether Feed Gal Hr/Ft^2	UNH M	HNO_3 M	Aqueous Overflow Gal Hr/Ft^2	UO_2^{++} M	HNO_3 M	Pentaether Overflow Gal Hr/Ft^2	UNH M	HNO_3 M
E-1*	PE	44.7	1.35	0.090	59.8	0	1.91	43.2	0.319	2.10	68.8	0.775	0.67
E-2**	PE	43.7	1.51	0.174	58.9	0	1.91	45.2	0.089	2.48	65.6	1.04	0.367
E-3**	PE	43.7	1.51	0.174	59.2	0	1.95	43.7	0.066	2.43	65.6	1.09	0.294

Run No.	Material Balance - % HNO_3	Material Balance - % UO_2^{++}	% Uranium Extracted into P. E. Stream	Pulse Length (inches)	Pulse Frequency (cycles/min)
E-1*	+39.9	+11.7	77.1	0.875	56.3
E-2**	+13.6	- 8.15	94.9	0.312	21.5
E-3**	+ 2.13	+12.3	95.7	0.312	21.5

Remarks

M = molarity

* = 5-foot column, stainless steel plates 0.062-inch perforations, 1-inch spacing.

** = 5-foot column, Teflon plates with 0.040-inch holes, 1-inch spacing.

Table II-b

PULSE COLUMN EXPERIMENTS

Re-Extraction*

Run No.	Cont. Phase	Aqueous Feed Gal/Hr/ft^2	Aqueous Feed UO_2^{++} M	Aqueous Feed HNO_3 M	Pentaether Feed Gal/Hr/ft^2	Pentaether Feed UNH M	Pentaether Feed HNO_3 M	Aqueous Overflow Gal/Hr/ft^2	Aqueous Overflow UO_2^{++} M	Aqueous Overflow HNO_3 M	Pentaether Overflow Gal/Hr/ft^2	Pentaether Overflow UNH M	Pentaether Overflow HNO_3 M
R-1	Aq.	42.6	0	0	31.8	0.660	0.300	56.0	0.366	0.245	29.2	0.0015	0.053
R-2	Aq.	35.9	0	0	31.4	0.660	0.300	45.2	0.416	0.320	27.7	0.0039	0.062
R-3	Aq.	88.9	0	0	76.7	0.416	0.275	93.8	0.340	0.222	81.7	0.0005	0.012
R-4	Aq.	87.8	0	0	78.7	0.536	0.378	107.7	0.392	0.221	75.8	0.0007	0.065
R-5	Aq.	32.5	0	0	33.2	0.512	0.346	43.7	0.392	0.240	25.5	0.0040	0.082
R-6	Aq.	91.0	0	0	75.9	0.484	0.338	105.0	0.350	0.203	73.0	0.0027	0.048
R-7	Aq.	91.7	0	0	77.3	0.484	0.338	118.0	0.361	0.189	66.0	0.0009	0.034

Run No.	Material Balance - % HNO_3	Material Balance - % UO_2^{++}	% Uranium Extracted into Aqueous Stream	Pulse Length (inches)	Pulse Frequency (cycles/min)
R-1	+58.4	+2.1	99.8	1.0	27.0
R-2	+69.7	-8.5	99.5	1.75	23.5
R-3	+3.4	+0.2	99.9	0.94	30.0
R-4	-3.6	-	99.9	0.75	42.5
R-5	+9.5	+1.0	99.4	0.875	42.5
R-6	-3.1	-	99.5	0.75	21.0
R-7	-6.0	+14.5	99.8	0.75	30.0

*5-foot column, inverted feed, aqueous extraction of uranium from PE solution. Teflon plates spaced 1-inch apart containing 0.040-inch perforations.

M = molarity.

Table II-c

PULSE COLUMN EXPERIMENTS

Center Feed Extraction

Run No.	Cont. Phase	Top Aqueous Feed Gal Hr/Ft^2	UO_2^{++} M	HNO_3 M	UNH Center Feed Gal Hr/Ft^2	UNH M	HNO_3 M	Bottom PE Feed Gal Hr/Ft^2	UNH M	HNO_3 M
C-1*	Aq	14.0	0	0	29.2	2.09	0.127	59.5	0.74	2.04
C-2**	Aq	5.8	0	0	14.0	1.92	0.113	25.7	0	1.90
C-3**	Aq	7.3	0	0	13.4	1.92	0.113	28.9	0	1.91
C-4**	Aq	14.6	0	0	30.6	2.04	0.100	67.2	0	1.85

Run No.	PE Overflow Gal Hr/Ft^2	UNH M	HNO_3 M	Aqueous Bottoms Gal Hr/Ft^2	UO_2^{++} M	HNO_3 M	Material Balance HNO_3	Material Balance UO_2^{++}	% U Recovered	Pulse length (in.)	Pulse Freq. (cycles/min)
C-1*	59.9	0.541	0.27	54.0	0.728	2.38	+19.9	+9.8	49.5	2.0	12
C-2**	29.2	0.800	0.50	19.9	0.283	2.00	+8.2	+7.4	86.7	2.0	11
C-3**	30.6	0.708	0.43	21.9	0.184	2.18	+7.4	-0.27	84.3	1.0	34
C-4**	71.5	0.841	0.53	40.8	0.205	2.04	-2.4	+9.8	67.3	1.5	26

Aqueous Phase Column Samples

Scrub Section UO_2^{++} M	Scrub Section HNO_3 M	Extraction Section UNH M	Extraction Section HNO_3 M	Feed Plate UNH M	Feed Plate HNO_3	Run No.
0.87	0.38	1.28	1.11	1.53	0.61	C-1*
0.77	0.74	0.53	1.59	1.00	0.84	C-2**
0.77	0.64	0.54	1.50	1.04	0.78	C-3**
0.82	-	0.50	-	0.97	-	C-4**

Remarks

M = molarity

* = 62-inch extraction section, 31.5-inch rectifying section, 0.040-inch Teflon plates, 1-inch spacing.

**= 1-inch plate spacing, extraction section steel plates, scrub section Teflon plates.

V. CALCULATIONS AND DISCUSSION

In order to facilitate use of the equilibrium data presented in Figs. 2 through 5, concentration plots were made of organic uranium versus aqueous uranium with aqueous nitric acid as a parameter, and of organic acid versus aqueous acid with aqueous uranium as a parameter. These plots are presented in Figs. 10 and 11. Concentration values obtained from the smoothed curves of these plots were then used in the activity calculations. These data are given in Table XI of the Appendix.

Activity Coefficients for Uranyl Nitrate

Theoretical Method. Thermodynamic uranyl nitrate activities were calculated for the three-component system uranyl nitrate-water-pentaether, based on the data obtained by Robinson[3] for the uranyl nitrate-water system and given in Table III.

Table III

Activity Data for Aqueous Uranyl Nitrate

Molarity $c_{u\ell}$	Molality $m_{u\ell}$	Activity Coefficient $\gamma_{u\ell}$	Water Activity a_w
0.098	0.1	0.573	0.995
0.197	0.2	0.543	0.990
0.292	0.3	0.540	0.985
0.482	0.5	0.564	0.973
0.660	0.7	0.616	0.960
0.931	1.0	0.721	0.938
1.361	1.5	0.959	0.896
1.755	2.0	1.288	0.848

The calculations are based on molarities (moles per liter) rather than molalities (moles per 1000 grams solvent). Equation (9) is thus expressed

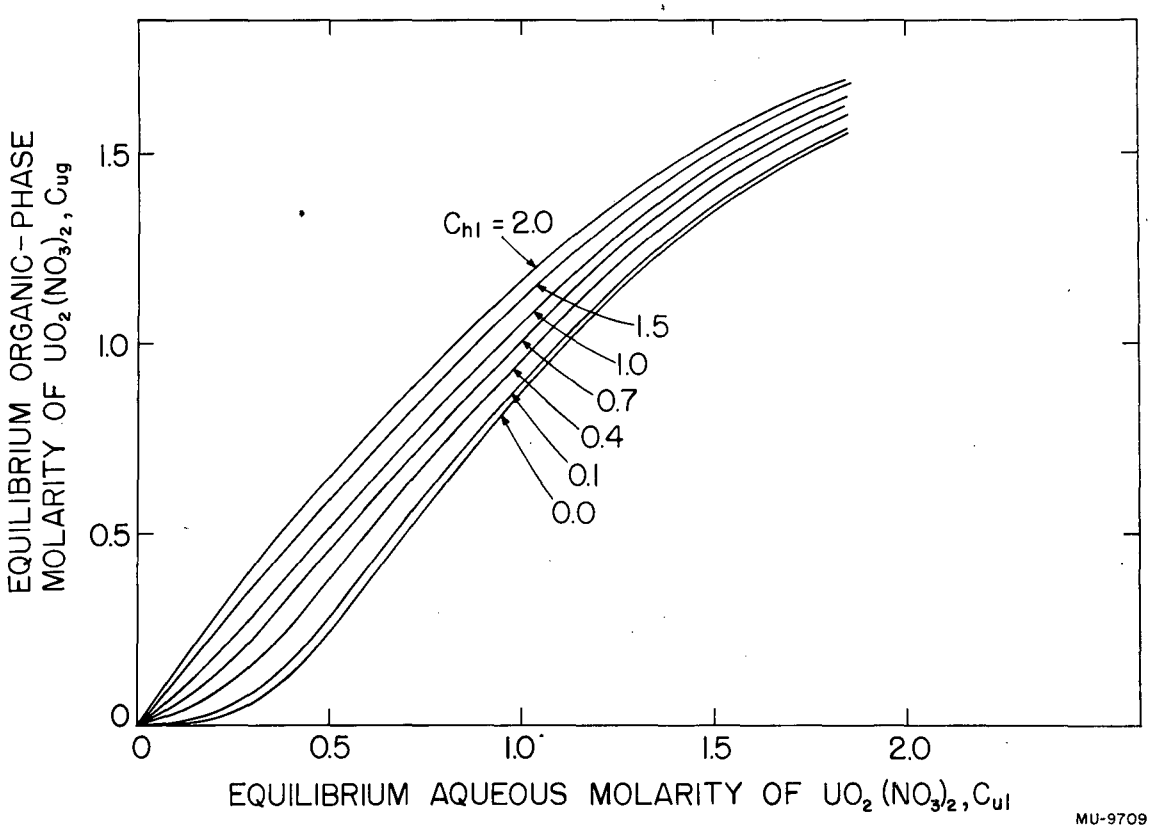


Fig. 10. Uranium distribution at constant aqueous HNO_3.

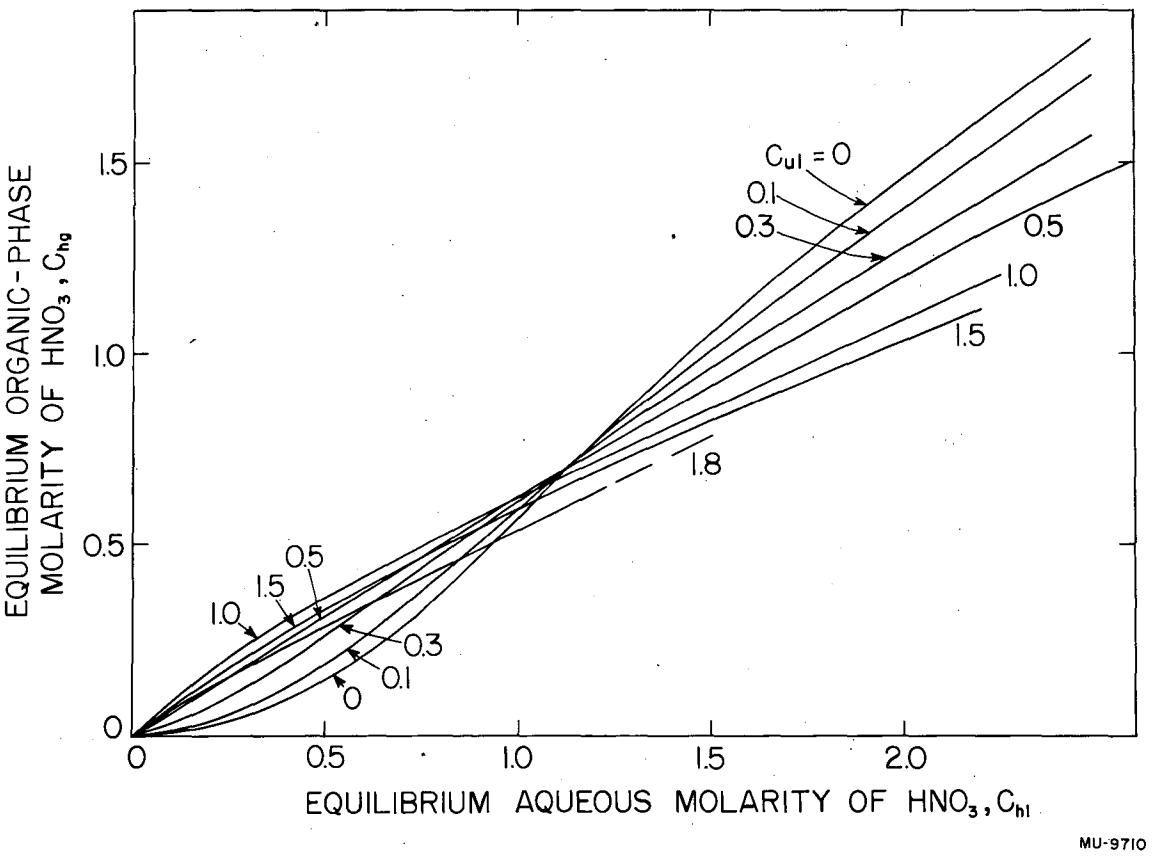


Fig. 11. Nitric acid distribution at constant aqueous $UO_2(NO_3)_2$.

$$c_{u\ell}^{3}\ \gamma_{u\ell}^{3}\ a_{w}^{4} = K_{e}'\ c_{ug}\ \gamma_{ug}. \qquad (61)$$

The uranyl nitrate aqueous activity will be defined

$$a_{u\ell} = \frac{(c_{u\ell}\ \gamma_{u\ell}\ a_{w}^{4/3})^{3}}{K_{e}'} \qquad (62)$$

The organic uranyl nitrate activity coefficients were calculated from the activity data of Table III and our four-component equilibrium data extrapolated to zero acid concentration and given in Table XII of the Appendix. By plotting $c_u\ \gamma_u\ a_w^{4/3}$ versus c_{ug} on logarithmic paper as shown in Fig. 12, we may easily obtain values of γ_{ug}. If the linear portion of the experimental curve is extrapolated, γ_{ug} at any point is equal to the ratio, at fixed $c_u\ \gamma_u\ a_w^{4/3}$, of c_{ug} (extrapolated) to c_{ug} (experimental). The equilibrium constant, K_e, of Eqs. (61) and (62) was calculated from the extrapolated linear curve to be 0.064, thus aqueous activities as defined by Eq. (62) may be determined. The results of the calculations are given in Table IV. For comparison purposes the experimental equilibrium data of Stover and of Glueckauf and associates presented in Tables IX and X of the Appendix are also plotted in Fig. 12.

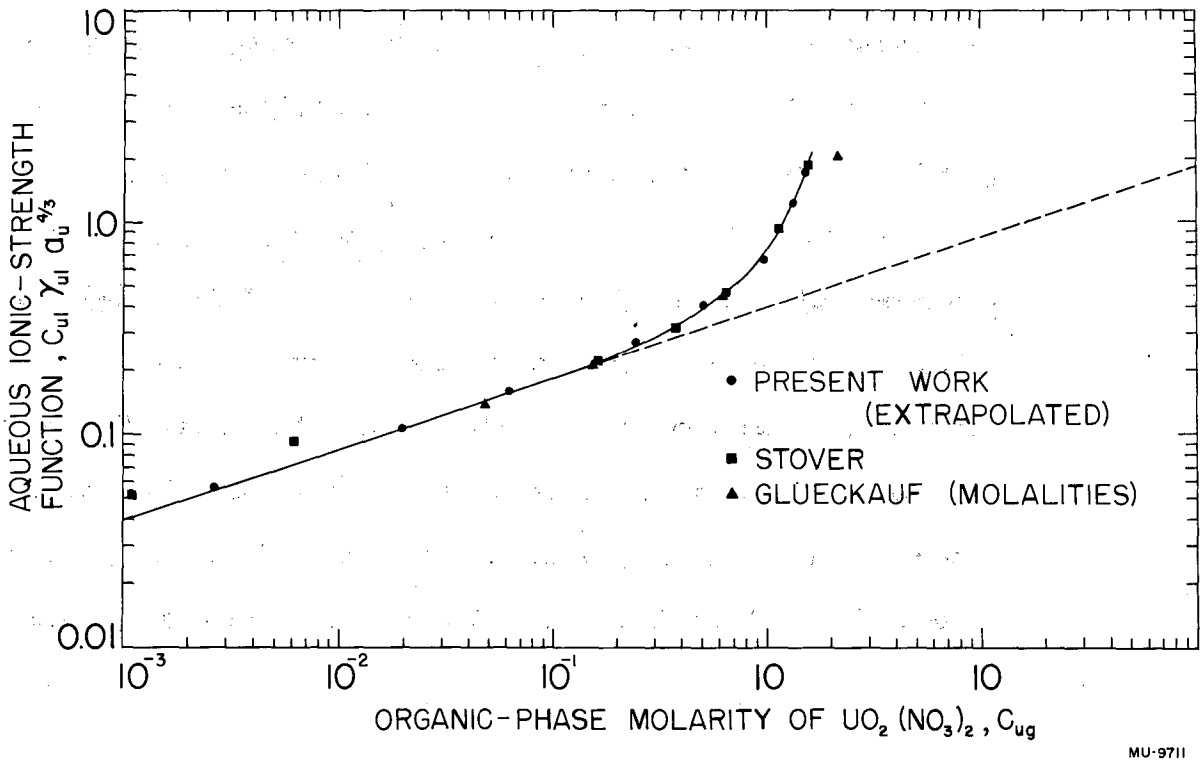


Fig. 12. Partition of uranyl nitrate without free nitric acid.

Table IV

Thermodynamic Activity Data for Uranyl Nitrate - Water - Pentaether System

$UO_2(NO_3)_2$ Molarities*		Aqueous $UO_2(NO_3)_2$	Organic $UO_2(NO_3)_2$
Aqueous, $c_{u\ell}$	Organic, c_{ug}	Activities Eq.(62)	Activity Coeff. γ_{ug}
0.1	0.00264	0.00298	1.0
0.2	0.0198	0.0192	1.0
0.3	0.062	0.0628	1.01
0.5	0.242	0.314	1.155
0.7	0.502	1.05	2.035
1.0	0.872	4.68	5.37
1.5	1.346	29.8	22.2
1.8	1.530	80.9	52.9

*Extrapolated data

In calculating the quantity $c_u \gamma_u a_w^{4/3}$, the activity data of Robinson given in molal units were used at the equivalent molar concentrations also shown in Table III. Since $c_u \longrightarrow m_u$ as $\gamma_{ug} \longrightarrow 1$, therefore, at low concentrations, the calculated equilibrium constant will be the same; however, some error will be introduced into γ_g at moderate and high uranyl nitrate concentrations.

Comparing modified forms of Eqs. (9) and (61), we have

$$c_{u\ell}^2 = \frac{K'_e (\gamma_{ug})_c}{(\gamma_{u\ell})_c^3} \quad \frac{c_{ug}}{c_{u\ell}} \quad \frac{1}{a_w^4} \tag{63}$$

and

$$m_{u\ell}^2 = \frac{K'_e (\gamma_{ug})_m}{(\gamma_{u\ell})_m^3} \cdot \frac{m_{ug}}{m_{u\ell}} \quad \frac{1}{a_w^4} \quad , \tag{64}$$

where the activity coefficient subscripts c and m refer to molar and molal units respectively.

Also, since

$$\frac{c_{ug}}{c_{u\ell}} = \frac{m_{ug}}{m_{u\ell}} , \tag{65}$$

and if we incorporate a_w^4, which is near unity, into a new equilibrium constant K''_e, then

$$c_u^2 = K''_e \frac{(\gamma_{ug})_c}{(\gamma_{u\ell})_c^3} \tag{66}$$

and

$$m_u^2 = K''_2 \frac{(\gamma_{ug})_m}{(\gamma_{u\ell})_m^3} . \tag{67}$$

Since we have $m_u^2 > c_u^2$ for equivalent concentrations, $(\gamma_u)_c$ must be greater than $(\gamma_u)_m$ to preserve K''_e, which is constant for both Eqs. (66) and (67).

In the light of the latest careful study of aqueous uranyl nitrate solutions by Robinson and Lim,[8] the activity data of Robinson in Table III should be reduced by 4% to 5%. Thus the data, when used as described, will automatically include a correction factor for the molar units.

Further, when our data were converted to their equivalent molal concentrations and used with the data of Robinson, the final correlation obtained was less satisfactory in that there was a greater spread in the data from the smooth curves of Fig. 13 and Fig. 14.

In calculating activity data for the four-component system it was assumed as before that pentaether is essentially insoluble in the aqueous phase and that the aqueous activity would be proportional to the ionic strength. Substituting molar units in Eq. (62), we have

$$a_u = \frac{\left[\left(c_{u\ell} + \frac{1}{3} c_{h\ell}\right)\left(\gamma_{u\ell} a_w^{4/3}\right)\right]^3}{K'_e} \tag{68}$$

The values of $\gamma_{u\ell}$ and a_w given in Table III for various aqueous

uranyl nitrate concentrations were then applied to aqueous acetic-uranyl nitrate solutions of equivalent ionic strength ($c_{u\ell} + c_{h\ell}/3$). Aqueous uranyl nitrate activities were then calculated using our equilibrium data and setting $K'_e = 0.064$ as previously determined. Since at equilibrium we have $a_{u\ell} = a_{ug}$ and $a_{ug} = c_{ug}\gamma_{ug}$, the organic uranyl nitrate activity coefficients were easily calculated. The results were graphically correlated by plotting $(c_{u\ell} + \frac{c_{h\ell}}{3})$ and $(c_{ug} + \frac{c_{hg}}{3})$ against $\gamma_{ug} - 1$ on logarithmic paper as illustrated in Figs. 13 and 14. The tabulated results are presented in Table V.

Table V

Thermodynamic Uranyl Nitrate-Activity Data for the System Uranyl Nitrate-Water - Pentaether - Nitric Acid - 25°C

Aqueous Phase Molarities			Organic Phase Molarities			Organic $UO_2(NO_3)_2$ Activity Coeff - 1
UO_2^{++}	HNO_3	$UO_2^{++} + (HNO_3/3)$	UO_2^{++}	HNO_3	$UO_2^{++} + (HNO_3/3)$	$\gamma_{ug} - 1$
0.5	0.5	0.667	0.419	0.315	0.524	1.05
0.5	1.0	0.833	0.522	0.621	0.729	3.08
0.5	1.5	1.000	0.602	0.903	0.903	6.58
1.0	0.5	1.167	0.974	0.362	1.095	8.23
1.0	1.0	1.333	1.052	0.621	1.259	14.7
1.0	1.5	1.500	1.117	0.849	1.400	25.8
1.5	0.5	1.667	1.418	0.333	1.529	34.3
1.5	1.0	1.833	1.469	0.586	1.664	58.2
1.5	1.5	2.000	1.508	0.822	1.782	89.9

Empirical Method. The calculations may be conveniently broken down into four steps as follows.

(1) Calculation of the infinitely dilute reference activity coefficients.

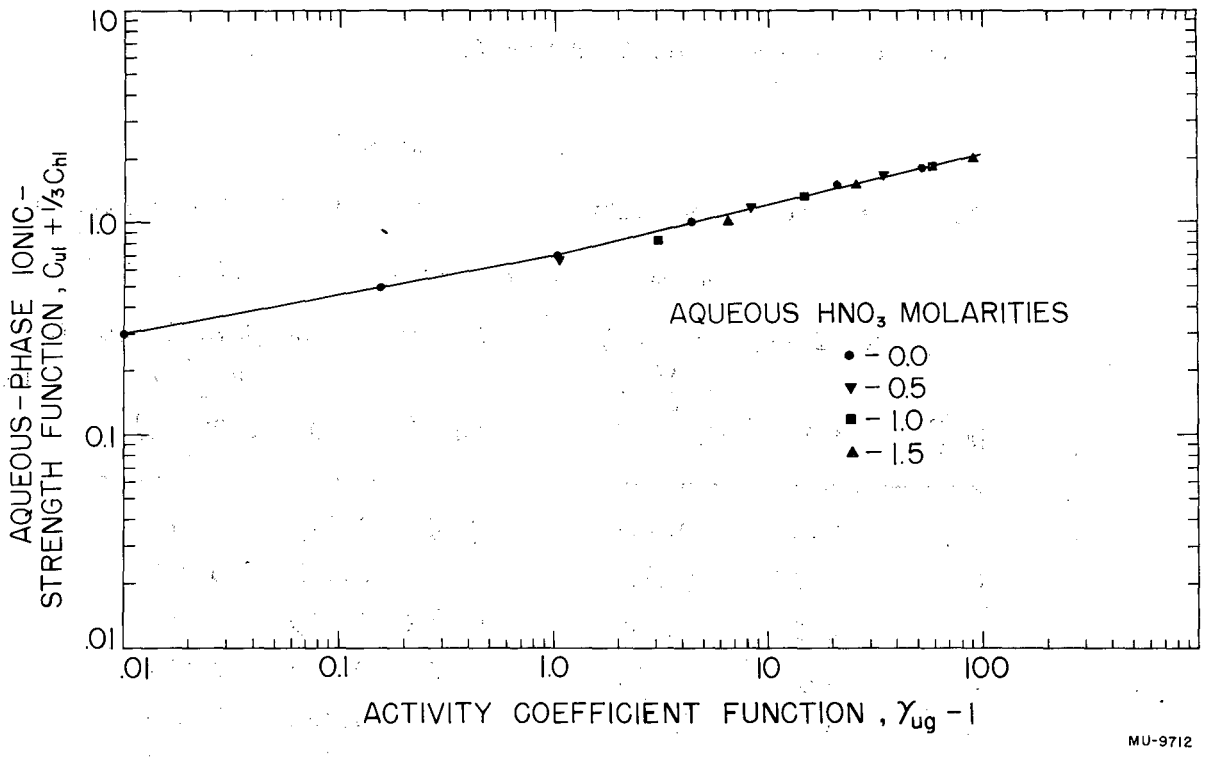


Fig. 13. Organic-phase activity coefficients for $UO_2(NO_3)_2$ in relation to aqueous-phase ionic strength.

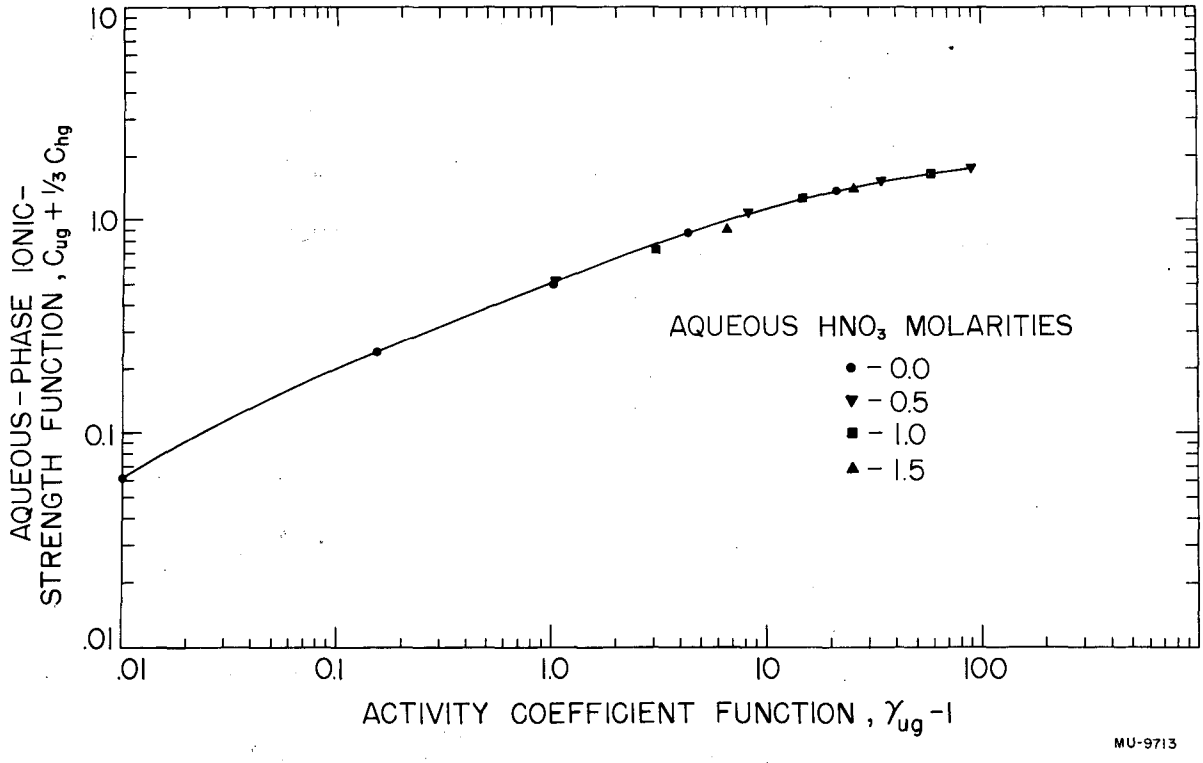


Fig. 14. Organic-phase activity coefficients for $UO_2(NO_3)_2$ in relation to organic-phase ionic strength.

(2) Calculation of the constants needed to satisfy infinitely dilute acid conditions.

(3) Calculation of the constants required to satisfy infinitely dilute uranyl nitrate conditions.

(4) Calculation of constants on cross-product terms required to satisfy all other conditions.

It is convenient in most cases to set the activity coefficient of the organic phase equal to unity at infinite dilution. Inspection of the zero acid uranium distribution curve in Fig. 10 shows that the curve approaches the point of infinite dilution asymmetrically along the aqueous axis. Therefore, the activity coefficient in the infinitely dilute aqueous solution was taken as zero. Thus at infinite dilution,

$$(E_u^o)_{h=0} = \frac{\gamma_{u\ell}^o}{\gamma_{ug}^o} = \frac{0}{1} = 0. \qquad (69)$$

For uranyl nitrate in the absence of acid, the equation for the uranium distribution coefficient is expressed:

$$(E_u)_{h=0} = \frac{c_{ug}}{c_{u\ell}} = \left(\frac{\gamma_{u\ell}}{\gamma_{ug}}\right)_{h=0} = \frac{A'c_{u\ell} + B'c_{u\ell}^2 + C'c_{u\ell}^3}{1 + Ac_{ug} + Bc_{ug}^2}. \qquad (70)$$

Equating on activities through Eq. (13), Eq. (70) becomes

$$c_{ug} + Ac_{ug}^2 + Bc_{ug}^3 = A'c_{u\ell}^2 + B'c_{u\ell}^3 + C'c_{u\ell}^4 \qquad (71)$$

The constants of Eq. (71) were determined by substituting equilibrium values taken from the zero acid curve of Fig. 5 and using a modified method of averages. This consisted of solving five simultaneous equations. The first equation was written for 0. M aqueous uranium, the second was the sum of three equations written for 0.2, 0.3, and 0.4 M aqueous uranium respectively, the third was the sum of five equations written for 0.5, 0.6,

0.7, 0.8, and 0.9 M aqueous uranium respectively, the fourth was the sum of five equations written for 1.0, 1.1, 1.2, 1.3, and 1.4 M aqueous uranium respectively, and the fifth and last simultaneous equation was the sum of five equations written for 1.5, 1.6, 1.7, 1.8, and 1.9 M aqueous uranium respectively. Solving the equations, we may express the uranium activity coefficient equations in the absence of acid:

$$(\gamma_{u\ell})_{h=0} = 0.01347\ c_{u\ell} + 2.59928\ c^2_{u\ell} - 0.92343\ c^3_{u\ell}\ , \qquad (72)$$

$$(\gamma_{ug})_{h=0} = 1 + 0.22786\ c_{ug} + 0.96423\ c^2_{ug}\ . \qquad (73)$$

It is necessary to take the 0.1 M aqueous uranium point for one of the simultaneous equations because of the very low concentration of organic uranyl nitrate at this point. If this point is incorporated with several others as in the subsequent simultaneous equations, the value for organic uranium is so low as to have no significant effect in the simultaneous equation thus formed and the constants resulting from such a solution will yield appreciable error in the very low concentration region.

Distribution coefficients expressed as $\frac{\gamma_{u\ell}}{\gamma_{ug}}$ were calculated by substituting the equilibrium data used in formation of the simultaneous equations into Eqs. (72) and (73) and compared to the values given by $E_u = \frac{c_{ug}}{c_{u\ell}}$. For the 19 points the probable error as expressed by the Gaussian distribution law was 0.00304 or 0.593%. The maximum error was 0.008 at 0.4 M aqueous uranium equivalent to 2.37%.

Solutions for Eq. (71) were also obtained by solving five simultaneous equations written for five selected points and by the method of least squares. In both cases the constants obtained yielded solutions having a greater average probable error than the solution obtained by

the previously described modified method of averages. A weighted-least-squares method was also attempted; however, the results were poor, since no satisfactory method was found for weighing each point in the construction of the normal equations. Although polynomial equations of the type $y = f(x)$ are readily solvable by the weighted-least-square method, a general least-square method has not yet been developed which can adequately handle equations of the type $f(y) = f(x)$ where $f(y)$ and $f(x)$ are polynomials in x and y respectively.[9]

In infinitely dilute uranium solutions, the uranium distribution coefficient may be expressed:

$$E_u^o = \left(\frac{\partial c_{ug}}{\partial c_u}\right)_h \text{ as } c_u \longrightarrow 0 = \frac{D' c_h \ell + E' c_h^2 \ell + F' c_h^3 \ell}{1 + D\, c_{hg} + E\, c_{hg}^2} \quad . \qquad (74)$$

where D, E, D', E', and F' are constants to be determined. In order to solve Eq. (74) values of E_u^o were obtained from the uranium distribution curves of Fig. 10 at the point of infinite dilution and plotted as a function of nitric acid concentration as illustrated in Fig. 15. Points from the smooth curve of Fig. 15 were then used to calculate the constants in Eq. (74), by the modified method of averages previously described to yield Eq. (75):

$$E_u^o = \frac{0.50235 c_h \ell + 0.35578 c_h^2 \ell - 0.12098 c_h^3 \ell}{1 - 0.10449\, c_{hg} + 0.10242\, c_{hg}^2} \quad . \qquad (75)$$

Comparison of calculated distribution coefficients using Eq. (75) with the 20 selected points from Fig. 15 gave a probable error based on the Gaussian distribution law of 0.272% and a maximum error of 0.91%.

If cross-product terms in the activity coefficients are neglected, the general activity equations for aqueous and organic uranium are now expressed:

$$a_{u\ell} = c_{u\ell}(0.01347c_{u\ell} + 2.59928c_{u\ell}^2 - 0.92343c_{u\ell}^3 + 0.502.35_{h\ell} + 0.35578c_{h\ell}^2 - 0.12098c_{h\ell}^3, \quad (76)$$

$$a_{ug} = c_{ug}(1 + 0.22786c_{ug} + 0.96428c_{ug}^2 - 0.10449c_{hg} + 0.10242c_{hg}^2) \quad . \quad (77)$$

In order to determine the necessary cross-product terms for the activity coefficients, the uranium activities were calculated for both phases using the above equations and data from thirty-six selected equilibrium points of Figs. 10 and 11. These data are presented in Table XI of the Appendix. The difference between the calculated aqueous and organic uranium activities for each equilibrium point -- as given by Eqs. (76) and (77) -- was then attributed to cross-product terms in the activity coefficients. Since the equations for the aqueous and organic activity coefficients as so far developed contain no higher-order terms than third and second order respectively, it was assumed that the cross-product terms would be of no higher order. Thus the available cross-product terms for the aqueous activity coefficient were $c_{u\ell}h_{u\ell}$, $c_{u\ell}^2 h_{u\ell}$ and $c_{u\ell}h_{u\ell}^2$. The only term available for the organic activity coefficient was $c_{ug}\ h_{ug}$.

If corrections are to be applied to each phase, some knowledge must be had of the error in each phase in order that the coefficients for the cross-product terms for each phase may be calculated independently. If this restriction is not imposed, the only remaining restriction is that the difference between the activity corrections resulting from cross-product activity coefficient terms will equal the difference given by Eq. (76) and (77) for equilibrium points. Coefficients calculated in this manner may be very large which, would yield activity corrections to Eqs. (76) and (77) entirely out of proportion to the activities calculated without cross-product correction terms.

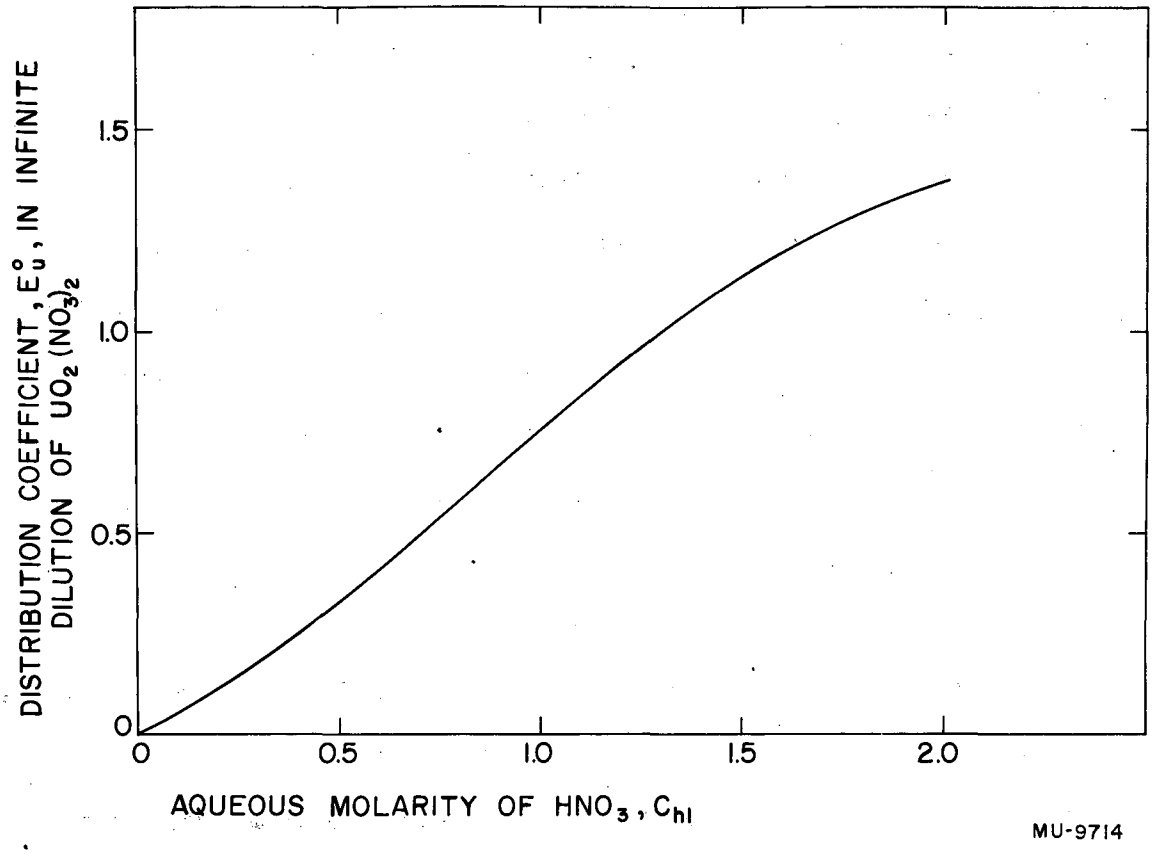


Fig. 15. Effect of HNO_3 upon extrapolated uranium distribution coefficients.

Since there is no method of determining which equation is more nearly correct, it was postulated that greater deviations from the limiting conditions could be expected from polar solutions, therefore, all the error was charged to the aqueous phase. This is considered valid, since all activities and activity coefficients calculated from the final equations are only relative values, and as long as they fulfill the conditions of the defining equations they are justified.

In order to calculate the coefficients of the aqueous activity-coefficient cross-product terms $c_{u\ell}^2 c_{h\ell}$ and $c_{u\ell} c_{h\ell}^2$, the activity differences as calculated from Eqs. (76) and (77) for the thirty-six selected equilibrium points were divided by $c_{u\ell} c_{h\ell}$. These results were then plotted on coordinate paper as a function of $c_{u\ell}$ with $c_{h\ell}$ as a parameter and as a function of $c_{h\ell}$ with $c_{u\ell}$ as a parameter. The average slopes of these curves in the more concentrated regions of the plots were read as -0.15 and -0.12 respectively. Thus, two of the activity-coefficient cross-product terms were established as $-0.15\ c_{u\ell}^2 c_{h\ell}$ and $-0.12\ c_{u\ell} c_{h\ell}^2$. After these correction terms were applied to the equations, the activity difference for the thirty-six selected equilibrium points was again calculated. The remaining difference was then charged to the aqueous activity coefficient term $c_{u\ell} h_{u\ell}$, and by application of the method of averages it was found that the correction $0.273\ c_{u\ell} h_{u\ell}$ best fit the data. The final uranium activity coefficients are then expressed:

$$\gamma_{u\ell} = 0.01347\ c_{u\ell} + 2.59928\ c_{u\ell}^2 - 0.92343\ c_{u\ell}^3 + 0.50235\ c_{h\ell} + 0.35578\ c_{h\ell}^2 - 0.12098\ c_{h\ell}^3 + 0.273\ c_{u\ell} c_{h\ell} - 0.15\ c_{u\ell}^2 c_{h\ell} - 0.12\ c_{u\ell} c_{h\ell}^2, \quad (78)$$

$$\gamma_{ug} = 1 + 0.22786\ c_{ug} + 0.96423\ c_{ug}^2 - 0.10449\ c_{hg} + 0.10242\ c_{hg}^2, \quad (79)$$

where

$$a_u = a_{ug},\ a_{u\ell} = c_{u\ell}\gamma_{u\ell},\ a_{ug} = c_{ug}\gamma_{ug}.$$

For the eighteen selected equilibrium points in which the aqueous uranium concentration was equal to or greater than 1.0 M, the maximum percent variation based on the organic phase between the calculated organic and aqueous uranium activities using Eqs. (78) and (79) was -3.93%, the standard deviation was 1.29%, and the probable error was 1.09%.

For the eighteen equilibrium points where the aqueous uranium concentration was less than 1.0 M, the standard deviation based on the organic phase was 7.74%, the deviation being greater than 10% in four cases. It was found at a late stage that addition of a constant numerical term to the aqueous activity coefficient considerably reduced the error in this range. This term was not evaluated in conjunction with the other constants, but a value of 0.05 was found by inspection to apply with the constants as previously determined for Eq. (78). For acidic aqueous uranyl nitrate solutions in the concentration range 0.05 M to 0.75 M, the preferred equation for uranium activity becomes

$$\begin{aligned} a_{u\ell} = c_{u\ell}\,(&0.05 + 0.01347\,c_{u\ell} + 2.59928\,c_{u\ell}^2 - 0.92343\,c_{u\ell}^3 + \\ &0.50235\,c_{h\ell} + 0.35578\,c_{h\ell}^2 - 0.12098\,c_{h\ell}^3 + 0.273\,c_{u\ell}\,c_{h\ell} - \\ &0.15\,c_{u\ell}^2\,c_{h\ell} - 0.12\,c_{u\ell}\,c_{h\ell}^2\,) \end{aligned} \qquad (80)$$

Eq. (80) has a standard deviation based on the organic phase of 3.91%, a probable error based on Gaussian distribution of 3.30%, and a maximum error of 7.79% for seventeen selected points. Where the uranyl nitrate and nitric acid concentrations in the aqueous phase are both equal to or less than 0.1 M, Eq. (79) again applies.

Development of Empirical Equations for Nitric Acid Activity

In order to evaluate the nitric acid distribution coefficient in infinitely dilute solutions, the slope of the zero uranium acid distribution curve of Fig. 11 was read as 0.015 at the point of infinite dilution. Since the reference value of 1 was established for the activity coefficient in infinitely dilute organic solutions, the corresponding activity coefficient for the infinitely dilute aqueous solution becomes 0.015; therefore, at infinite dilution we have

$$(E_h^o)_u = 0 = \frac{\gamma_h^o}{\gamma_{hg}^o} = 0.015. \qquad (81)$$

For nitric acid in the absence of uranium, the equation for the acid distribution coefficient may now be expressed

$$(E_h)_{u=0} = \frac{c_{hg}}{c_h} = \left(\frac{\gamma_h}{\gamma_{hg}}\right)_{u=0} = \frac{0.015 + A'c_h + B'c_h^2 + C'c_h^3}{1 + Ac_{hg} + Bc_{hg}^2} \qquad (82)$$

If we equate activities through Eq. (13), Eq. (82) becomes

$$c_{hg} + Ac_{hg}^2 + Bc_{hg}^3 = 0.015\ c_{h\ell} + A'c_{h\ell}^2 + B'c_{h\ell}^3 + C'c_{h\ell}^4 \quad . \qquad (83)$$

The constants of Eq. (82) were determined by substituting equilibrium values taken from the zero uranium curve of Fig. 11 into Eq. (83) and solving for the constants, using the previously described method of averages. The equations for the nitric acid activity coefficients for the aqueous and organic phases respectively become

$$\gamma_{h\ell} = 0.015 + 0.56211\ c_{h\ell} - 0.08795\ c_{h\ell}^2 + 0.03014\ c_{h\ell}^3 \quad , \qquad (84)$$

$$\gamma_{hg} = 1 - 0.41985\ c_{hg} + 0.47871\ c_{hg}^2 \qquad (85)$$

In infinitely dilute nitric acid solutions, the nitric acid distribution coefficient may be expressed

$$(E_h^o)_{h=0} = \left(\frac{c_{ug}}{c_{u\ell}}\right)_{h=0} = \frac{0.015 + D'c_{u\ell} + E'c_{u\ell}^2 + F'c_{u\ell}^3}{1 + D\,c_{ug} + E\,c_{ug}^2} \quad , \qquad (86)$$

where D', E', F', D and E are constants to be determined. In order to solve Eq. (86) one reads values of E_h^o as the slopes of the acid distribution curves of Fig. 11 at the point of infinite dilution and plotted as a function of aqueous uranyl nitrate as illustrated in Fig. 16. Points from the smooth curve of Fig. 16 were then used to calculate the constants of Eq. (86) by the method of averages, and gave

$$(E_h^o)_{h=0} = \frac{0.015 + 0.17834\,c_{u\ell} + 2.96113\,c_{u\ell}^2 - 1.36182\,c_{u\ell}^3}{1 + 0.51709\,c_{ug} + 0.76608\,c_{ug}^2} \qquad (87)$$

When cross-product terms in the activity coefficients are neglected, the general activity equations for nitric acid in the aqueous and organic phases respectively are

$$a_{h\ell} = c_{h\ell}\,(0.015 + 0.56211\,c_{h\ell} - 0.08795\,c_{h\ell}^2 + 0.03014\,c_{h\ell}^3 + 0.17834\,c_{u\ell} + 2.96113\,c_{u\ell}^2 - 1.36182\,c_{u\ell}^3) \quad , \qquad (88)$$

$$a_{hg} = c_{hg}\,(1 - 0.41985\,c_{hg} + 0.47871\,c_{hg}^2 + 0.51709\,c_{uh} + 0.76608\,c_{ug}^2 . \qquad (89)$$

In order to calculate the coefficients for the activity coefficient cross-product terms, the activity differences R calculated from Eqs. (88) and (89) for the thirty-six equilibrium points were equated to cross-product terms, and the equation was divided by $c_h^2\,c_u$ to yield:

$$L + M\,c_{u\ell} + N\,c_{h\ell} - O\,\frac{c_{hg}^2 c_{ug}}{c_{h\ell}^2\,c_{u\ell}} = R/c_{h\ell}^2\,c_{u\ell} = R' \; . \qquad (90)$$

With use of the data from the thirty-six selected equilibrium points, Eq. (90) was solved by the method of least squares.[9] The nitric-acid activity equations then become for the aqueous and organic phases, respectively,

$$a_{h\ell} = c_{h\ell}\,(0.015 + 0.56211\,c_{h\ell} - 0.08795\,c_{h\ell}^2 + 0.03014\,c_{h\ell}^3 + 0.17834\,c_{u\ell} + 2.96113\,c_{u\ell}^2 - 1.36182\,c_{u\ell}^3 + 0.30207\,c_{h\ell}\,c_{u\ell} - 0.14890\,c_{h\ell}\,c_{u\ell}^2 + 0.02885\,c_{h\ell}^2\,c_{u\ell}), \quad (91)$$

$$a_{hg} = c_{hg}\,(1 - 0.41985\,c_{hg} + 0.47871\,c_{hg}^2 + 0.51709\,c_{ug} + 0.76608\,c_{ug}^2 + 1.75474\,c_{ug}\,c_{hg}) \quad (92)$$

Although the activity equations (91) and (92) are an improvement over the activities calculated from Eqs. (88) and (89), they do not represent the best solutions obtainable, since it is not possible to use a weighted least square in the solution. Therefore, to improve further the equations, additional corrections were made to the aqueous activity-coefficient equation.

Activity differences, R'', were calculated for the thirty-six equilibrium points using Eqs. (91) and (92), divided by $c_{u\ell}\,c_{h\ell}$, and the results plotted as a function of $c_{u\ell}$. The equation for the smooth curve drawn through the points as calculated by the method of averages is expressed

$$R'' = c_{u\ell}\,c_{h\ell}\,(0.34237 - 1.18348\,c_{u\ell} + 0.59811\,c_{u\ell}^2). \quad (93)$$

The general activity equation for aqueous nitric acid then becomes

$$a_{h\ell} = c_{h\ell}\,(0.015 + 0.56211\,c_{h\ell} - 0.08795\,c_{h\ell}^2 + 0.03014\,c_{h\ell}^3 + 0.52071\,c_{u\ell} + 1.77765\,c_{u\ell}^2 - 0.76371\,c_{u\ell}^3 + 0.30207\,c_{h\ell}\,c_{u\ell} - 0.14890\,c_{h\ell}\,c_{u\ell}^2 + 0.02885\,c_{h\ell}^2\,c_{u\ell}). \quad (94)$$

It should be noted that the final corrections to the aqueous acid activities do not disappear in the limiting case when the acid concen-

tration approaches zero. Therefore, new values of E_h^o were calculated from Eq. (86) and plotted on coordinate paper as a function of the aqueous uranyl nitrate concentration. Comparison of the original extrapolated values with the revised values of E_h^o are shown in Fig. 16.

Comparison of organic and aqueous acid activities calculated from equations (92) and (94) for the thirty-six selected equilibrium points showed the probable error to be 3.37% and the standard deviation 3.99%, both based on the organic activity. In three cases the error was greater than 10%. Two of these were for 0.1 N aqueous acid solutions where the uranyl nitrate concentration was respectively 0.3 M and 1.0 M. The calculated activity differences for these two points were respectively 0.005 and 0.022. Such small differences are certainly within the error limits of the equations, since the data used in deriving the equations cannot be considered valid beyond the second decimal place.

The third error of greater than 10% was obtained for the equilibrium point where the aqueous concentrations were 2.0 N and 1.0 M for nitric acid and uranyl nitrate respectively. Since this represents the limit of the range for which data were available, the derived activity equations may naturally be expected to yield greater errors in this region. Complete data are presented in Table XI of the Appendix.

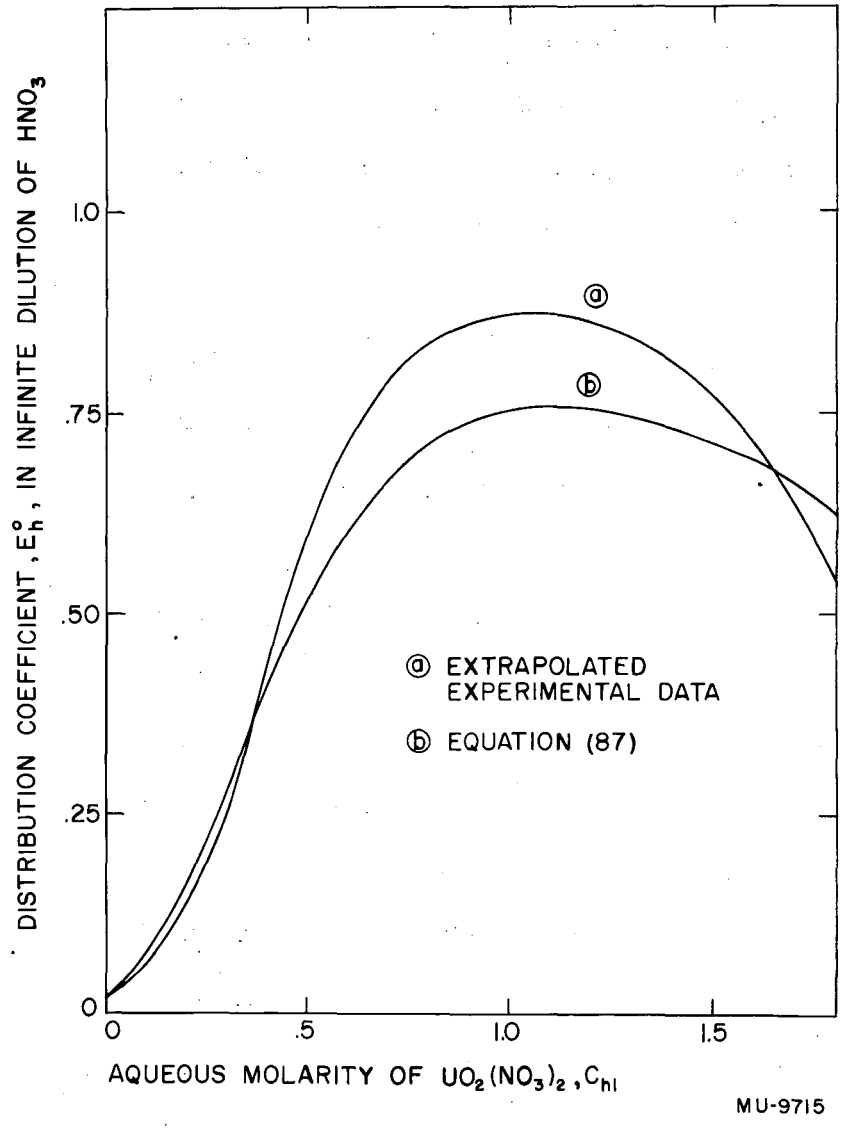


Fig. 16. Effect of $UO_2(NO_3)_2$ upon extrapolated nitric-acid distribution coefficients.

Tower Calculations

Because the material balances obtained in the several runs were poor, calculations were made only on pulse-column Run #46-I-11, principally to illustrate the method of calculating multicomponent transfer systems, rather than to obtain significant engineering data.

Operating Data. Material balances based on measured flow rates and concentrations failed to balance by only + 0.27% for uranyl nitrate and by - 7.42% for nitric acid, when a positive quantity refers to gain in the tower. Since only aqueous-phase samples were obtained from the several sample points within the column, the corresponding organic concentrations were calculated by material balance. Further, it was assumed for the aqueous-phase sample from the feedplate that mixing with the feed had not yet occurred. Since a small volume change occurs in the system, it was also necessary to assume minor changes in flow rates at the several sample points within the column. The measured overflow and feed rates and the assumed internal flow rates, together with aqueous sample analyses and calculated organic concentrations are shown in Fig. 17. Flow rates are given in gal/hr/ft^2.

In order to obtain additional operating data for other points in the tower for use in transfer unit calculations, plots were made on the same coordinate grid and scale of $c_{u\ell}$ versus c_{ug}, c_{hg} versus $c_{h\ell}$, and $c_{u\ell}$ versus $c_{h\ell}$ for both stripping and rectifying sections. Thus for any chosen value of $c_{u\ell}$, the corresponding c_{ug} and $c_{h\ell}$ were read from the appropriate curve; and from $c_{h\ell}$, c_{hg} was similarly obtained. These plots are shown in Figs. 18 and 19. The operating concentration data obtained together with other pertinent data for Run #C3 are given in Table VI.

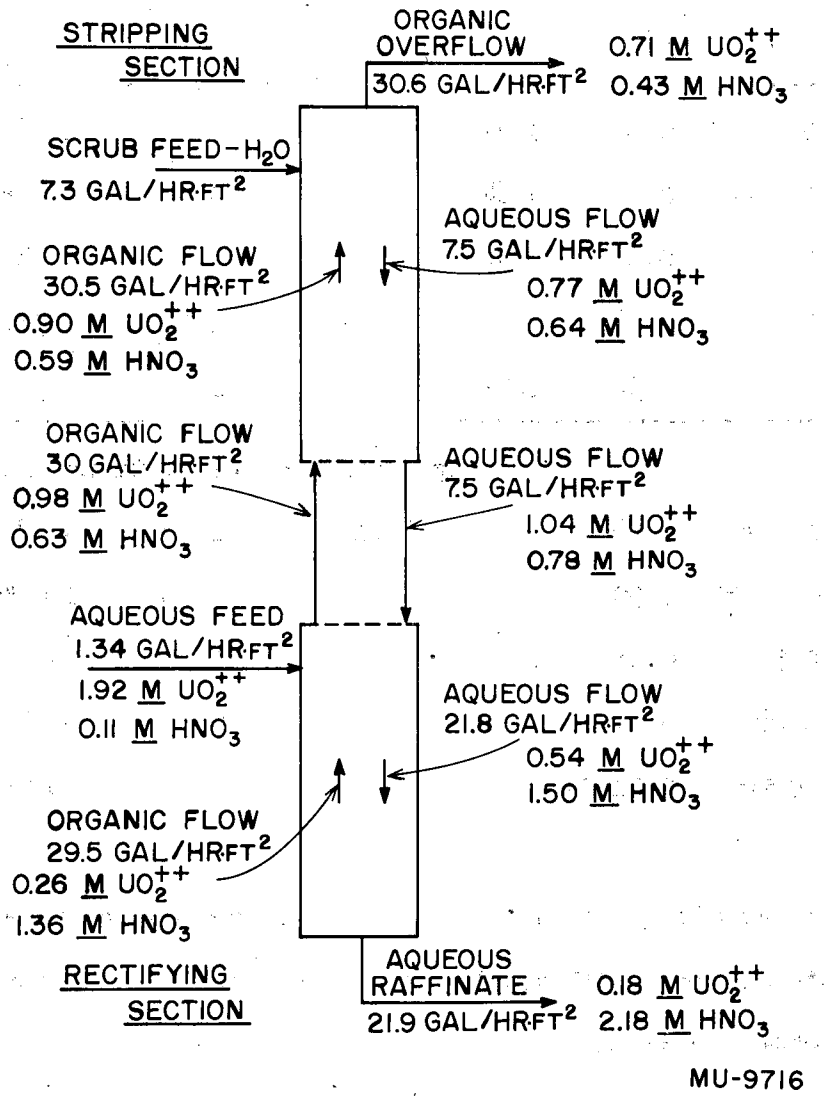


Fig. 17. Flow diagram pulse column Run C-3.

Table VI

Operating, Equilibrium and Pseudoequilibrium Data

Pulse Column Run C-3

Rectifying Section Concentrations (moles/liter)

$c_{u\ell}$	c_{ug}	c_{ug_i}	c'_{ug}*	c'_{ug}**	$c_{h\ell}$	c_{hg}	c_{hg_i}
0.18***	0.0***	0.27	1.09	0.26	2.18***	1.91***	1.45
0.54***	0.26	0.64	1.55	0.84	1.50***	1.36	0.91
1.00	0.60	1.04	2.57	1.61	0.94	0.96	0.59
1.36	0.84	1.32	3.77	2.13	0.58	0.74	0.39
1.60	0.98	1.47	4.73	2.34	0.35	0.63	0.23

Stripping Section Concentrations (moles/liter)

1.04***	0.98	1.06	1.16	1.12	0.78***	0.63	0.51
0.77***	0.90	0.75	0.42	0.63	0.64***	0.59	0.42
0.55	0.84	0.48	0.15	0.32	0.51	0.55	0.32
0.28	0.77	0.12	0.02	0.07	0.30	0.50	0.13
0***	0.71***	0	0	0	0***	0.43***	0

* Pseudoequilibrium based on thermodynamic correlation.

** Pseudoequilibrium based on empirical correlation.

***Experimental Data.

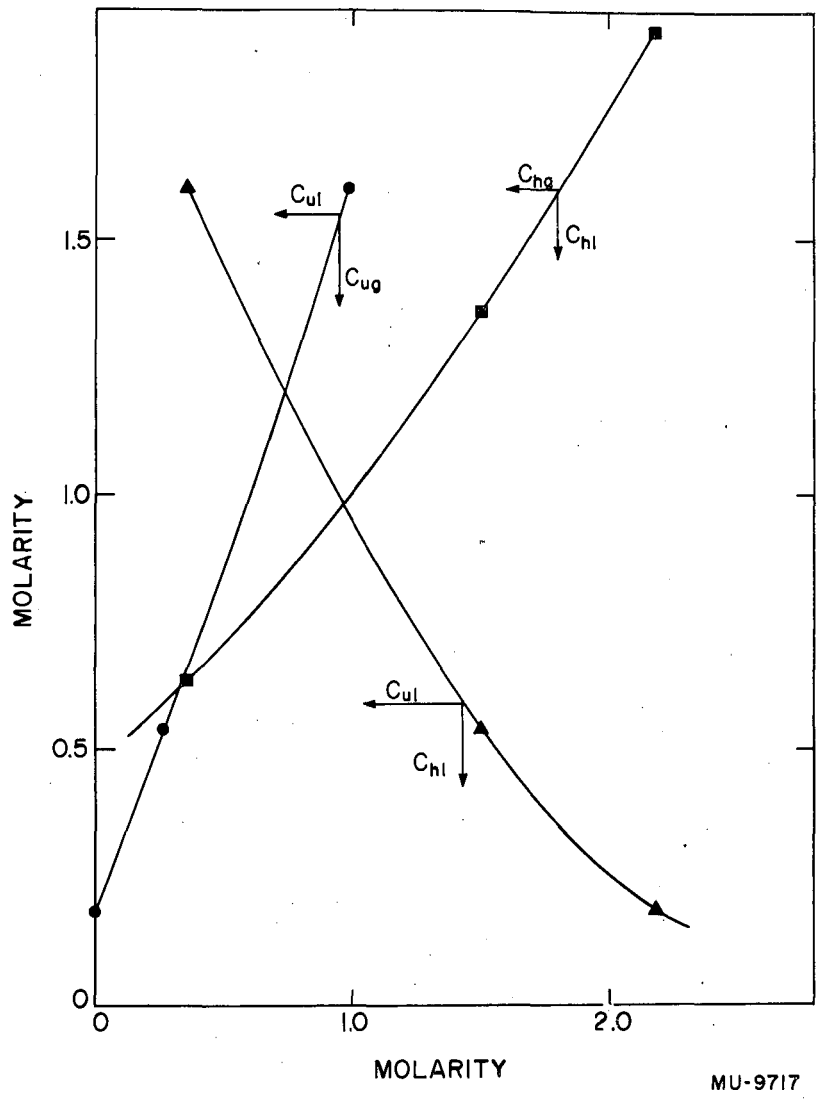


Fig. 18. Operating curves for rectifying section, Run C-3.

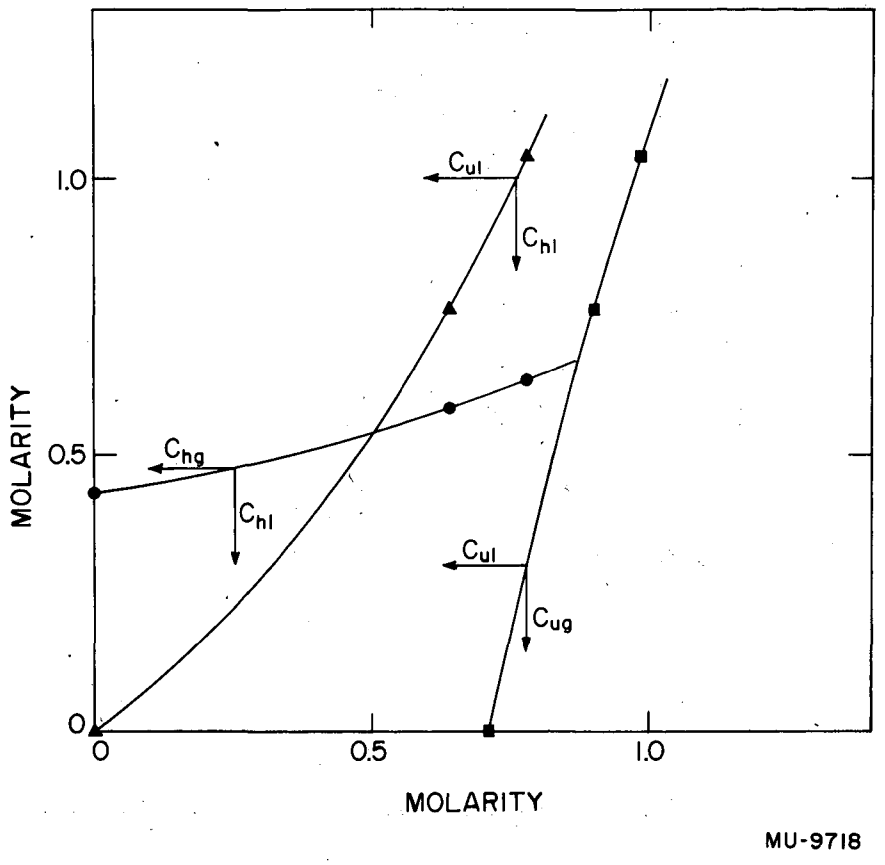


Fig. 19. Operating curves for stripping section, Run C-3.

Equilibrium Data. It was assumed that all resistance to mass transfer was in the organic film, hence the bulk-phase aqueous concentrations were taken as the aqueous interfacial concentrations. Equilibrium organic interfacial concentrations were then read from the equilibrium diagrams in Fig. 10 and 11.

Pseudoequilibrium Data. By use of the thermodynamic method, uranyl nitrate aqueous activities were calculated from Eq. (68) by the method previously described. Organic bulk-phase activity coefficients were obtained from Fig. 14. Since $a_{u\ell} = a_{u\ell_i} = a_{ug_i}$ for this case, the pseudoequilibrium concentrations were obtained from the relation

$$c'_{ug} = \frac{a_{ug_i}}{\gamma_{ug}}$$

and are presented in Table VI.

An alternative set of uranyl nitrate pseudoequilibrium data was calculated by the use of the empirical equations (79) and (80), and the above relations. The data are given in Table VI. Similarly pseudo-equilibrium values may be determined for nitric acid.

In order to illustrate the significance of the thermodynamic driving force on mass-transfer calculations, the uranium operating, equilibrium, and pseudoequilibrium lines are shown for the rectifying and stripping sections respectively in Figs. 20 and 21. In the development of tower calculations it has been customary to assume that the vertical distance between the operating and equilibrium lines is representative of the driving force for mass transfer throughout the film when all resistance lies in the organic phase. This concept, however, is not valid in multicomponent transfer systems when all or several of the transferring components affect the equilibrium. Hence for the system under study

the vertical distance between the operating and pseudoequilibrium lines $(c_{ug} - c'_{ug})$ is representative of the true driving force for mass transfer. From visual inspection of the curves, it will become apparent that transfer units based on the pseudoequilibrium concept will vary significantly from those calculated based on the true equilibrium line.

There is an appreciable difference between the two pseudoequilibrium curves, and from inspection of their shape it was concluded that pseudoequilibrium values determined from thermodynamic data and correlations are to be preferred over values obtained from empirical equations. However, in the absence of basic thermodynamic data, the empirical activity equations will still be indicative of the change in driving force resulting from multicomponent mass transfer.

Transfer Units. It was postulated from Eq. (58) that if the ratio $\gamma_{ug}/\gamma_{ug_m}$ varied significantly throughout a tower, mean film values were to be preferred in transfer unit calculations, as their use would tend to preserve the constancy of the mass-transfer film coefficient. Inspection of the ratios in Table VII shows a significant variation, particularly in the stripping section, hence the following equations employing mean film values were employed in calculating approximate and exact numbers of transfer units:

$$(N_{OG})_u = \int_{c_1}^{c_2} \frac{\gamma_{ugm} dc_{ug}}{(a_{ugi} - a_{ug})} , \tag{59}$$

and

$$(N_{OG})_u = \int_{c_1}^{c_2} \frac{(1 - c_{hg}\bar{v}_h)}{(1 - c_{hg}\bar{v}_h)_m} \frac{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)_m}{(1 - c_{ug}\bar{v}_u - c_{hg}\bar{v}_h)} \frac{\gamma_{ugm} dc_{ug}}{(a_{ugi} - a_{ug})} \tag{95}$$

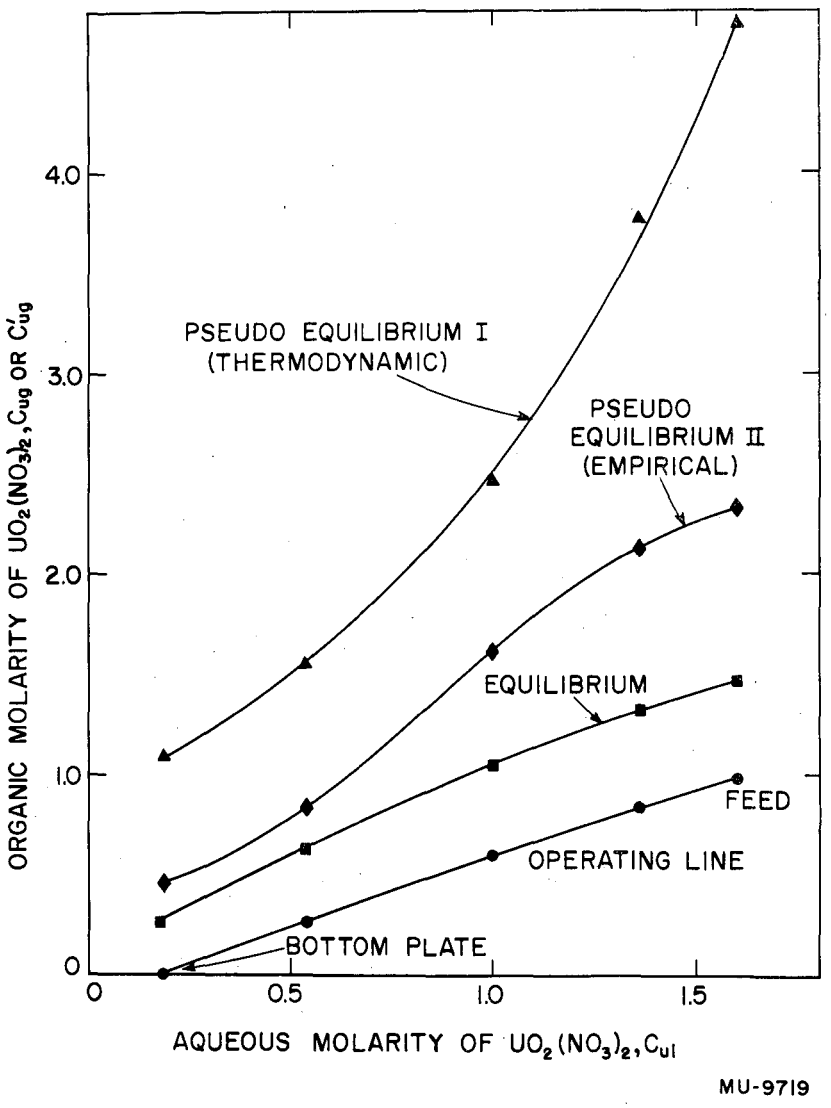


Fig. 20. Uranium molarities in rectifying section, Run C-3.

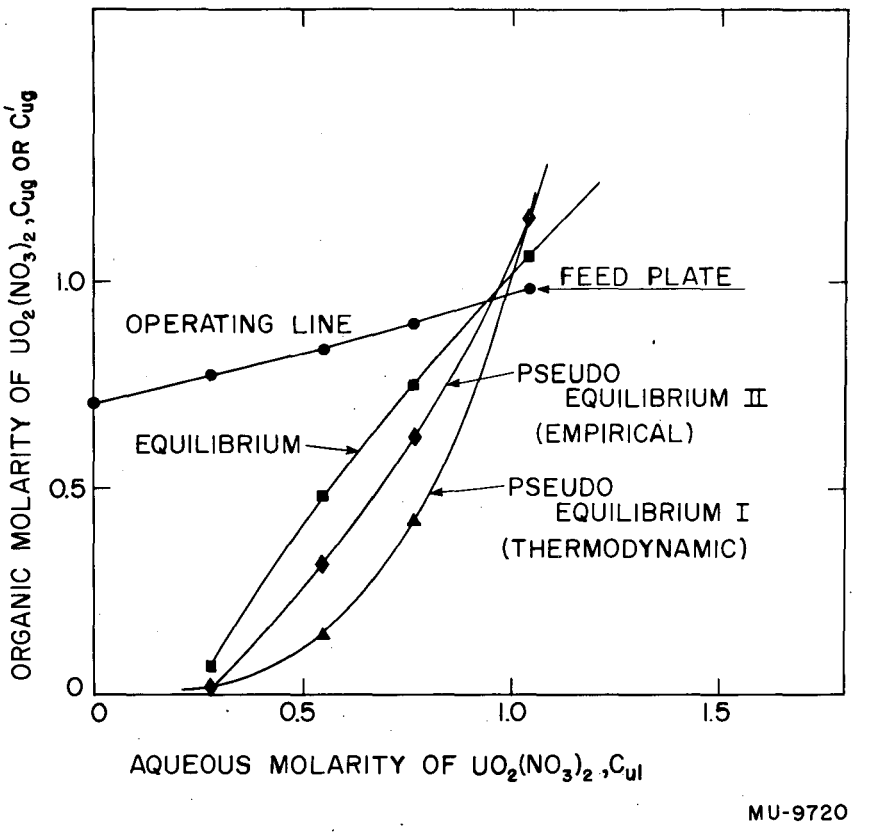


Fig. 21. Uranium molarities in stripping section, Run C-3.

Table VII

Data for Transfer Unit Calculations Pulse Column Run C-3

c_{ug}	γ_{ugi}	γ_{ug}	γ_{ugm}	$\frac{\gamma_{ug}}{\gamma_{ugm}}$	a_{ug}	a_{ugi}	$\frac{\gamma_{ugm}}{a_{ug} - a_{ugi}}$	N_{OG} Correction Factor
				Rectifying Section				
0	2.81	11.4	6.14	1.86	0	3.07	2.00	1.24
0.26	3.45	8.42	5.58	1.51	0.90	5.36	1.25	1.16
0.60	6.07	15.0	9.72	1.54	3.64	15.6	0.82	1.12
0.84	9.60	26.7	16.7	1.60	8.07	36.2	0.59	1.09
0.98	12.8	41.1	24.3	1.69	12.6	60.4	0.51	1.07
				Stripping Section				
0.98	12.8	14.6	13.75	1.06	12.6	14.9	-5.94	1.09
0.90	9.8	5.52	7.45	0.74	8.80	4.14	1.63	1.07
0.84	8.1	2.47	4.75	0.52	6.78	1.19	0.85	1.06
0.77	6.3	1.24	3.12	0.40	4.86	0.13	0.66	1.05
0.71	5.04	1.0	2.50	0.40	3.56	0	0.70	1.03

The partial-molal-volume data necessary for solution of Eq. (95) were found by substituting the equilibrium data of Stover into Eq. (30),

$$1 = c_{ug}\bar{v}_u + c_{hg}\bar{v}_h + c_{pg}\bar{v}_p,$$

where the subscript "p" refers to pentaether and there is no free water in the organic phase. The molal volume of pentaether was first found from the limiting data of the acid-free system as the uranyl nitrate concentration approaches zero. By use of $\bar{v}_p$, the average molal volume of uranyl nitrate was calculated for the acid-free system from the relation

$$\sum c_{hg}\bar{v}_{hg} = \sum (1 - c_{pg}\bar{v}_{pg} - c_{ug}\bar{v}_{ug}).$$

The constants as determined by this method were $\bar{v}_{ug} = 0.177$, $\bar{v}_{pg} = 0.319$ and $\bar{v}_{hg} = 0.115$. The data of Stover with these constants corresponded to Eq. (30) with an average deviation of -0.013, and a maximum deviation of -0.064 (except for one point, believed incorrect, where the error was 0.136). These molal volumes were then used in calculating the HTU correction factor which is represented by the first two terms of Eq. (95).

The activity data necessary for solution of Eqs. (59) and (95) were calculated by use of the preferred thermodynamic equations and correlations and are presented in Table VII. Graphical integration of the data yielded the results given in Table VIII.

Table VIII

Results of Transfer Unit Calculations

Pulse Column Run C-3

	$(N_{OG})_u$		$(H_{OG})_u$, feet	
	Approx.	Exact	Approx.	Exact
Rectifying Section	0.987	1.083	5.25	5.02
Partial Stripping Sect.	0.159	0.167	8.26	7.88
Total Stripping Section	0.318	0.334	8.26	7.88

From inspection of Fig. 21 it is observed that the uranium operating line and all "equilibrium" lines converge in the stripping section resulting in a "pinch point". By use of conventional calculation methods, this would result in an infinite number of transfer units. However, since this case is analogous to multicomponent distillation, it is reasonable to expect pinch points to occur and a finite number of transfer units must exist. Unfortunately, no precise methods have been developed to calculate infinite sections in extraction towers and the stepwise calculation methods used for analogous cases in plate distillation towers are not applicable.

The transfer unit equation, as previously shown, may be expressed

$$(N_{OG})_u = \int \frac{\gamma_m \, d\, c_{ug}}{\gamma_{ug} \, (c'_{ug} - c_{ug})} \quad . \tag{95a}$$

The change in the driving force $d(c'_{ug} - c_{ug})$ is not due just to changes in c_{ug} and $c_{u\ell}$, by way of mass transfer, but is also due to changes in c'_{ug} as a result of mass-transfer changes in c_{hg} and $c_{h\ell}$.

Hence, we may express the rate of change of c'_{ug} with respect to column height

$$\frac{d\, c'_{ug}}{dH} = A \frac{dc_{hg}}{dH} + B \frac{d\, c_{ug}}{dH} \tag{96}$$

In the region where c_{hg} changes slowly compared to c_{ug}, transfer units can be evaluated in terms of uranium only, if the contribution of acid transfer is neglected. In the region where $(c'_{ug} - c_{ug})$ driving force is practically zero, the transfer-unit calculation does not appear to have significance. There should be a refined way of correcting for $\frac{d\, c_{hg}}{dH}$, and its effect on $(c'_{ug} - c_{ug})$, throughout the column that would give

a finite number of transfer units for the entire column. Since we lack it, transfer units may be calculated for partial sections and multiplied by the height ratio of total section to partial section to obtain the total number of transfer units in the section.

CONCLUSIONS

Extraction of Uranyl Nitrate by Pentaether in Packed Plate Towers

Pentaether is an excellent extractant for uranyl nitrate from aqueous solutions; however, it is impractical for use in continuous countercurrent pulsed plate extraction towers because the high viscosity of uranyl nitrate pentaether solutions impedes flow and hinders rapid mass transfer, resulting in low column capacities.

Fundamental Mass-Transfer Concepts

From a study of multicomponent mass transfer involving the system uranyl nitrate-pentaether-nitric acid-water, it has been concluded that the basic equation for mass transfer of a single component through an interfacial film should express the mass-transfer driving force in terms of thermodynamic potential rather than concentration gradient. It may be shown, for systems containing several diffusing components all affecting the equilibrium, that expressing the driving force through the film in terms of the concentration gradient within the film for one diffusing component takes no cognizance of the nonequilibrium distribution within the film of the remaining diffusing components. Hence it is necessary to express the driving force in terms of a thermodynamic potential that will account for the nonequilibrium distribution of all diffusing components.

This concept may also be applied to three-component extraction systems containing only one diffusing component, which deviate from ideal solution behavior. For ideal solutions, where the activity may be defined by concentration, the concentration gradient will express the true driving force. In most systems, however, the activity coefficient will vary through the interfacial film, hence the concentration gradient is no longer a true

measure of the driving force for mass transfer. It is necessary to revert to a more fundamental concept which will express the driving force in terms of thermodynamic potential. The following expression is proposed to accomplish this purpose:

$$dM_t = \frac{k'_g dS}{\gamma_{gm}} (a_{gi} - a_g) = \frac{k'_\ell \, dS(a_{\ell i} - a_\ell)}{\gamma_{\ell m}} .$$

Since data for multicomponent mass transfer are quite rare, it is recommended that this concept be applied to nonideal three-component systems for which considerable data are available. It is anticipated that transfer units and mass-transfer coefficients so calculated will exhibit greater consistency and permit simpler correlations than have previously been obtained.

NOMENCLATURE

A,B,C,D,E,F	Organic-phase constants of empirical activity equations.
A',B',C',D',E',F'	Aqueous-phase constants of empirical activity equations.
a	Activity
C	Number of components (phase rule)
c	Concentration, lb moles/liter
c'	Pseudoequilibrium concentration, lb moles/liter
c*	Equilibrium concentration as defined by Eq. (4) and Eq. (6)
c°	Concentration of pure materials, lb moles/liter
d	Differential operator
E	Distribution coefficient
E°	Distribution coefficient at infinite dilution
F	Degrees of freedom (phase rule)
h	Height of tower, ft
H_T	Height of transfer unit
K	Overall mass-transfer film coefficient $\frac{(\text{lb moles})}{(\text{hr ft}^2)\ (\frac{\text{lb moles}}{\text{liter}})}$
Ka	Overall mass-transfer film coefficient $\frac{(\text{lb moles})}{(\text{hr ft}^3)\ (\frac{\text{lb moles}}{\text{liter}})}$
K'a	Overall mass-transfer film coefficient based on pseudoequilibrium concentration gradient Eq. (39).
K''a	Overall mass-transfer film coefficient based on pseudoequilibrium mean film values
K_f	Flow constant, moles per hour
k,k'	Mass-transfer film coefficient $\frac{(\text{lb moles})}{(\text{hr ft}^3)\ (\frac{\text{lb moles}}{\text{liter}})}$
K_e , K'_e, K''_e	Equilibrium constants

NOMENCLATURE

(-2-)

$\underline{M}$	Molarity, moles per liter
m	Molality, moles per 1000 grams solvent
M_f	Mass flow rate, lb moles/hr
M_t	Mass transfer rate, lb moles/hr
N	Number of overall mass-transfer units
n	Number of moles
P	Number of phases (phase rule)
S	Cross-sectional area perpendicular to the direction of diffusion, ft^2
V	Volume, liters
v	Flow rate, liters per hour
$\bar{v}$	Partial molal volume, liters per mole
x	Mole fraction in aqueous phase
y	Mole fraction in organic phase
Z	Ionic charge

Greek Letters

γ	Mean molal activity coefficient
γ°	Mean molal activity coefficient at reference state
μ	Ionic strength

Subscripts

f	Refers to flow
G,g	Phase designation, organic
h	Nitric acid
i	Interface
ℓ	Aqueous phase designations

NOMENCLATURE

(-3-)

m	Log mean
OL, OG	Overall resistance in G and L phases, respectively
o	Refers to conditions at one end of column
u	Uranyl nitrate
w	Water

Superscripts

*	Refers to equilibrium using overall film resistance concept.
'	Refers to pseudoequilibrium concept
h	Hydration constant

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APPENDIX

Table IX

Experimental Equilibrium Data of C. Stover[10]

Uranyl Nitrate-Nitric Acid-Pentaether-Water 25°C

Aqueous Phase, Moles per Liter				Organic Phase, Moles per Liter			
HNO_3	P.E.	H_2O	u	HNO_3	P.E.	H_2O	u
0	0.04	54.89	0.091	0	3.14	2.24	0.0011
0	0.04	54.44	0.1738	0	3.08	2.40	0.0061
0	0.02	53.56	0.4135	0	3.08	3.03	0.1610
0	0.02	52.72	0.5774	0	2.91	4.02	0.374
0	0.02	52.17	0.7797	0	2.75	5.15	0.649
0	0.02	50.56	1.255	0	2.44	6.27	1.146
0	0.02	47.94	1.894	0	2.33	6.88	1.593
.7137	0.09	52.59	0.0623	0.358	2.80	4.40	0.0349
.646	0.14	51.02	0.2746	0.410	2.71	5.28	0.2283
.634	0.16	49.72	0.5076	0.436	2.57	5.92	0.4976
.572	0.16	50.33	0.5446	0.421	2.47	5.88	0.5685
1.248	0.04	53.55	0.0476	0.812	2.67	6.76	0.538
1.241	0.04	53.22	0.2283	0.812	2.69	6.70	0.225
1.270	0.04	52.11	0.4524	0.790	2.57	6.78	0.535
1.227	0.04	52.53	0.518	0.761	2.56	6.65	0.609
1.246	0.04	51.84	0.635	0.747	2.50	6.83	0.742
0.994	0.04	48.58	1.625	0.412	2.30	6.75	1.543
2.439	0.16	48.36	0.0356	1.794	2.39	9.53	0.0581
2.485	0.14	47.62	0.1742	1.607	2.43	8.37	0.298
2.700	0.14	47.17	0.3590	1.597	2.35	7.69	0.588

Table X

Equilibrium Data of Glueckauf[3] and Associates

$UO_2(NO_3)_2$-HNO_3-P.E.-H_2O 25°C

	Uranyl Molalities			
Aqueous Phase	0.26	0.396	0.765	2.00
Organic Phase	0.476	0.153	0.630	2.16

Table XI

Selected Equilibrium Data

and Calculated Uranyl Nitrate and Nitric Acid Activities

$c_{u\ell}$	c_{ug}	$c_{h\ell}$	c_{hg}	$a_{u\ell}$	a_{ug}	% Difference in U Activities	$a_{h\ell}$	a_{hg}	% Difference in Acid Activities
0.1	0.009	0.1	0.013	0.00826	0.00901	+8.42	0.0722	0.0130	6.15
0.1	0.031	0.4	0.128	0.0329	0.0309	-6.48	0.115	0.125	8.00
0.1	0.056	0.7	0.334	0.0562	0.0556	-1.08	0.326	0.326	0.00
0.1	0.082	1.0	0.588	0.0826	0.0821	-0.61	0.620	0.618	-0.32
0.1	0.119	1.5	1.005	0.123	0.124	4.81	1.32	1.35	+2.22
0.1	0.142	2.0	1.380	0.154	0.157	+1.91	2.33	2.44	+4.51
0.3	0.088	0.1	0.031	0.097	0.090	-7.79	0.0374	0.0324	+15.42
0.3	0.162	0.4	0.193	0.161	0.169	+4.73	0.222	0.211	-5.22
0.3	0.229	0.7	0.401	0.233	0.247	+5.67	0.511	0.493	-3.67
0.3	0.287	1.0	0.610	0.310	0.321	+3.43	0.901	0.879	-8.50
0.3	0.366	1.5	0.935	0.429	0.441	+2.72	1.79	1.79	+0.00
0.3	0.419	2.0	1.28	0.519	0.545	+4.77	3.03	3.23	+6.19
0.5	0.282	0.1	0.059	0.328	0.320	-2.50	0.0691	0.0691	0
0.5	0.384	0.4	0.251	0.437	0.465	+6.02	0.354	0.353	0.28
0.5	0.461	0.7	0.438	0.558	0.594	+6.07	0.750	0.729	2.88
0.5	0.522	1.0	0.621	0.685	0.710	+3.52	1.26	1.22	3.28
0.5	0.602	1.5	0.903	0.875	0.890	+1.69	2.36	2.31	2.16
0.5	0.653	2.0	1.203	1.005	1.032	+2.62	3.85	3.88	0.77
1.0	0.894	0.1	0.085	1.75	1.76	+0.57	0.162	0.184	11.95
1.0	0.956	0.4	0.303	1.97	1.99	+1.00	0.731	0.794	7.93
1.0	1.006	0.7	0.469	2.20	2.19	-0.46	1.42	1.42	0
1.0	1.052	1.0	0.621	2.43	2.40	-1.25	2.24	2.15	4.19
1.0	1.117	1.5	0.849	2.75	2.73	-0.73	3.89	3.55	9.59
1.0	1.165	2.0	1.089	2.92	3.01	+2.99	5.97	5.42	10.15
1.5	1.361	0.1	0.075	4.22	4.20	-0.48	0.239	0.250	4.40
1.5	1.404	0.4	0.274	4.51	4.49	-0.45	0.994	1.050	5.33
1.5	1.440	0.7	0.438	4.85	4.75	-2.11	1.88	1.90	1.05
1.5	1.469	1.0	0.586	5.07	4.98	-1.81	2.88	2.84	1.41
1.5	1.508	1.5	0.822	5.40	5.31	-1.70	4.86	4.66	4.30
1.5	1.534	2.0	1.038	5.45	5.55	+1.80	7.28	6.72	8.33
1.8	1.543	0.1	0.067	5.52	5.62	1.78	0.232	0.253	8.30
1.8	1.580	0.4	0.232	5.92	5.92	0	1.00	0.998	0.20
1.8	1.608	0.7	0.386	6.20	6.17	-0.49	1.88	1.85	1.62
1.8	1.631	1.0	0.539	6.46	6.38	-1.25	2.86	2.88	0.70
1.8	1.661	1.5	0.781	6.71	6.68	+0.45	4.82	4.85	0.62
1.8	1.678	1.8	1.016	6.60	6.87	-3.93	7.20	7.20	0

Table XII

Uranyl Nitrate and Nitric Acid

Distribution Coefficients in Infinitely Dilute Acid Solutions

System $UO_2(NO_3)_2$-PE-H_2O-HNO_3 25°C

$c_{u\ell}$ (1)	c_{ug} (1)	$(E_u)_{h=0}$ (2)	$(E_u)_{h=0}$ (3)	$(E_h)_{h=0}$ (4)
0.1	0.00264	0.0264	0.0264	0.062
0.2	0.01975	0.0988	0.0988	0.135
0.3	0.0620	0.207	0.209	0.248
0.4	0.135	0.338	0.346	0.465
0.5	0.242	0.484	0.487	0.600
0.6	0.372	0.611	0.620	0.715
0.7	0.502	0.716	0.712	0.789
0.8	0.628	0.785	0.789	0.838
0.9	0.752	0.835	0.841	0.862
1.0	0.872	0.872	0.874	0.873
1.1	0.984	0.895	0.895	0.873
1.2	1.088	0.907	0.906	0.864
1.3	1.183	0.910	0.909	0.843
1.4	1.270	0.907	0.907	0.813
1.5	1.346	0.897	0.901	0.768
1.6	1.412	0.883	0.892	0.712
1.7	1.473	0.866	0.875	0.636
1.8	1.530	0.850	0.849	0.549

(1) From Figure 10

(2) $E_o = c_{ug}/c_{u\ell}$

(3) Equation (70)

(4) From Figure 16a

Table XIII

Uranyl Nitrate and Nitric Acid

Distribution Coefficients in Infinitely Dilute Uranium Solutions

System $UO_2(NO_3)_2$-PE-H_2O-HNO_3 25°C

c_{he} (1)	c_{hg} (1)	$(E_h)_{u=0}$ (2)	(E_u^o) (3)	(E_u^o) (4)
0.1	0.0078	0.071	0.054	0.054
0.2	0.026	0.126	0.113	0.114
0.3	0.054	0.180	0.181	0.180
0.4	0.093	0.236	0.252	0.252
0.5	0.145	0.293	0.330	0.329
0.6	0.209	0.351	0.412	0.410
0.7	0.284	0.409	0.496	0.495
0.8	0.372	0.466	0.582	0.582
0.9	0.469	0.519	0.670	0.670
1.0	0.570	0.567	0.753	0.757
1.1	0.669	0.608	0.841	0.842
1.2	0.769	0.640	0.925	0.924
1.3	0.866	0.666	1.003	1.002
1.4	0.959	0.686	1.075	1.075
1.5	1.052	0.700	1.142	1.142
1.6	1.139	0.711	1.202	1.202
1.7	1.224	0.719	1.253	1.256
1.8	1.305	0.725	1.299	1.301
1.9	1.384	0.728	1.340	1.340
2.0	1.461	0.730	1.376	1.370

(1) Figure 11

(2) Calc. Eq. (82)

(3) Figure 15

(4) Calc. Eq. (75)

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