ORNL MASTER COPY DEC 6 1990

ORNL/TM-11365

ornl

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

Determination of Nitric Acid and Uranium Concentrations in Aqueous Solution from Measurements of Electrical Conductivity, Density, and Temperature

B. B. Spencer
M. E. Whatley

5/20/2013 OK for public release.

CONSOLIDATED FUEL REPROCESSING PROGRAM

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-11365
Dist. Category UC-526
(Applied)

Consolidated Fuel Reprocessing Program

DETERMINATION OF NITRIC ACID AND URANIUM CONCENTRATIONS IN AQUEOUS SOLUTION FROM MEASUREMENTS OF ELECTRICAL CONDUCTIVITY, DENSITY, AND TEMPERATURE

B. B. Spencer
M. E. Whatley*
Robotics and Process Systems Division

Date Published–November 1990

Prepared for the
Office of Facilities, Fuel Cycle,
and Test Programs

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

*Retired.

CONTENTS

LIST OF FIGURES v

LIST OF TABLES vii

ABSTRACT ix

1. INTRODUCTION 1
   1.1 BACKGROUND 1
   1.2 CONSTRAINTS AND SPECIFICATIONS FOR THE EQUATIONS 1

2. CORRELATIONS 3
   2.1 NITRIC ACID-WATER SYSTEM 4
      2.1.1 Density 4
      2.1.2 Conductivity 11
      2.1.3 Equations for Process Use 21
   2.2 NITRIC ACID-URANIUM-WATER SYSTEM 26
      2.2.1 Density 31
      2.2.2 Conductivity 35
      2.2.3 Equations for Process Use 43

3. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS 55

REFERENCES 59

NOMENCLATURE 61

APPENDIXES
APPENDIX A: DENSITY OF AQUEOUS NITRIC ACID SOLUTIONS 63
APPENDIX B: CONDUCTIVITY OF AQUEOUS NITRIC ACID SOLUTIONS 71
APPENDIX C: CONDUCTIVITY AND DENSITY OF AQUEOUS NITRIC ACID-URANIUM SOLUTIONS 77

LIST OF FIGURES

Fig. 2.1. Density of aqueous nitric acid solutions as a function of wt % acid at various temperatures 5

Fig. 2.2. Density of nitric acid solutions as a function of molar concentration at 25°C 6

Fig. 2.3. Reciprocal density of nitric acid solutions as a function of molar concentration at 25°C 7

Fig. 2.4. Electrical conductivity of aqueous nitric acid 12

Fig. 2.5. Conductivity of dilute and concentrated aqueous nitric acid at 18°C—log scale 13

Fig. 2.6. K-values for nitric acid 14

Fig. 2.7. Temperature effect on electrical conductivity of aqueous nitric acid 17

Fig. 2.8. Comparison of electrical conductivity data for nitric acid solutions with the correlation 24

Fig. 2.9. Change in density with nitric acid concentration at various uranium concentrations at 25°C 33

Fig. 2.10. Change in density with nitric acid concentration at various uranium concentrations at 95°C 34

Fig. 2.11. Density of uranyl nitrate solutions at 17°C 35

Fig. 2.12. Change in density with uranium concentration at various nitric acid concentrations at 25°C 36

Fig. 2.13. Change in density with uranium concentration at various nitric acid concentrations at 95°C 37

Fig. 2.14. Conductivity of aqueous nitric acid-uranium solutions at various temperatures 42

Fig. 2.15. Comparison of experimental electrical conductivity of aqueous nitric acid-uranium solutions at 25° to correlation 48

Fig. 2.16. Comparison of experimental electrical conductivity of aqueous nitric acid-uranium solutions at 60° to correlation 49

Fig. 2.17. Comparison of experimental electrical conductivity of aqueous nitric acid-uranium solutions at 95° to correlation 50

LIST OF TABLES

Table 2.1. Correlation of reciprocal density with weight percent at 25°C 8

Table 2.2. Correlation of reciprocal density with molar concentration at 25°C 9

Table 2.3. Regression analysis for the volumetric expansion coefficient 10

Table 2.4. Correlation of K with concentration at 18°C 15

Table 2.5. Correlation of K with concentration at 25°C 16

Table 2.6. Regression models for dependent variable K 19

Table 2.7. Summary of forward selection procedure for dependent variable K 21

Table 2.8. Summary of data in conductivity correlation and percentage error 22

Table 2.9. BASIC computer program segment that solves Eq. (2.5) by iteration 26

Table 2.10. Percentage error in calculating concentration from density measurements 27

Table 2.11. Regression models for density of aqueous nitric acid-uranium solutions 38

Table 2.12. Comparison of density data with predictions from correlation 40

Table 2.13. Summary of forward selection procedure for dependent variable g with constant term excluded 43

Table 2.14. Regression models for dependent variable g′ where an intercept is required 44

Table 2.15. Comparison of conductivity data with calculations made from correlation 46

Table 2.16. FORTRAN program for calculating nitric acid and uranium concentrations from electrical conductivity, density, and temperature 51

Table 2.17. Comparison of acid and uranium concentrations inferred from conductivity, density, and temperature with data 53

Table A.1. Density of aqueous nitric acid solution at various weight percent acid and temperatures 64

Table A.2. Molarity of aqueous nitric acid solution at various weight percent acid and temperatures 67

Table B.1. Conductivity of concentrated and dilute aqueous nitric acid solution at 18°C 72

Table B.2. K-values of dilute aqueous nitric acid solutions at different temperatures 73

Table B.3. Conductivity of dilute aqueous nitric acid solutions at different temperatures 73

Table B.4. Conductivity of concentrated and dilute aqueous nitric acid solutions at 25°C 74

Table B.5. Conductivity of dilute aqueous nitric acid solutions at 20°C 75

Table B.6. Electrical conductivity of concentrated aqueous nitric acid solution at various temperatures 76

Table C.1. Density of uranyl nitrate solutions at 17°C 78

Table C.2. Density and freezing point data for UNH-H_2O-HNO_3 systems at 25°C 79

Table C.3. Electrical conductivity and density of aqueous nitric acid-uranium solutions 80

ABSTRACT

Electrical conductivity and density for the aqueous nitric acid and aqueous nitric acid-uranium systems have been modeled as functions of composition and temperature. These equations permit the ascertaining of composition (nitric acid and uranium concentration) from measurements of electrical conductivity, density, and temperature in the processing system. Algorithms based on the correlations and suitable for real-time process control have been developed.

1. INTRODUCTION

Aqueous solutions of nitric acid and nitric acid-uranium are handled in large quantities in both nuclear fuel reprocessing plants and uranium milling operations. Automatic control of process operations requires reliable measurements of the concentration of these solutes. Concentration is difficult to measure directly but can be inferred from easily measured physical properties or conditions. Solution density and electrical conductivity vary markedly with both the concentration of acid and the concentration of uranium. Additionally, these properties are also temperature-dependent. Electrical conductivity, density, and temperature may be measured with high accuracy using relatively simple and inexpensive devices. Were there good correlations between these measured quantities and composition, acid and uranium concentrations could be readily calculated from measurements of electrical conductivity, density, and temperature. The purpose of this report is to summarize the available data and develop the appropriate correlations.

1.1 BACKGROUND

The effort to produce the described correlations was initiated to satisfy the requirements for automating the processing systems in the Integrated Equipment Test (IET) Facility. Operation of this chemical plant without the need for human intervention mandated that the control system rapidly and reliably obtain information on the concentration of nitric acid and uranium in process solutions. Instrumentation to measure electrical conductivity, density, and temperature of process solutions was installed when the plant was built but at that time correlations to make effective use of these data were only in the early stages of development. Laboratory data on electrical conductivity and density at various solution concentrations and temperatures were obtained and correlations developed prior to the collaborative program between the U.S. Department of Energy and the Power Reactor and Nuclear Fuel Development Corporation of Japan. Documentation of both the data and the correlations was performed under the auspices of the collaboration. This report describes the development of the correlating equations now in use.

Automation of a large portion of the IET chemical plant has been successfully implemented. Control of the feed adjustment system and the uranium product evaporator relies on the use of correlations to extract nitric acid and uranium concentration from measurements of electrical conductivity, density, and temperature. For example, the uranium concentration in product batches has been controlled to within 0.5% of target values.[1]

1.2 CONSTRAINTS AND SPECIFICATIONS FOR THE EQUATIONS

The specifications on the correlating equations have largely been established by implication. The two uses for the equations can be examined to establish the rules.

The primary use for the equations will take place in a process control computer in a real-time mode and there are general constraints, both on the computation time required to make the calculation and on the amount of program that can fit in the available computer memory. While these constraints are loosely understood, the incentive for simplicity is real. However, the most

meager requirement for accuracy (which will be addressed in Sect. 2.) pushes the correlation into a regime of complexity (indeed, nonlinearity) that precludes an explicit inversion. The set of equations that explicitly generates conductivity and density from temperature, uranium concentration, and nitric acid concentration cannot be solved for uranium and nitric acid concentrations as explicit functions of temperature, density, and conductivity. This unfortunate reality has now been accepted.

A secondary use for the equations involves process modeling. For this use, there will be frequent requirements for an accurate inversion. Given temperature, uranium and nitric acid concentrations, it should be possible to calculate values for density and conductivity, which can be used as input to a calculation that will generate the original uranium and nitric acid concentrations. Implied is the necessity for an iterative algorithm. The alternative method of producing a correlation to obtain an approximate inverse has a disadvantage in that repeated calculations tend to "walk" away from the correct value, because such an inverse will be accurate to only three or four digits. An iterative method can easily produce values to the precision of the computing machine.

Further criteria can be imposed on the correlations. The equations should be smooth and regular over the range of applications, exhibiting neither discontinuities nor spurious inflection points. The equations should behave well in extrapolations beyond, yet in the vicinity of, the range of application so as to obviate dangerous responses to either signal errors or fallacious input. It is desirable for the equations to reduce to known states in the limit. For example, when the uranium concentration goes to zero, the equation for conductivity should fit the pure acid case and when the acid goes to zero, the equation should fit the pure uranium case. Restrictions of this type were placed on all equations developed in this work, except where a lack of data prevented it or a limiting of the range of application offered substantial simplification.

2. CORRELATIONS

All correlations presented in this report are developed first by plotting the data and examining the shape of the curve from which a functional form may be chosen, albeit somewhat subjectively. This process is augmented by the use of conventional correlation forms or theory, where they seem to work well.

Second, the dependent variable is fit to a linear combination of independent variables, independent variables raised to various powers, and/or cross products of independent variables by linear regression. Two statistical quantities (the correlation coefficient and the Mallow C(p) statistic) are used to gauge the goodness of fit.

The correlation coefficient, r^2, measures how much of the variation in the dependent variable can be accounted for by the model. It is defined as

$$r^2 = \frac{\text{sum-of-squares for the model}}{\text{sum-of-squares for the corrected total}} \tag{2.1}$$

$$= \frac{\Sigma(\hat{y}_i - \bar{y})^2}{\Sigma(y_i - \bar{y})^2} \quad ,$$

where

$\hat{y}_i =$ the value of the dependent variable computed by the model,

$y_i =$ the experimental value of the dependent variable,

$\bar{y} =$ the average value of the experimental dependent variable.

Values of r^2 will range from 0 to 1. Generally, the larger the value of r^2, the better the model fits the data.[3]

The Mallow C(p) statistic is used to measure the total squared error between the data and the model. It is defined as

$$C(p) = \left(\frac{SSE_p}{s^2}\right) - (n - 2p) \quad , \tag{2.2}$$

where

SSE = sum-of-squares error for the model (see ref. 3 for the matrix mathematical definition),

$s^2 =$ mean square error for the full model,

$$= \Sigma \frac{(y_i - \hat{y}_i)^2}{(n - m - 1)} \quad ,$$

n = number of observations,

m = number of independent variables,

p = number of parameters (independent variables) in the model plus the intercept, if any (which is essentially the number of adjustable coefficients in the model).

Mallow recommends using the model where C(p) first approaches the value of p.

Third, direct comparisons are made to see how well the correlation or model predicts the quantities of interest. Equations are recommended for use in process control applications.

2.1 NITRIC ACID-WATER SYSTEM

The use of density or electrical conductivity to ascertain nitric acid concentration in aqueous solution is not new. In fact, instruments can be purchased that are precalibrated to make such measurements, usually over narrow ranges. Because the ultimate goal is to develop correlations for the nitric acid-uranium-water system, the various forms that the correlations take for the nitric acid-water system are important for the limiting case of zero uranium concentration. Therein lies the major purpose of this section of the report. A second and perhaps equally important purpose is to develop correlations that are highly accurate over a wide range of concentrations.

2.1.1 Density

The density of aqueous nitric acid solutions has been measured and tabulated for a wide range of concentrations (from 0 to 100 wt %) over a broad range of temperatures (from 0 to 100°C).[4-7] These data are summarized in Appendix A. Figure 2.1 displays the density as a function of wt % nitric acid for different temperatures. The figure shows a family of curves, each having a similar shape, but displaced vertically along the density coordinate. Additionally, the displacement is not constant with concentration but appears to widen with increasing concentration. The method of attack now is to determine how density varies with concentration at a fixed temperature. Once this dependence is adequately modeled, then terms can be added for temperature correction.

The curves of Fig. 2.1 show inflection points at ~30 wt % acid and above 90 wt % acid. Concentration expressed as wt % has certain advantages. One advantage is that the value of concentration does not change with temperature. However, concentration can also be expressed in molar units and, for HNO_3, the conversion may be written as

$$C = \frac{10\rho w}{63.02} , \tag{2.3}$$

where

C = concentration, *M*,

ρ = density, g/cm^3,

w = concentration, wt %,

The value of 63.02 is the mol. wt of nitric acid and the 10 results from the conversion from wt % and the shift from cm^3 basis to liters. Conversion back to wt % from molarity concentration and density is easily accomplished by rearranging Eq. (2.3). There is an advantage in using molar concentration; density can be more accurately modeled with the same number of coefficients than if wt % is the independent variable. A detailed discussion is provided later in this section.

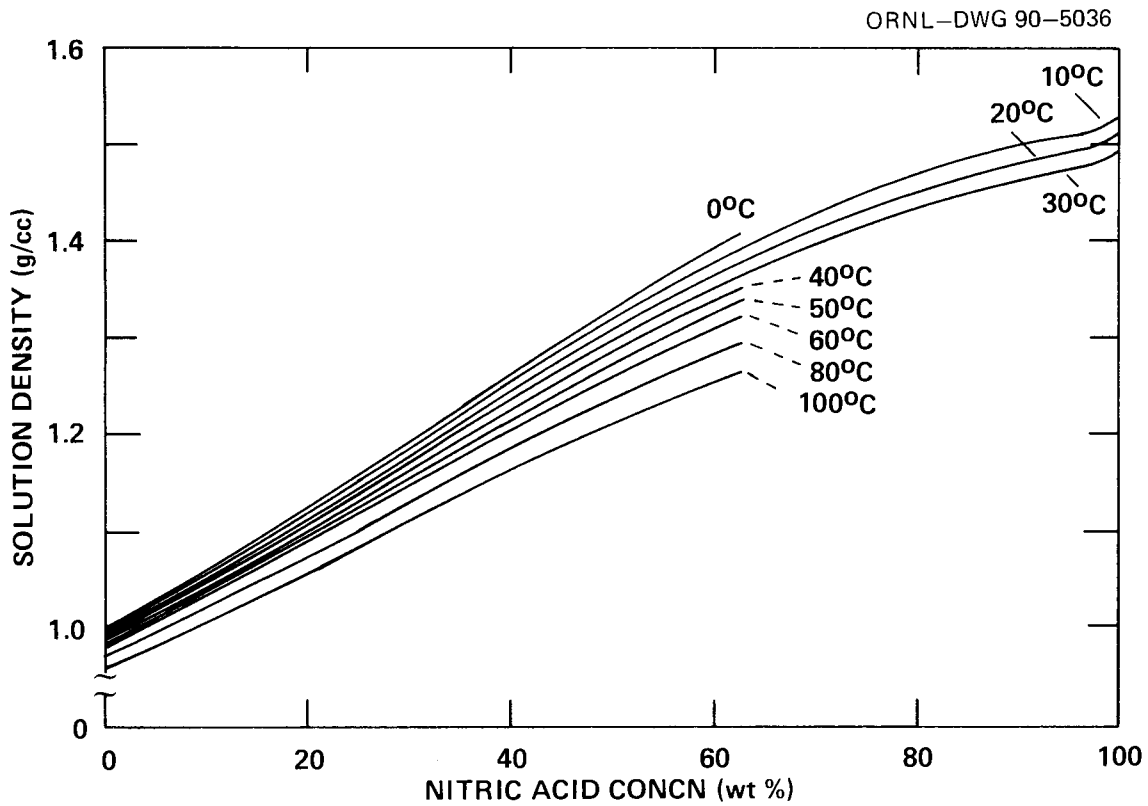

Fig. 2.1. Density of aqueous nitric acid solutions as a function of wt % acid at various temperatures.

If inverse (or reciprocal) density is used instead of density, the curve that correlates density with molar concentration assumes a simple shape (shown in Figs. 2.2 and 2.3 for the data at 25°C). The curvature shown in Fig. 2.3 suggests that reciprocal density will depend on concentration to the first and second powers. Other terms, such as third order or reciprocal concentration, may also be tested.

The very highest concentrations exhibit a definite change in the functional form above ~95 wt %. Because most process applications will not involve such high acid concentrations, it seemed that a small reduction in the range might considerably simplify the functional form. Consequently, a decision was made to test an equation having the form

$$\frac{1}{\rho} = a_0 + a_1C + a_2C^2 + a_3C^3 + a_4C^4 + \frac{a_5}{C} + \ldots , \tag{2.4}$$

over a range from 0 to 21.2 *M* (from 0 to 90 wt %) and at a temperature of 25°C. The correlation coefficient and Mallow C(p) statistic were calculated for all possible regression combinations of the variables shown in Eq. (2.4) using the Statistical Analysis System (SAS).[3] Results from the best five models from each group (group defined as the number of independent variables in the model) are provided in Tables 2.1 and 2.2.

For models having more than two independent parameters, the C(p) statistic clearly shows that molar concentration is the better unit to use than wt %. The correlation coefficient does not strongly distinguish between the two units.

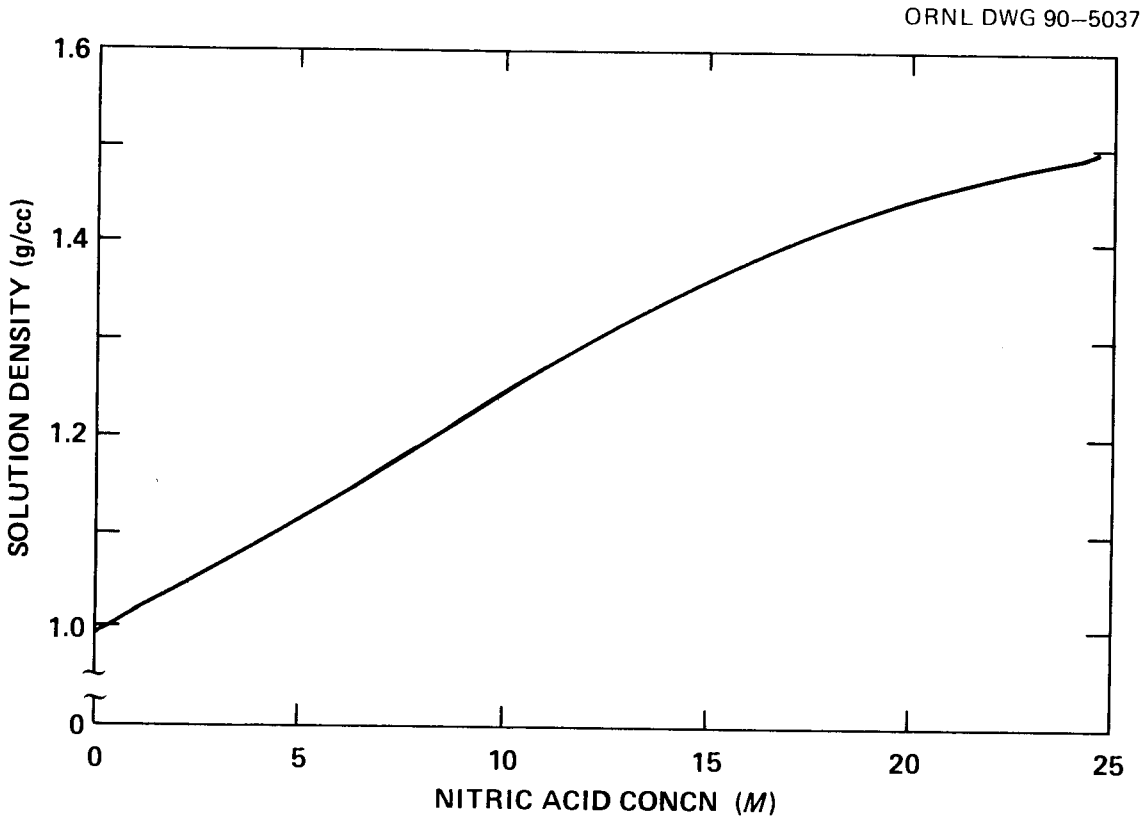

Fig. 2.2. Density of nitric acid solutions as a function of molar concentration at 25°C.

Based on the values of the statistics given in Table 2.2, and in keeping with simplicity, the best model is

$$\frac{1}{\rho_{25}} = a_0 + a_1 C + a_2 C^2 + a_3 C^3 \quad , \tag{2.5}$$

and the coefficients are

$a_o =$ 1.003124,

$a_1 =$ -3.364529×10^{-2},

$a_2 =$ 1.219254×10^{-3},

$a_3 =$ -1.681279×10^{-5}.

This equation is for the density of nitric acid at 25°C and covers the range from 0 to 21.2 *M* (from 0 to 90 wt %). It deviates a maximum of 0.05% from the data, with the preponderance of errors being much smaller than the maximum.

The next step is to develop a method to incorporate temperature correction into the correlation. Many liquids expand when the temperature is raised. A coefficient of volumetric expansion, β, is sometimes used to model this phenomena and is defined by the equation

$$V_2 = V_1[1 + \beta(T_2 - T_1)] \quad , \tag{2.6}$$

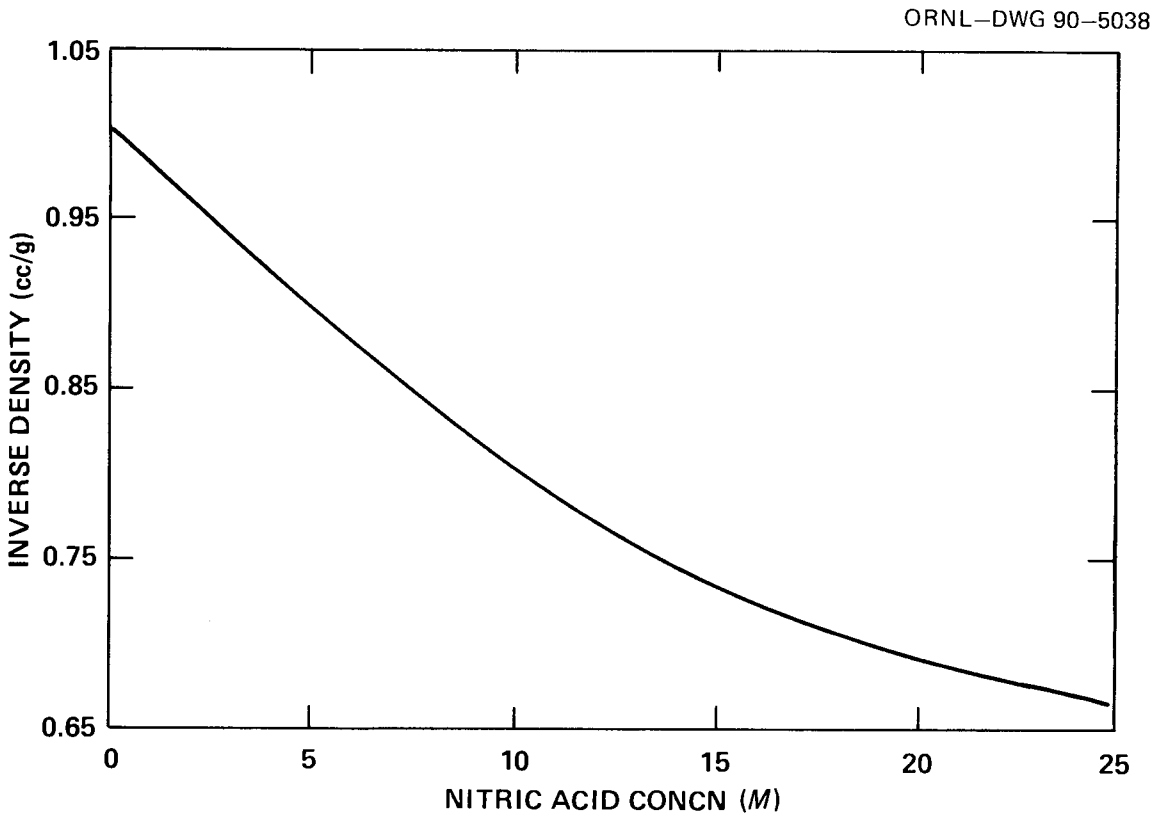

Fig. 2.3. Reciprocal density of nitric acid solutions as a function of molar concentration at 25°C.

where

V = volume,

T = temperature.

The subscripts 1 and 2 represent conditions at two different temperatures. Values of β usually vary with temperature for pure substances. For water at 15°C, its value is 0.00018/°C.[8] Density is defined as the ratio of mass to volume,

$$\rho = m/V \quad . \tag{2.7}$$

In nonrelativistic physics, mass does not change with temperature, so the dependence of density on temperature may be written

$$\frac{1}{\rho} = \left(\frac{1}{\rho_0}\right)[1 + \beta(T - T_0)] \quad , \tag{2.8}$$

where the subscript 0 refers to a reference temperature. It is very likely that β is a function of both temperature and concentration for nitric acid. If β depended only linearly on concentration C, combining Eqs. (2.5) and (2.8) to obtain a correlation over all values of temperature and composition would result in the final correlation being at least fourth-order in concentration. This result can be avoided by choosing β as a function of temperature and density at 25°C, since density is a measure of concentration. As a first approximation, it may be assumed that

Table 2.1. Correlation of reciprocal density with weight percent at 25°C

Number of variables in model	r^2	C(p)	Independent variables				
1	0.30946902	12229577.0	w^{-1}				
1	0.58959258	7268443.0	w^4				
1	0.69437237	5412738.0	w^3				
1	0.82842973	3038513.0	w^2				
1	0.96874188	553512.0	w				
2	0.97526334	438015.0	w	w^{-1}			
2	0.97784730	392252.0	w^2	w^3			
2	0.99855373	25530.2	w	w^4			
2	0.99963490	6382.2	w	w^2			
2	0.99970945	5061.8	w	w^3			
3	0.99972883	4720.5	w	w^3	w^{-1}		
3	0.99978303	3760.6	w	w^2	w^{-1}		
3	0.99984436	2674.4	w	w^2	w^4		
3	0.99988670	1924.5	w	w^3	w^2		
3	0.99995527	710.2	w	w^3	w^4		
4	0.99826532	30642.0	w^2	w^3	w^4	w^{-1}	
4	0.99988097	2028.1	w	w^2	w^4	w^{-1}	
4	0.99990589	1586.8	w	w^3	w^2	w^{-1}	
4	0.99996383	560.6	w	w^3	w^4	w^{-1}	
4	0.99999307	42.8	w	w^3	w^4	w^2	
5	0.99999526	6.0	w	w^3	w^4	w^2	w^{-1}

$$\beta = a_0 + a_1\rho_0 + a_2 T \quad . \tag{2.9}$$

Cross-product terms may be readily added. Values of β may be obtained from rearrangement of Eq. (2.8), thus

$$\beta = \frac{\rho_0 / \rho - 1}{T - T_0} \quad . \tag{2.10}$$

Table 2.2. Correlation of reciprocal density with molar concentration at 25°C

Number of variables in model	r^2	C(p)	Independent variables				
1	0.30603219	32294596.0	C^{-1}				
1	0.52384719	22158296.0	C^4				
1	0.62704240	17355974.0	C^3				
1	0.76862514	10767240.0	C^2				
1	0.94075574	2756922.0	C				
2	0.95024004	2315559.0	C^2	C^3			
2	0.95687296	2006888.0	C	C^{-1}			
2	0.99004352	463254.0	C	C^4			
2	0.99486520	238871.0	C	C^3			
2	0.99901680	45670.3	C	C^2			
3	0.99635612	169491.0	C	C^3	C^{-1}		
3	0.99923301	35610.8	C	C^2	C^{-1}		
3	0.99961736	17724.5	C	C^3	C^4		
3	0.99999030	369.5	C	C^2	C^4		
3[a]	0.99999690	62.5	C	C^2	C^3		
4	0.99362076	296786.0	C^2	C^3	C^4	C^{-1}	
4	0.99975715	11221.5	C	C^3	C^4	C^{-1}	
4	0.99999260	264.5	C	C^2	C^4	C^{-1}	
4	0.99999723	49.1	C	C^2	C^3	C^{-1}	
4	0.99999819	4.0	C	C^2	C^3	C^4	
5	0.99999819	6.0	C	C^2	C^3	C^4	C^{-1}

[a]Chosen model.

The form of Eq. (2.10) precludes the data at the reference temperature from being included in the regression (i.e., the denominator and numerator become zero). It is of no consequence, however, because the form of Eq. (2.8) collapses to the value of the reference density at the reference temperature. The remaining density-concentration data in Appendix A were correlated with SAS using Eqs. (2.9) and (2.10), where ρ_0 was calculated for $T_0 = 25°C$ using Eq. (2.5). (Since 25°C was the chosen reference, ρ_0 may now be replaced with the notation ρ_{25}, etc.) The results are provided in Table 2.3.

Table 2.3. Regression analysis for the volumetric expansion coefficient

Number of variables in model	r^2	C(p)	Independent variables			
1	0.00304427	57949.4	T			
1	0.00306711	57948.0	T^2			
1	0.02541402	56630.3	$T\rho_o$			
1	0.93282401	3126.0	ρ_o			
2	0.11045808	51617.8	$T\rho_o$	T^2		
2	0.48149439	29740.1	$T\rho_o$	T		
2	0.98020626	334.1	ρ_o	T^2		
2	0.98038073	323.8	ρ_o	$T\rho_o$		
2[a]	0.98323068	155.8	ρ_o	T		
3	0.48277862	29666.4	$T\rho_o$	T	T^2	
3	0.98151522	258.9	ρ_o	$T\rho_o$	T^2	
3	0.98332892	152.0	ρ_o	T	T^2	
3	0.98580576	5.9	ρ_o	T	$T\rho_o$	
4	0.98585574	5.0	ρ_o	T	$T\rho_o$	T^2

[a]Chosen model.

The C(p) statistic indicates that the four-variable model is the best selection for β. However, the correlation coefficient is hardly better than that for the best two-variable model. Because the two-variable model will lead to the simplest inverse, it was selected for use. The density dependence on temperature may now be written, by combining Eq. (2.9) with Eq. (2.8), as

$$\frac{1}{\rho} = \left(\frac{1}{\rho_{25}}\right)[1 + (a_0 + a_1\rho_{25} + a_2 T)(T - 25)] \quad , \tag{2.11}$$

where

$a_0 = -1.647365 \times 10^{-3}$,

$a_1 = 1.897063 \times 10^{-3}$,

$a_2 = 2.017796 \times 10^{-6}$.

Again, this covers the range of from 0 to ~22 *M* (from 0 to 90 wt %) and deviates a maximum of 0.6% from the data, with most of the errors being much smaller than the maximum. The largest

errors occur at temperatures far from 25°C (for example, 0 and 100°C) and at the lowest concentrations (under ~0.8 *M* or 5 wt %). [Interestingly, the volumetric expansion coefficient implied by Eq. (2.11) is 0.00028/°C for water at 15°C, which is not far from the true value.]

2.1.2 Conductivity

The literature does not contain as large a body of data for electrical conductivity of aqueous nitric acid as it does for the density of that acid. The available data do span a considerable range of temperatures (from 0 to 306°C) and concentrations (from 0 to 24 *M* HNO_3) with most of the data measured near room temperature.[5,9-12] These data are summarized in Appendix B.

The data having the widest range of concentration at a fixed temperature are shown in Fig. 2.4. Electrical conductivity is shown to rise rapidly with concentration, reaching a maximum at ~6 *M*. Conductivity then decreases beyond the point of the maximum to quite low values well beyond the azeotrope. This bell-shaped curvature means that there is not a unique value of concentration for a given value of conductivity. Conductivity can be used to infer concentration only when it is known to which side of the peak the true value lies. Additionally, the conductivity is seen to have a strong temperature-dependence.

The available data extend to very low concentrations and are not easily plotted on the linear scale of Fig. 2.4. The data at 18°C have been plotted on a log-log scale in Fig. 2.5 so that the entire range may be more easily examined. At nitric acid concentrations below ~0.5 *M*, the conductivity varies with the first power of concentration. This, together with a downward concavity at the maximum, suggests fitting the data to a polynomial,

$$c = a_0 + a_1C + a_2C^2 + a_3C^3 + \ldots , \tag{2.12}$$

where c is electrical conductivity, mS/cm. A built-in advantage here is that values of C below unity cause the higher power terms to rapidly vanish, leaving only the first power term.

Fitting the conductivity over the entire range of concentration turned out to be a difficult problem. The benefit from the effort did not seem to justify development of such an equation, especially in view of the range of concentrations to which the correlation would be applied. Most of the solutions in the reprocessing plant, toward which this work is directed, contain both nitric acid and uranium. Acid concentration would typically be in the range of 0.5 to 7 *M*. Smooth extrapolation outside this range was considered desirable, so a decision was made to fit the data in the 0.1 to 10.0 *M* concentration range. A linear regression on polynomials like Eq. (2.12) led to values for the constant term in the vicinity of -100 to -200. The electrical conductance cannot be less than zero even when the concentration nears zero. In fact, the electrical conductivity of pure water at 18°C is 4×10^{-5} mS/cm.[6] Compared to the hundreds of millisiemens of conductance exhibited by acid solutions, the conductivity of pure water is essentially zero. The constant term in Eq. (2.12) can be forced to zero so that the conductivity will be zero when the concentration assumes a value of zero. The method chosen was to make the definition

$$K = \frac{c}{C} = a_1 + a_2C + a_3C^2 + \ldots . \tag{2.13}$$

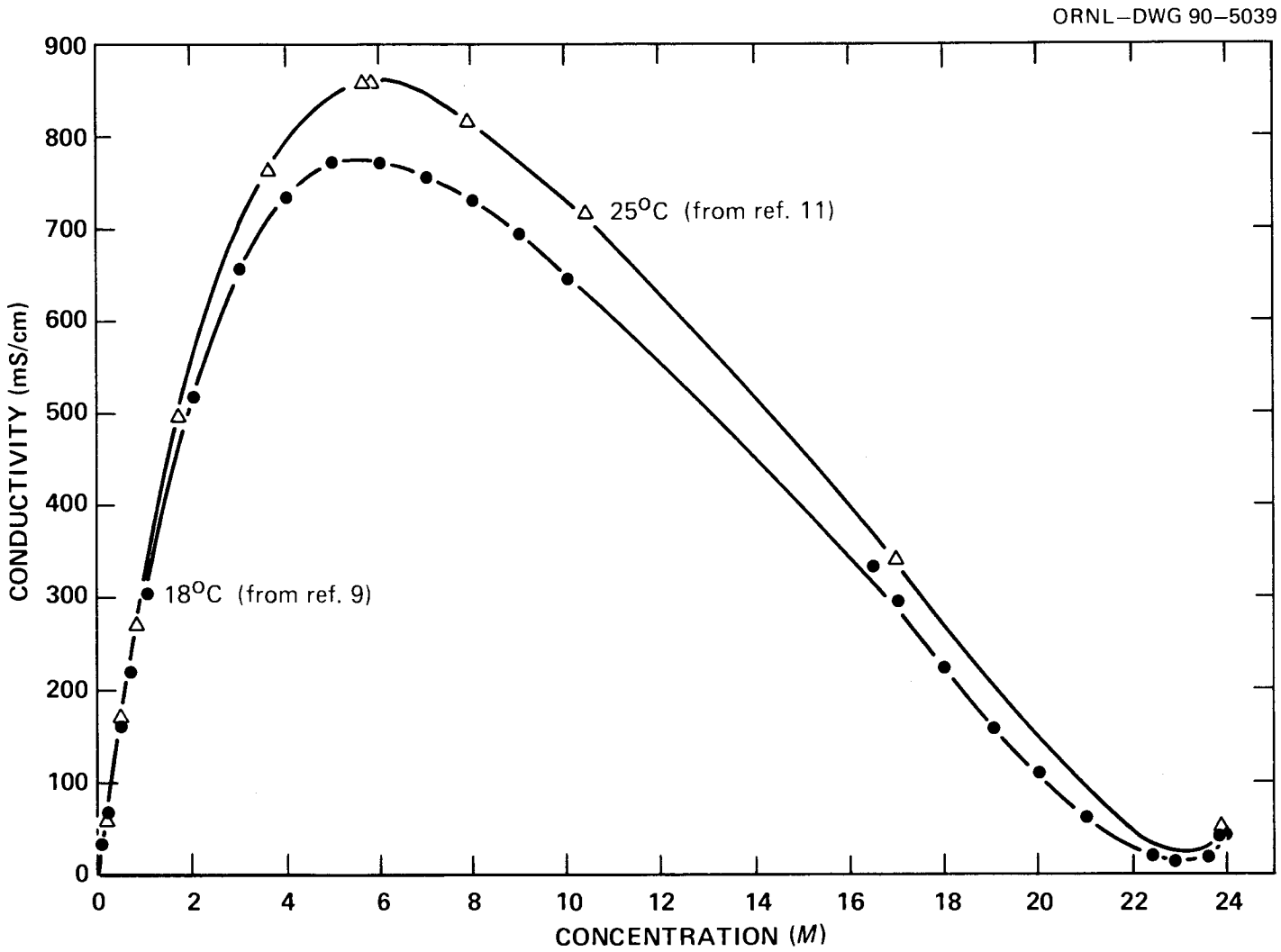

Fig. 2.4. Electrical conductivity of aqueous nitric acid.

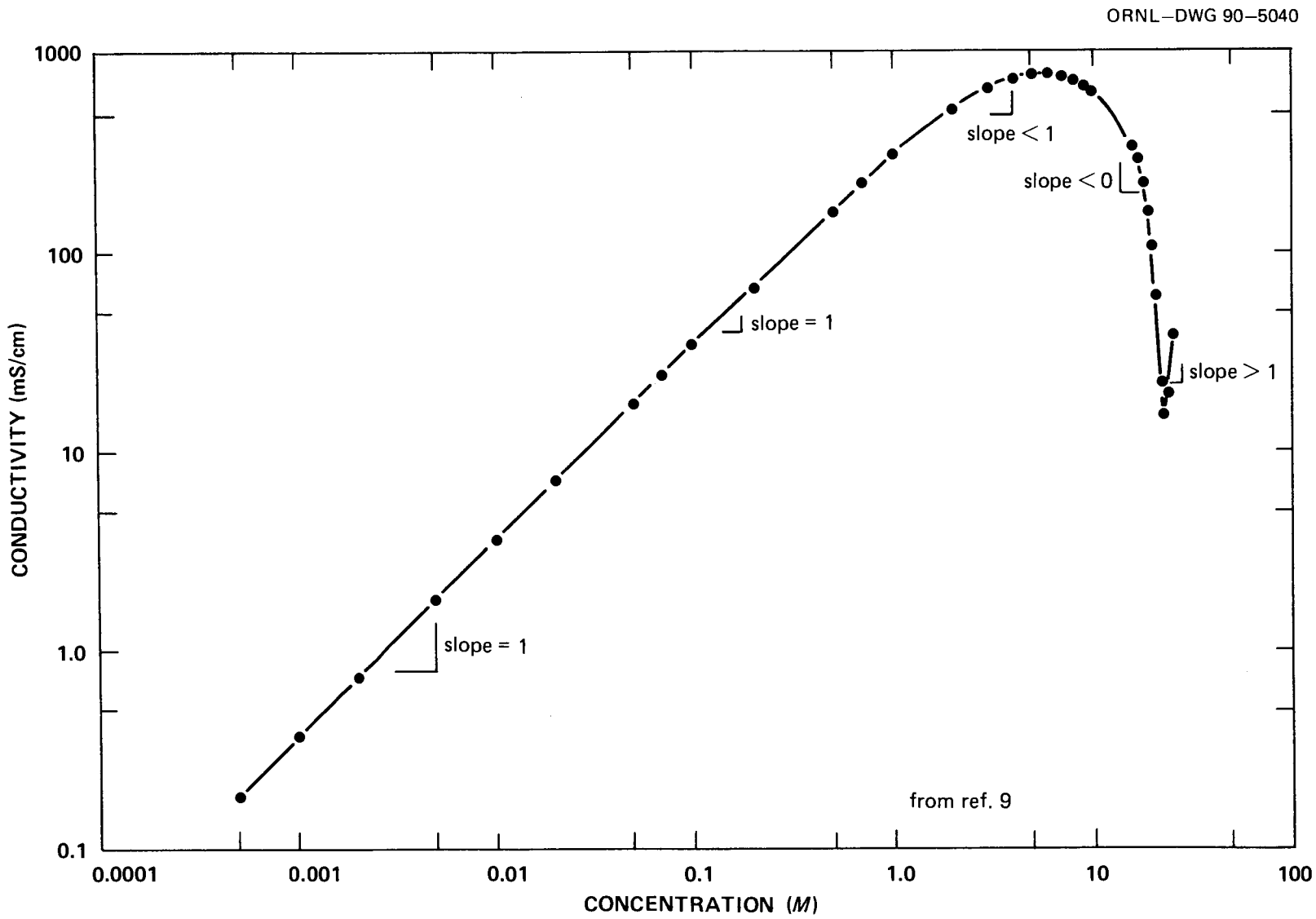

Fig. 2.5. Conductivity of dilute and concentrated aqueous nitric acid at 18°C—log scale.

This definition of K is consistent with that sometimes found in the literature.[9] The data (see Fig. 2.4) have been transformed to a plot of K-values vs concentration in Fig. 2.6. As shown, the curve is smooth and lends itself well to regression analysis. Finally, expansion of Eq. (2.13) to solve for conductivity, c, produces the desired low concentration limit.

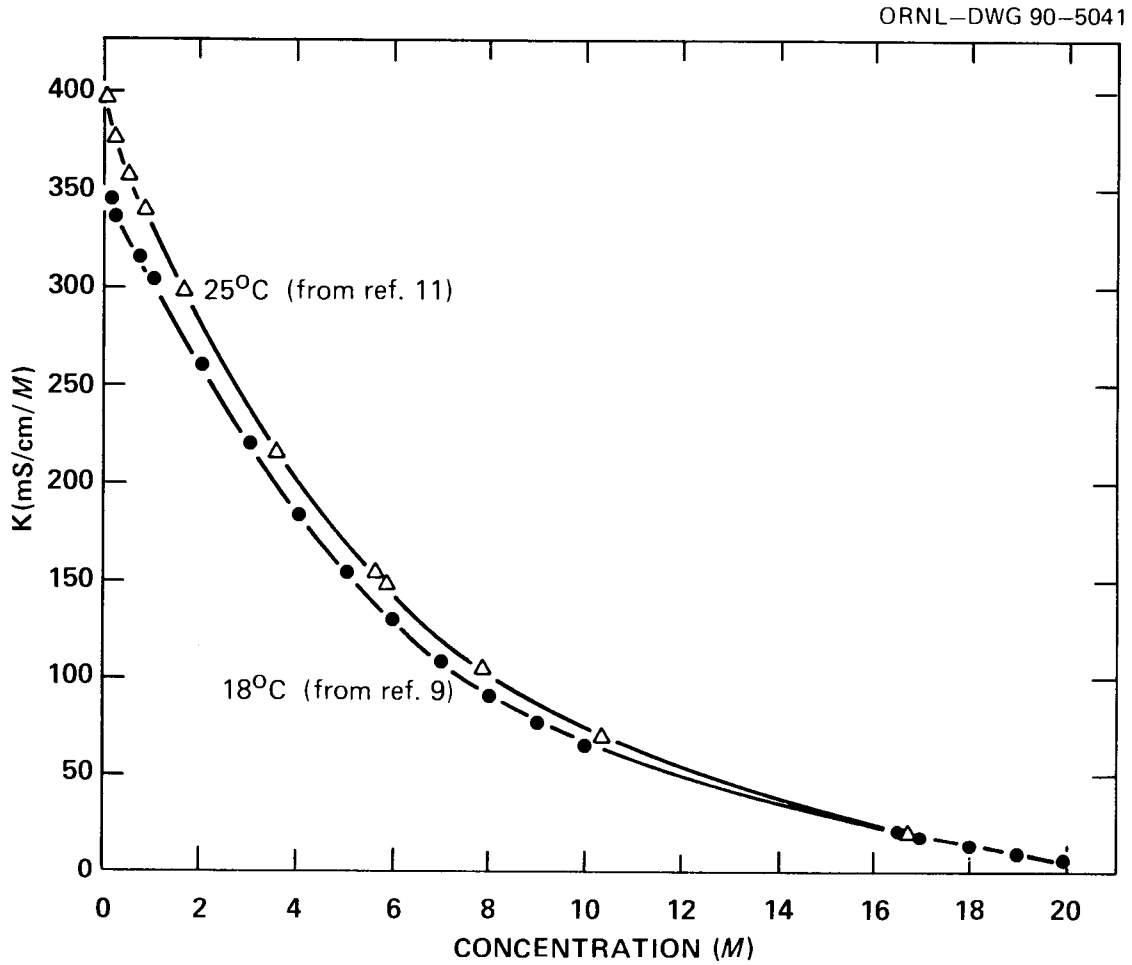

Fig. 2.6. K-values for nitric acid.

The data at 18 and 25°C, and between 0.1 and 10.0 *M* nitric acid were fit to equations having the form of Eq. (2.13) by using SAS. Again, every combination of powers of concentration up to fourth power was checked. The results are shown in Tables 2.4 and 2.5.

These results show rather decisively that K should be correlated with concentration to the first and second powers. Adding terms of higher power seems to make a marginal improvement, as evidenced by the correlation coefficient. (Subsequent work to include temperature effects in the correlation indicated that the addition of the third power term made a significant improvement, as will be described in detail in this section.) Conductivity at a constant temperature was, therefore, correlated with the function

$$c = a_1C + a_2C^2 + a_3C^3 + a_4C^4 \quad . \tag{2.14}$$

Table 2.4. Correlation of K with concentration at 18°C

Number of variables in model	r^2	C(p)	Independent variables			
1	0.56928055	16628.0	C^4			
1	0.67342934	12605.0	C^3			
1	0.81380055	7182.5	C^2			
1	0.96848423	1207.4	C			
2	0.95120861	1876.7	C^2	C^4		
2	0.96849062	1209.1	C^2	C^3		
2	0.99668380	120.1	C	C^4		
2	0.99857441	47.1	C	C^3		
2	0.99964906	5.6	C	C^2		
3	0.99328223	253.5	C^2	C^3	C^4	
3[a]	0.99966423	7.0	C	C^2	C^3	
3	0.99967546	6.5	C	C^2	C^4	
3	0.99976698	3.0	C	C^3	C^4	
4	0.99976701	5.0	C	C^2	C^4	C^3

[a]Chosen model.

At a temperature of 18°C the coefficients of Eq. (2.14) are

$a_1 = 348.8490,$

$a_2 = -49.89165,$

$a_3 = 2.346735,$

$a_4 = -1.843778 \times 10^{-2}.$

The data are correlated to within 1.95%. At 25°C, the coefficients are

$a_1 = 385.7028,$

$a_2 = -59.85647,$

$a_3 = 3.811007,$

$a_4 = -9.486139 \times 10^{-2}.$

The data are correlated to within 0.77%. Note that the values of a_1 correspond remarkably well with the slope of the curves (see Fig. 2.4) near a concentration of zero.

Table 2.5. Correlation of K with concentration at 25°C

Number of variables in model	r^2	C(p)	Independent variables			
1	0.49772585	19655.0	C^4			
1	0.60799146	15339.0	C^3			
1	0.77153994	8937.4	C^2			
1	0.95693759	1680.5	C			
2	0.94950903	1973.3	C^2	C^4		
2	0.96527934	1356.0	C^2	C^3		
2	0.99515633	186.6	C	C^4		
2	0.99743667	97.3	C	C^3		
2	0.99950376	16.4	C	C^2		
3	0.99072728	362.0	C^2	C^3	C^4	
3	0.99971148	10.3	C	C^3	C^4	
3	0.99989540	3.1	C	C^2	C^4	
3[a]	0.99989709	3.0	C	C^2	C^3	
4	0.99989781	5.0	C	C^2	C^3	C^4

[a]Chosen model.

The next step was to include the temperature dependence of conductivity. Figure 2.7 illustrates how conductivity varies with temperature at fixed values of concentration. The graph shows that conductivity increases almost linearly with temperature, with the slope decreasing as higher temperatures are approached and the curvature becoming more pronounced at higher temperatures.

Because it is assumed that all conductivity curves have an intercept of zero at zero concentration, there is not a family of curves with a predictable offset from one another as in the density correlation described in Sect. 2.1.1. (There is a family of curves, to be sure, but of a different variety.) Instead, it seems that the coefficients, a_i, of Eq. (2.13) or of Eq. (2.14) are functions of temperature. This suggests that coefficients could be obtained at each temperature and then the coefficients correlated with temperature. However, lack of sufficient data precludes obtaining reliable coefficients at each temperature. A different tactic was used. It may be assumed that the coefficients in the conductivity equation, a_i, are of the form

$$a_i = b_{0,i} + b_{1,i}T + \ldots , \tag{2.15}$$

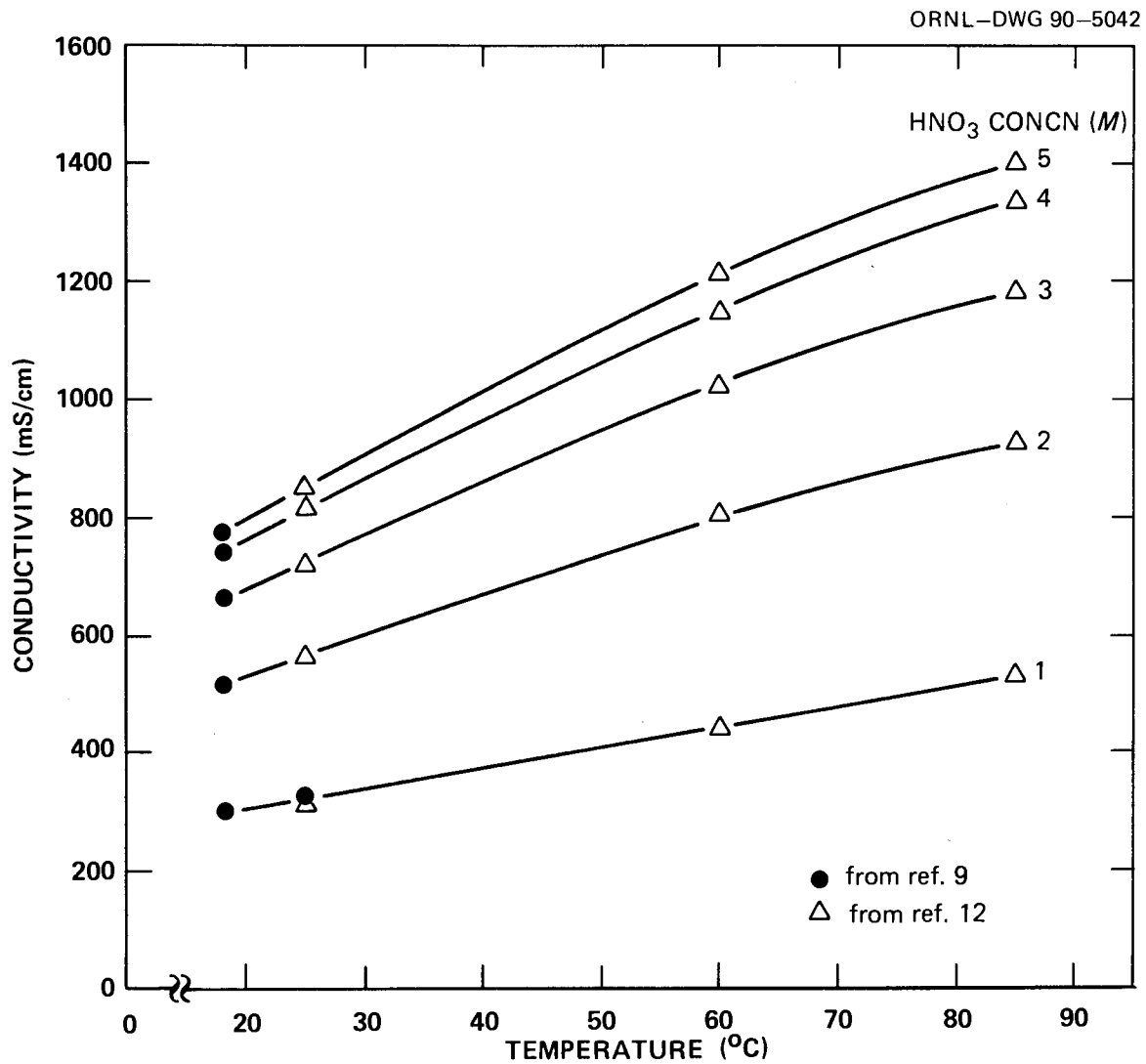

Fig. 2.7. Temperature effect on electrical conductivity of aqueous nitric acid.

Insert Eq. (2.15) into Eq. (2.14) to obtain

$$K = \frac{c}{C} = (b_{0,1} + b_{1,1}T) + (b_{0,2} + b_{1,2}T)C + (b_{0,3} + b_{1,3}T)C^2 + (b_{0,4} + b_{1,4}T)C^3 + \ldots . \tag{2.16}$$

This form can be expanded to

$$K = \frac{c}{C} = b_{0,1} + b_{1,1}T + b_{0,2}C + b_{1,2}TC + b_{0,3}C^2 + b_{1,3}TC^2 + \ldots . \tag{2.17}$$

which can be fit to all the available data in a single pass. At a given value of temperature Eqs. (2.16) and (2.17) collapse to the form of Eq. (2.14) that previously gave the best results.

All combinations of terms in Eq. (2.14) and Eq. (2.15), through second order in temperature, were tested by using SAS. The results are shown in Table 2.6. The Mallow statistic indicates

$$K = \frac{c}{C} = b_{0,1} + b_{1,1}T + b_{2,1}T^2 + (b_{0,2} + b_{1,2}T)\,C + (b_{0,3} + b_{1,3}T)\,C^2 + b_{1,4}TC^3 \quad , \tag{2.18}$$

is the best equation form, and does not include the $b_{0,4}C^3$ term. Table 2.7 shows the result of a forward selection procedure in which terms were initially selected (step 0) and more terms were added by using SAS until no further significant improvement in the data fit was obtained. The correlation coefficient, r^2, does not significantly improve with additional terms, so Eq. (2.18) appears to be the best equation form to fit the conductivity over the temperature and concentration range of interest. The coefficients for Eq. (2.18) are

$b_{0,1} =$ 255.7921,

$b_{1,1} =$ 5.446796,

$b_{2,1} =$ -8.49695×10^{-3},

$b_{0,2} =$ -36.42003,

$b_{1,2} =$ -1.043629,

$b_{0,3} =$ 1.437531,

$b_{1,3} =$ 1.310446×10^{-1},

$b_{1,4} =$ -6.48670×10^{-3}.

The data are correlated within a maximum error of 4.6% over a concentration range of 0.1 to 10.0 *M* and a temperature range of 0° to 100°C. Usually the error is much smaller. Table 2.8 summarizes the data correlated by Eq. (2.18) and shows the percentage error in calculating the conductivity. The error between the data and the equation is small and is probably on the order of the error in the data. The largest errors occur at the highest concentrations (from ~8 to 10 *M*). The fourth order term in Eq. (2.18), being negative, causes the calculated conductivity to fall sharply at the higher concentrations. Beyond 10 *M*, the curve falls off faster than the data would indicate. However, using terms of up to only third order in concentration results in a curve that turns up sharply at ~10 *M*, which is clearly in opposition to the established data. The present model is adequate for determining concentration from conductivity measurements. A comparison of the conductivity data to the conductivity calculated from Eq. (2.18) is shown graphically in Fig. 2.8.

Note that earlier versions of the conductivity equation implemented in the IET used the form for the temperature dependence of the coefficients

$$a_i = b_{0,i} + \frac{b_{1,i}}{T_k} \quad , \tag{2.19}$$

where

$$T_k = T + 273.15^2 \quad .$$

With an eight constant equation, the data were fit with a value of r^2 only slightly smaller than that obtained for Eq. (2.18), both having the same number of coefficients. However, the reciprocal

Table 2.6. Regression models for dependent variable K

Number of variables in model	r^2	C(p)	Independent variables				
1	0.25163145	19699.0	TC^3				
1	0.26595436	19321.0	TC^2				
1	0.44449276	14604.0	C^3				
1	0.53325619	12259.0	C^2				
1	0.62884012	9733.2	C				
2	0.79758136	5277.0	C^2	T			
2	0.85713607	3703.5	T^2	TC			
2	0.88960244	2845.8	T	TC			
2	0.90469119	2447.1	C	T^2			
2	0.91989398	2045.4	C	T			
3	0.94917106	1273.9	T	TC	T^2C		
3	0.95708887	1064.7	T	TC	T^2C^3		
3	0.96637653	819.3	C	T	T^2C		
3	0.96712108	799.7	C	T	TC		
3	0.97129121	689.5	T	TC	T^2C^2		
4	0.98883556	228.0	C	T	TC	C^3	
4	0.99091126	173.1	C	T	T^2C	C^2	
4	0.99132661	162.2	C	T	TC	C^2	
4	0.99297612	118.6	C	T	TC	TC^3	
4	0.99474437	71.9	C	T	TC	TC^2	
5	0.99518703	62.2	C	T	TC	TC^2	T^2C^2
5	0.99531977	58.7	C	T	TC	TC^2	T^2
5	0.99534535	58.0	C	T	TC	TC^2	C^3
5	0.99567768	49.2	C	T	TC	TC^2	C^2
5	0.99589499	43.5	C	T	TC	TC^2	T^2C^3

Table 2.6. (continued)

Number of variables in model	r^2	C(p)	Independent variables										
6	0.99637203	32.9	C	T	TC	TC^2	C^2	T^2					
6	0.99646599	30.4	C	T	TC	TC^2	T^2C^3	T^2C^2					
6	0.99653212	28.6	C	T	TC	TC^2	C^2	TC^3					
6	0.99666407	25.1	C	T	TC	TC^2	C^3	TC^3					
6	0.99676981	22.3	C	T	T^2C	C^2	T^2C^2	TC^3					
7	0.99711092	15.3	C	T	T^2C	C^2	T^2C^2	T^2C^3	TC^2				
7	0.99717082	13.7	C	T	TC	C^2	T^2C^3	T^2C	T^2C^2				
7	0.99724059	11.9	C	T	TC	TC^2	T^2C^3	T^2C^2	T^2				
7[a]	0.99735211	9.0	C	T	TC	TC^2	C^2	TC^3	T^2				
7	0.99747196	5.8	C	T	TC	TC^2	C^3	TC^3	T^2				
8	0.99747376	7.7	C	T	TC	TC^2	C^3	TC^3	T^2	T^2C			
8	0.99747779	7.6	C	T	TC	TC^2	T^2C^3	T^2	TC^3	C^3			
8	0.99748014	7.6	C	T	TC	TC^2	C^3	TC^3	T^2	T^2C^2			
8	0.99749562	7.2	C	T	TC	TC^2	C^2	TC^3	T^2	C^3			
8	0.99749972	7.1	C	T	TC	C^2	T^2C^3	T^2	T^2C^2	T^2C			
9	0.99749988	9.1	C	T	TC	TC^2	T^2C^3	T^2	TC^3	C^3	C^2		
9	0.99750053	9.0	C	T	TC	TC^2	C^3	TC^3	T^2	T^2C^2	T^2C		
9	0.99750128	9.0	C	T	TC	C^2	T^2C^3	T^2	C^3	T^2C	T^2C^2		
9	0.99752141	8.5	C	T	TC	TC^3	C^2	T^2	T^2C^2	T^2C	T^2C^3		
9	0.99753767	8.1	C	T	TC	TC^2	T^2C^3	T^2C^2	T^2	C^2	T^2C		
10	0.99750987	10.8	C	T	T^2C	C^2	T^2C^2	TC^3	T^2	T^2C^3	TC^2	C^3	
10	0.99752326	10.4	C	T	TC	TC^2	T^2C^3	T^2C^2	T^2	C^3	TC^3	T^2C	
10	0.99753779	10.1	C	T	TC	TC^2	T^2C^3	T^2C^2	T^2	C^2	T^2C	TC^3	
10	0.99753810	10.0	C	T	TC	TC^2	T^2C^3	T^2C^2	T^2	C^2	T^2C	C^3	
10	0.99753968	10.0	C	T	TC	TC^3	C^2	C^3	T^2	T^2C^2	T^2C^3	T^2C	
11	0.99753978	12.0	C	T	TC	TC^2	T^2C^3	T^2C^2	T^2	C^2	T^2C	C^3	TC^3

[a]Chosen model

Table 2.7. Summary of forward selection procedure for dependent variable K

Step	Variable(s) entered	Number in model	Partial r^2	Model r^2	C(p)
0	$C\ C^2$	2	0.6419	0.6419	9390.00
1	T	3	0.3061	0.9480	1305.37
2	TC	4	0.0443	0.9913	162.15
3	TC^2	5	0.0044	0.9957	49.20
4	TC^3	6	0.0009	0.9965	28.62
5	T^2	7	0.0008	0.9974	8.96
6	C^3	8	0.0001	0.9975	7.17[a]

[a]Violates the Mallow criteria.

temperature scale gives a curvature that becomes less pronounced as temperature increases. This finding is directly opposite to the behavior of the curves observed in Fig. 2.7 but does show that the curvature must be slight. A second order temperature term like that in Eq. (2.18) is now thought to more appropriately model the data and does not require transformation of temperature to the absolute scale.

2.1.3 Equations for Process Use

Density and electrical conductivity were correlated for nitric acid solutions as functions of concentration and temperature in Sects. 2.1.1 and 2.1.2. Process control applications will require the inverse equation; that is, given temperature and density or conductivity, calculate the concentration.

The algorithm for obtaining nitric acid concentration, C, from measurements of temperature, T, and density, ρ, involves the inverse of Eqs. (2.11) and (2.5). Measured density can be corrected to the density that the solution would have at 25°C by rearranging Eq. (2.11)

$$\rho_{25} = \frac{\rho[1 + (a_0 + a_2 T)(T - 25)]}{1 - a_1 \rho (T - 25)} , \tag{2.20}$$

where the constants (a) are defined in Eq. (2.11). Now the concentration at 25°C, C_{25}, can be calculated by solving Eq. (2.5), which is a cubic equation. The concentration can then be readjusted to correspond to the temperature at which the measurements were made by

$$C = \frac{C_{25}\rho}{\rho_{25}} . \tag{2.21}$$

The analytic solution of Eq. (2.5) shows that there is only one positive real root in the range of $0 \leq \rho \leq 2$, so the choice of one of the possible three solutions is easy. However, the analytic solution involves the differences of large numbers (on the order of 10^4). Having carried seven-digit precision in the constants, which is more than is justified by the data, one can only

Table 2.8. Summary of data in conductivity correlation and percentage error

T (°C)	HNO_3 (*M*)	Conductivity (mS/cm)	Calculation of $c = f(C,T)^a$ (% error)	Calculation of $C = f^{-1}(c,T)^b$ (% error)
0.0	0.1000	24.53	-2.80	2.76
0.0	0.2000	48.26	-3.01	3.01
18.0	0.1000	34.57	0.03	-0.03
18.0	0.2000	67.20	-1.25	1.27
18.0	0.5000	160.80	-0.87	0.94
18.0	0.7000	220.90	0.42	-0.47
18.0	1.0000	305.50	1.95	-2.37
18.0	2.0000	518.20	1.61	-2.45
18.0	3.0000	660.00	1.60	-3.29
18.0	4.0000	737.60	0.47	-1.44
18.0	5.0000	773.00	-0.50	2.78
18.0	6.0000	774.60	-1.70	-16.46
18.0	7.0000	760.20	-1.86	-7.04
18.0	8.0000	735.20	-0.79	-1.66
18.0	9.0000	698.40	1.27	1.66
18.0	10.0000	649.00	4.62	3.90
20.0	0.0790	28.40	0.74	-0.76
20.0	0.1590	56.10	0.14	-0.15
20.0	0.2400	84.70	1.45	-1.53
20.0	0.3200	108.00	-1.75	1.81
20.0	0.4010	138.00	1.49	-1.62
20.0	0.4830	160.00	-1.00	1.08
20.0	0.5650	184.00	-1.40	1.52
20.0	0.6480	213.00	0.86	-0.97
25.0	0.0973	37.60	1.51	-1.55
25.0	0.1000	38.60	1.44	-1.48
25.0	0.1000	38.42	0.98	-1.00
25.0	0.1591	60.00	0.08	-0.08
25.0	0.2000	75.22	0.47	-0.49
25.0	0.2000	74.88	0.02	-0.02
25.0	0.2023	74.40	-1.75	1.77
25.0	0.4823	172.00	-0.27	0.29
25.0	0.4921	172.00	-2.14	2.28
25.0	0.5000	178.30	0.01	-0.01
25.0	0.5000	178.30	0.01	-0.01
25.0	0.7000	242.90	0.53	-0.61
25.0	0.8125	275.00	-0.13	0.14
25.0	0.9438	317.50	1.39	-1.68
25.0	1.0000	329.80	0.34	-0.40
25.0	1.0000	333.20	1.35	-1.64
25.0	1.6698	498.00	1.20	-1.68
25.0	1.9806	560.00	0.94	-1.42
25.0	3.0269	720.00	0.73	-1.47
25.0	3.5300	763.00	-0.67	1.53
25.0	4.0150	812.50	0.60	-1.74

Table 2.8. (continued)

T (°C)	HNO_3 (*M*)	Conductivity (mS/cm)	Calculation of: $c = f(C,T)^a$ (% error)	Calculation of: $C = f^{-1}(c,T)^b$ (% error)
25.0	5.0426	850.00	-1.15	5.24
25.0	5.5997	861.00	-1.42	9.26
25.0	5.8188	862.00	-1.63	12.12
25.0	7.5209	835.00	-2.81	-8.46
25.0	7.8813	820.00	-3.21	-7.46
25.0	9.0409	780.00	-0.77	-0.98
25.0	10.3483	717.00	6.43	4.33
35.0	0.1000	43.26	0.88	-0.90
35.0	0.2000	83.80	-0.64	0.66
50.0	0.1000	51.47	3.22	-3.39
60.0	0.1022	54.00	-2.58	2.56
60.0	0.2038	105.50	-2.81	2.83
60.0	0.5028	255.00	0.52	-0.58
60.0	0.9808	440.00	-3.31	3.85
60.0	2.0421	800.00	1.66	-2.63
60.0	3.0595	1020.00	2.54	-5.40
60.0	4.1097	1145.00	1.27	-3.64
60.0	5.1246	1210.00	-0.10	0.37
60.0	7.8107	1205.00	-3.95	-10.74
60.0	9.1800	1147.50	-0.40	-0.41
75.0	0.1000	63.06	4.04	-4.29
85.0	0.1009	64.55	-0.80	0.81
85.0	0.2022	126.00	-1.52	1.55
85.0	0.5160	295.50	-4.09	4.33
85.0	1.0103	528.00	-3.94	4.63
85.0	2.0600	925.00	0.19	-0.31
85.0	3.1577	1177.50	0.70	-1.51
85.0	4.1235	1332.50	2.03	-6.19
85.0	5.1207	1400.00	0.38	-1.52
85.0	7.6733	1415.00	-2.28	-7.41
85.0	9.0229	1360.00	2.34	2.57
100.0	0.1000	72.70	3.50	-3.70

[a]This is to be interpreted as the calculation of conductivity from Eq. (2.18) with concentration and temperature as independent variables.

[b]This is to be interpreted as the calculation of concentration from the inversion of Eq. (2.18) with conductivity and temperature as the independent variables.

hope for a concentration value that is accurate to three digits. Based on these observations, a numerical solution will yield the best inversion. A simple Newton algorithm can be used, but it does require an initial estimate for the root. Two equations to provide the initial estimated were developed by a regression of concentration as a function of concentration at 25°C. The equations are

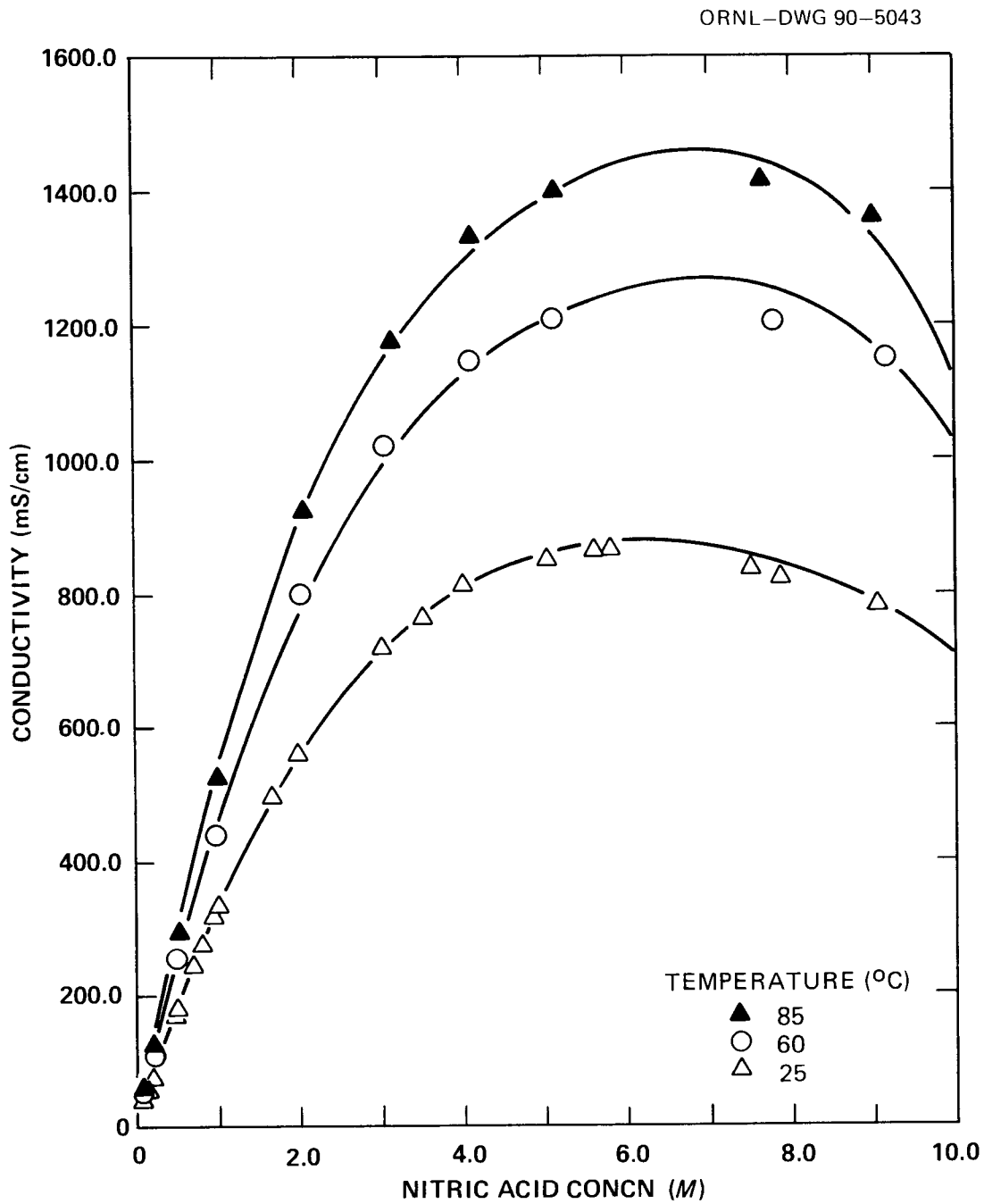

Fig. 2.8. Comparison of electrical conductivity data for nitric acid solutions with the correlation.

$$C_{25} = -25.17383 + 20.51090\rho_{25} + 47.49737\rho_{25}^2 \quad , \tag{2.22}$$

for $\rho_{25} \leq 1.064$ and

$$C_{25} = -285.8722 + 697.4225\rho_{25} - 580.6755\rho_{25}^2 + 168.7065\rho_{25}^3 \quad , \tag{2.23}$$

for $\rho_{25} > 1.064$.

Eq. (2.22) is accurate to within 0.23% over a rather narrow range of low concentration and Eq. (2.23) is accurate to ~10% over the remainder of the density range. The computer program provided in Table 2.9 iteratively solves Eq. (2.5) for C_{25} by the methods described. The program achieves four-digit precision in the result within only two iterations. Thereafter, it picks up ~3 or 4 more digits of precision for each iteration. Obviously, the iteration is both fast enough and precise enough to be of practical use. Table 2.10 shows the percentage error in molar concentration calculated from given values of temperature and density. (See Table A.2 in Appendix A for the corresponding values of concentration.) These results show that the algorithm extrapolated well up to 100% nitric acid and may be safely used for concentrations above ~0.8 *M*. If more accuracy at low concentrations is required, then a different correlation for that specific range could be developed using the equation forms described in this report.

To obtain nitric acid concentration from measurements of electrical conductivity, an inversion of Eq. (2.18) is required. At a given temperature, the equation reduces to a fourth-order polynomial in concentration, which is difficult to solve analytically. As in inverting the density correlation, it is necessary to solve for concentration numerically. A Newton approach is simple, providing rapid convergence with acceptable computation. However, there is an additional difficulty. Two positive real values of concentration within the range may have identical conductivities. Two methods to ensure a valid answer are (1) to generate an initial guess so close that only the correct root is possible and (2) to characterize the region in which the correct root lies and ensure the calculated root is within it. For many, if not all, solutions to which conductivity analysis may be applied in the fuel reprocessing plant, the acid concentration will be below ~6 *M*. This concentration represents a restriction to the region below the point of maximum conductivity.

To determine how closely the concentration could be calculated from conductivity and temperature, Eq. (2.18) was solved with the Newton method using the true value of concentration as the initial guess. See Table 2.8 for the percentage error between the calculated and true values, entered as the last column. Generally, the errors are small, under ~4%, except for points near the maximum conductivity. In this region, the concentration changes appreciably while conductivity changes little, making the calculation of concentration sensitive to small errors in conductivity.

Although knowing what the true value of concentration ought to be to test a correlation is useful, it does not address the problem in operating a plant where the instrumentation must reliably report an unknown concentration. Data between 0 and 6 *M* nitric acid were fit by linear regression to obtain concentration as a function of conductivity. Concentration may be estimated from measured values of conductivity and temperature using the function

$$\begin{aligned} C = {} & (4.117446 \times 10^{-3} - 7.379632 \times 10^{-5}T + 5.463200 \times 10^{-7}T^2)\, c \\ & + (6.244199 \times 10^{-7} - 2.377527 \times 10^{-8}T)\, c^2 \\ & + (5.397624 \times 10^{-9} - 4.335219 \times 10^{-11}T)\, c^3 \quad . \end{aligned} \tag{2.24}$$

The error is quite small at low concentrations and increases to ~25% at concentrations around 6 *M* and at the extremes of temperature. The estimate can be used for an initial guess to solve Eq. (2.18) by the Newton method.

Table 2.9. BASIC computer program segment that solves Eq. (2.5) by iteration

```
1000 'SUBROUTINE RHO2C
        'Given temperature, T (°C)
        '      and density, RHO (gm/cc)
        ' this calculates: the density corrected to 25°C, RHO25(gm/cc)
        '                    acid concentration at 25°C, C25(M)
        '    and acid concentration at given temperature, C(M)
        IF RHO < .9 OR RHO > 1.6 THEN PRINT "Value for density outside limits"
        'Correct density reading to that at 25°C
        RHO25 = RHO * (1. + (-1.647365E-03 + 2.017796E-06 * T) * (T - 25!))
        RHO25 = RHO25 / (1. - 1.897063E-03 * RHO * (T - 25!))
        'Calculate concentration using estimation formulas
        IF RHO25 <= 1.064 THEN
           C25 = -25.17383 + 20.5109 * RHO25 + 4.749737 * RHO25 * RHO25
          ELSE
           C25 = -285.8722 + 697.4225 * RHO25 - 580.6755 * RHO25 * RHO25
           C25 = C25 + 168.7065 * RHO25 * RHO25 * RHO25
        END IF
        'Solve cubic equation numerically using Newton method
        NITER = 0
        F = 1.
        WHILE ABS(F) > .0001 AND NITER < 10
        NITER = NITER + 1
        F = -1. / RHO25 + 1.003124 - 3.364529E-02 * C25 + 1.219254E-03 * C25 * C25
        F = F - 1.681279E-05 * C25 * C25 * C25
        FPRIME = -3.364529E-02 + 2. * 1.219254E-03 * C25 - 3. * 1.681279E-05 * C25 * C25
        C25 = C25 - F / FPRIME
        WEND
        C = C25 * RHO / RHO25
        LOCATE 2, 1: PRINT "NITER=", NITER
        RETURN
```

2.2 NITRIC ACID-URANIUM-WATER SYSTEM

Both density and electrical conductivity of aqueous solutions of uranyl nitrate hexahydrate (UNH) and nitric acid vary with concentrations of the salt and acid and with the temperature. The purpose here is to develop a method to determine both the uranium and nitric acid concentration from measured values of electrical conductivity, density, and temperature that parallels the method developed for the case of pure nitric acid. The addition of another component (the uranium specie) increases the dimensional order by one. Now there is no longer a choice of using either conductivity or density to ascertain the concentration, because both measurements must be made to simultaneously obtain the concentration of both uranium and acid.

In a reprocessing plant, the concentrations of actinides are often expressed in grams of heavy metal per liter of solution. Uranyl nitrate will probably exist in aqueous solution as UNH, but because there is only 1 uranium atom per UNH molecule, it will be convenient to express the concentration as gU/L, a convention used throughout this report. A simple ratio of molecular weights can be used to obtain the salt concentration.

Table 2.10. Percentage error in calculating concentration from density measurements

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
0[a]	-.09	-.06	-.03	-.01	-.00	0.01	0.01	0.01	-.01	-.03	-.11	-.22
1	49.88	32.33	18.10	7.63	0.69	-3.92	-5.16	-2.01	5.75	20.71	66.75	132.87
2	22.57	14.51	8.00	3.28	0.12	-1.97	-1.55	-1.12	2.53	9.73	31.05	61.05
3	13.84	8.69	4.74	1.92	0.07	-1.19	-.67	-.51	1.76	6.37	19.45	37.45
4	9.30	5.86	3.23	1.35	0.15	-.71	-.46	0.01	1.60	4.42	13.36	25.89
5	6.80	4.23	2.38	1.06	0.24	-.38	-.15	0.13	1.29	3.42	9.88	18.70
6	5.01	3.20	1.83	0.87	0.33	-.10	-.10	0.35	1.22	2.57	7.71	14.06
7	3.89	2.36	1.28	0.67	0.30	-.07	-.20	0.37	1.03	2.09	5.99	10.88
8	2.96	1.70	1.05	0.60	0.13	-.12	-.15	0.26	0.75	1.59	4.81	8.34
9	2.17	1.30	0.79	0.45	0.10	-.06	-.22	0.27	0.63	1.30	3.75	6.22
10	1.63	0.91	0.67	0.42	0.16	0.07	-.19	0.18	0.62	1.14	2.99	4.82
11	1.28	0.67	0.50	0.32	0.13	0.10	-.09	0.18	0.51	0.92	2.44	3.75
12	0.93	0.55	0.43	0.31	0.18	0.05	-.08	0.25	0.48	0.79	1.88	2.75
13	0.70	0.39	0.31	0.23	0.15	0.06	-.02	0.23	0.52	0.74	1.46	1.96
14	0.46	0.20	0.27	0.23	0.18	0.14	-.03	0.26	0.47	0.62	1.16	1.48
15	0.31	0.09	0.18	0.17	0.15	0.14	0.01	0.23	0.48	0.56	0.94	0.98
16	0.22	0.04	0.15	0.16	0.17	0.08	-.01	0.24	0.42	0.43	0.78	0.58
17	0.19	-.05	0.08	0.20	0.23	0.07	0.01	0.29	0.40	0.36	0.57	0.38
18	0.12	-.08	0.05	0.19	0.23	0.10	0.06	0.37	0.43	0.33	0.42	0.12
19	0.10	-.08	0.06	0.21	0.27	0.17	0.15	0.38	0.48	0.33	0.31	0.02
20	0.11	-.11	0.11	0.26	0.33	0.25	0.25	0.42	0.46	0.36	0.24	-.05
21	0.09	-.12	0.11	0.26	0.35	0.28	0.29	0.49	0.48	0.33	0.19	-.18
22	0.09	-.09	0.13	0.29	0.38	0.33	0.28	0.49	0.43	0.33	0.18	-.19
23	0.05	-.11	0.11	0.27	0.37	0.33	0.23	0.52	0.41	0.34	0.10	-.28
24	0.04	-.17	0.05	0.21	0.38	0.29	0.20	0.50	0.42	0.37	0.04	-.34
25	-.00	-.20	0.02	0.18	0.35	0.27	0.19	0.49	0.43	0.34	-.00	-.38
26	-.03	-.27	0.01	0.17	0.33	0.26	0.19	0.44	0.40	0.26	-.10	-.49
27	-.09	-.31	0.01	0.17	0.28	0.27	0.16	0.40	0.32	0.20	-.17	-.58
28	-.13	-.39	-.03	0.13	0.24	0.24	0.13	0.32	0.25	0.15	-.24	-.66
29	-.21	-.46	-.10	0.05	0.16	0.16	0.06	0.25	0.20	0.05	-.30	-.72
30	-.27	-.51	-.16	-.01	0.09	0.10	0.01	0.20	0.15	-.03	-.34	-.79

Table 2.10. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
31	-.31	-.59	-.21	-.06	0.04	0.05	-.04	0.15	0.12	-.11	-.39	-.85
32	-.40	-.67	-.25	-.11	-.01	-.04	-.08	0.06	0.03	-.18	-.43	-.90
33	-.47	-.78	-.33	-.19	-.09	-.13	-.11	-.02	-.05	-.24	-.52	-.96
34	-.58	-.88	-.45	-.31	-.22	-.20	-.19	-.14	-.17	-.36	-.62	-1.08
35	-.68	-.97	-.60	-.42	-.33	-.32	-.31	-.26	-.33	-.47	-.76	-1.25
36	-.62	-.94	-.54	-.37	-.28	-.31	-.29	-.25	-.31	-.44	-.70	-1.15
37	-.57	-.88	-.48	-.32	-.23	-.26	-.24	-.19	-.25	-.36	-.65	-1.06
38	-.52	-.78	-.44	-.28	-.19	-.21	-.20	-.15	-.20	-.30	-.57	-.99
39	-.44	-.70	-.36	-.20	-.12	-.14	-.16	-.07	-.12	-.26	-.50	-.88
40	-.37	-.63	-.30	-.14	-.06	-.08	-.10	-.01	-.05	-.18	-.44	-.79
41	-.32	-.57	-.24	-.09	-.01	-.03	-.05	0.04	-.03	-.16	-.40	-.72
42	-.31	-.52	-.20	-.05	0.03	0.01	-.01	0.08	0.01	-.11	-.33	-.62
43	-.28	-.49	-.18	-.03	0.05	0.03	0.01	0.10	0.04	-.07	-.28	-.54
44	-.26	-.43	-.16	-.02	0.06	0.04	0.02	0.11	0.05	-.06	-.25	-.48
45	-.26	-.43	-.16	-.03	0.05	0.03	0.01	0.10	0.04	-.06	-.24	-.44
46	-.27	-.44	-.15	-.05	0.03	0.00	-.02	0.07	0.02	-.08	-.24	-.42
47	-.30	-.44	-.18	-.08	-.01	-.04	-.06	0.03	-.03	-.12	-.27	-.47
48	-.35	-.49	-.23	-.14	-.07	-.09	-.15	-.03	-.09	-.18	-.32	-.50
49	-.44	-.55	-.30	-.21	-.18	-.17	-.23	-.15	-.17	-.30	-.43	-.60
50	-.40	-.51	-.27	-.17	-.14	-.13	-.19	-.11	-.16	-.28	-.40	-.54
51	-.38	-.46	-.25	-.16	-.13	-.12	-.18	-.09	-.14	-.26	-.35	-.51
52	-.36	-.43	-.23	-.14	-.10	-.10	-.15	-.06	-.14	-.22	-.34	-.51
53	-.35	-.40	-.23	-.14	-.10	-.10	-.15	-.06	-.14	-.20	-.34	-.49
54	-.35	-.39	-.22	-.13	-.10	-.09	-.14	-.05	-.12	-.22	-.34	-.50
55	-.33	-.38	-.21	-.12	-.09	-.08	-.13	-.07	-.13	-.22	-.37	-.50
56	-.32	-.36	-.19	-.10	-.07	-.06	-.11	-.08	-.14	-.22	-.38	-.52
57	-.30	-.34	-.20	-.11	-.08	-.07	-.08	-.08	-.14	-.25	-.38	-.54
58	-.31	-.32	-.21	-.12	-.08	-.07	-.08	-.11	-.16	-.26	-.42	-.58
59	-.28	-.30	-.22	-.13	-.09	-.07	-.08	-.11	-.18	-.31	-.45	-.62
60	-.26	-.27	-.19	-.13	-.09	-.07	-.08	-.13	-.20	-.36	-.51	-.65

Table 2.10. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
61	-.24	-.25	-.19	-.13	-.09	-.07	-.07	-.15	-.21	-.36	-.52	-.71
62	-.19	-.22	-.17	-.10	-.06	-.03	-.07	-.13	-.22	-.36	-.52	-.71
63	-.13	-.20	-.14	-.07	-.02	0.01	-.02	-.11	-.19	-.31	-.52	-.67
64		-.18	-.08	-.01	0.01	0.05	0.02					
65		-.15	-.02	0.03	0.05	0.09	0.07					
66		-.13	0.00	0.06	0.09	0.10	0.12					
67		-.08	0.03	0.09	0.13	0.11	0.17					
68		-.06	0.06	0.12	0.17	0.12	0.19					
69		-.03	0.09	0.16	0.21	0.13	0.21					
70		-.01	0.11	0.16	0.22	0.15	0.23					
71		0.01	0.14	0.19	0.23	0.17	0.26					
72		0.03	0.14	0.20	0.20	0.19	0.26					
73		0.05	0.14	0.21	0.22	0.18	0.22					
74		0.08	0.14	0.18	0.20	0.17	0.18					
75		0.07	0.14	0.19	0.19	0.16	0.15					
76		0.06	0.15	0.17	0.18	0.16	0.13					
77		0.06	0.12	0.16	0.14	0.13	0.11					
78		0.07	0.10	0.15	0.10	0.11	0.09					
79		0.08	0.09	0.14	0.07	0.09	0.05					
80		0.06	0.08	0.11	0.05	0.04	0.02					
81		0.05	0.08	0.09	0.04	0.01	-.05					
82		0.04	0.05	0.07	-.00	-.06	-.10					
83		0.05	0.03	0.03	-.03	-.11	-.14					
84		0.03	0.03	0.00	-.08	-.15	-.16					
85		0.02	0.04	-.01	-.08	-.18	-.21					
86		0.03	0.06	0.02	-.07	-.19	-.25					
87		0.06	0.10	0.04	-.04	-.18	-.26					
88		0.10	0.16	0.08	0.02	-.15	-.25					
89		0.16	0.23	0.17	0.09	-.05	-.18					
90		0.28	0.33	0.29	0.19	0.06	-.09					
91		0.42	0.45	0.43	0.35	0.16	-.00					
92		0.59	0.60	0.60	0.54	0.33	0.15					
93		0.92	0.92	0.94	0.87	0.69	0.49					

Table 2.10. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
94		1.21	1.23	1.24	1.15	0.99	0.78					
95		1.49	1.49	1.52	1.42	1.25	1.02					
96		1.72	1.75	1.76	1.67	1.45	1.25					
97		1.87	1.95	1.95	1.85	1.61	1.43					
98		1.65	1.68	1.68	1.56	1.33	1.13					
99		0.91	0.93	0.90	0.74	0.52	0.32					
100		-.73	-.76	-.77	-.98	-1.18	-1.43					

[a] Percentage error is undefined at a concentration of zero because concentration appears in the denominator. The numbers in this row are the calculated values of concentration, indicating that the absolute value of the error is quite low even for the low concentrations.

The general method of attack is to use laboratory data to develop functions wherein density and electrical conductivity are dependent on the independent variables of concentration and temperature. Thus

$$\rho = \rho\,(H,U,T) \quad , \tag{2.25}$$

$$c = c\,(H,U,T) \quad ,$$

where

H = concentration of nitric acid, *M* (here H is used instead of C as a reminder that uranium is present as the third component) and

U = concentration of uranium, g/L.

When ρ, c, and T are measured in the field, Eqs. (2.25) reduce to

$$\rho_m = \rho\,(H,U,T)\,|_T = \rho'(H,U) \tag{2.26}$$

$$c_m = c\,(H,U,T)\,|_T = c'(H,U) \quad ,$$

where the subscript m refers to a measured value. These equations may be solved simultaneously for H and U.

The applicable range of the variables is probably close to the range of the data available for correlation. The temperature of a usual process solution will probably never be below about 30°C, but it would be an error to not include room temperature. The temperature of process vessels may approach the boiling point (e.g., the collected stream from the bottoms of an evaporator or streams from the dissolver and digestors). It could be inferred that the higher temperatures apply only to the more concentrated solutions. The temperature range, without regard to concentration, is from 17 to 95°C, with expectation that extrapolations down to perhaps 10°C are good. Sparse data near the boiling point make upward extrapolations risky.

The applicable range of uranium and nitric acid concentrations is bounded on the upper side by the stability of solutions, since uranium concentrations above a few hundred grams per liter freeze at acidities above 5 or 6 *M* at temperatures of interest. While processes are thus limited, there is a tendency to push concentrations as close to instability as comfortable operation permits. Since a purpose of these correlations is to permit concentration determination in this dangerous region, the correlations should be reliable there. At lower acidities (perhaps 3 *M*) uranium concentrations as high as 450 g/L will be included, and at lower uranium concentrations (perhaps 200 g/L) acidities as high as 7 *M* will be included, although there is no apparent application over about 4 *M*, and a maximum in conductivity at acidities at about 6 *M* makes the system nearly useless there. Presently, in-plant applications for acidities below ~0.2 *M* have not been identified, although acidity, when uranium is quite dilute, may be measured by conductivity to very low levels (see Sect. 2.1.2).

2.2.1 Density

Densities of aqueous nitric acid-uranium solutions have been measured for temperatures ranging from 17 to 95°C, uranium concentrations ranging from 0 to 700 g/L, and acid concentrations ranging from 0 to 6 *M*.[13-15] The data are summarized in Appendix C.

In Sect. 2.1.1, the density of nitric acid solutions, without uranium, was correlated with concentrations to high accuracy. With that information, it is a natural step to write the density of the mixture as

$$\rho = f\,(\text{acid only})\ \ [+\text{ or }\times]\ \ g\,(\text{uranium})\ \ , \tag{2.27}$$

where the function f represents the previously developed correlation for acid alone and g is a function that describes the effect of adding uranium. Measured values of density may be appropriately modified by values from the function f, and the resulting residuals correlated with various functions g until a satisfactory fit is obtained. It is known that f is a cubic equation in acid concentration so that even a simple form for g causes Eq. (2.27) to be quite complex. The realization that the conductivity equation will be complicated and that it must be solved in conjunction with whatever density equation is chosen, encourages a search for a simpler density correlation.

Density at 25°C is plotted as a function of acid concentration for various fixed uranium concentrations, resulting in a family of lines as shown in Fig. 2.9. Over the rather narrow concentration range of 0 to 6 *M* the data are adequately represented by straight lines. The slopes of the lines indicated in the figure were computed from a linear least squares analysis. An increase in uranium concentration shifts the density lines upward and slightly modifies their slope. Fig. 2.10 is a similar plot of the data at 95°C. As shown, at the higher temperatures, density has decreased. The simplest implied functional form is

$$\rho = a_0 + a_1H + a_2f(U) + a_3T + a_4HU\ \ . \tag{2.28}$$

[The notation f(U) is used because the form of dependence on U has not yet been established.] Since the slope of the line also changed with temperature, there exists a temperature-dependence in the acid concentration coefficient, i.e. [$a_1 = a_1(T)$].

The next step is to establish the dependence of density on uranium concentration. Density for a solution containing no acid and at a temperature of 17°C is plotted as a function of the uranium concentration, in Fig. 2.11. There are, relatively, many points covering the entire practical range. These data are fit to a straight line and have a correlation coefficient of 0.9997, indicating that the dependence is very well modeled as linear. Densities of solutions containing both uranium and acid are plotted in Figs. 2.12 and 2.13 as a function of uranium concentration, with acid concentration as a parameter. The slopes of the lines indicated on the figures are computed by linear regression. Again, density varies linearly with uranium concentration and the effect of increased acid concentration is to shift the density lines upward and to slightly modify their slope. Curiously, the slope of the lines remain constant when temperature increases, as evidenced by comparing the two figures. This means that the uranium concentration coefficient has little or no temperature-dependence.

Combining this information with Eq. (2.28) provides the functional form with which to correlate density

$$\rho = a_0 + a_1H + a_2U + a_3T + a_4HU\ \ , \tag{2.29}$$

where a_1 is a function of T, [i.e., $a_1 = a_1(T)$]. A simple linear form for a_1 may be chosen (e.g., $a_1 = b_{1,0} + b_{1,1}T$).

ORNL–DWG 90–5044

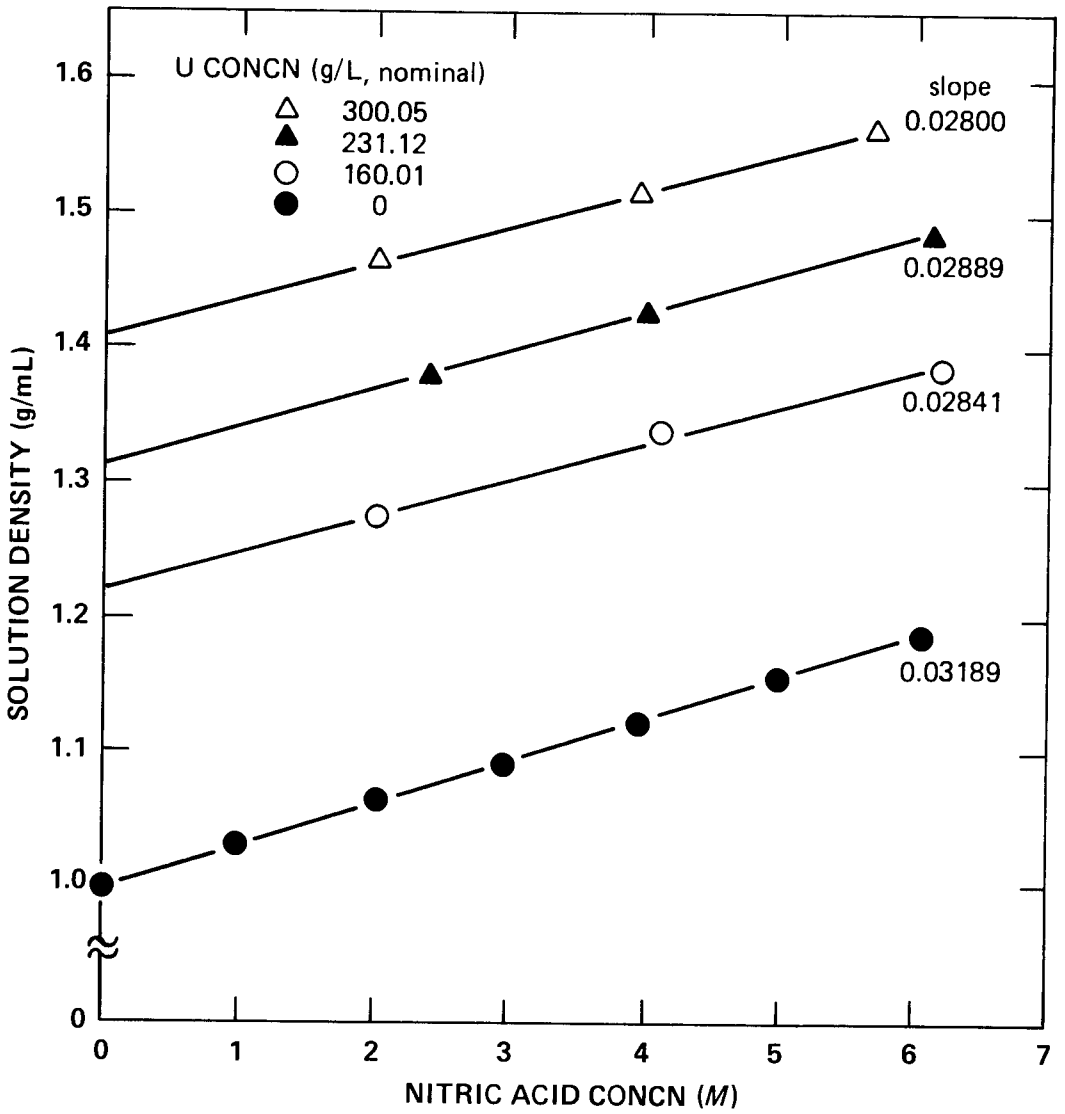

Fig. 2.9. Change in density with nitric acid concentration at various uranium concentrations at 25°C.

All possible regression combinations of the terms in Eq. (2.29), plus some higher order terms, were tested using SAS. The results are given in Table 2.11. Beyond the best four-parameter model, the addition of higher order terms make an insignificant improvement in the correlation coefficient. The Mallow statistic does not improve much beyond this, either. Even the cross-product term, HU, appears to add little to the data fit. Therefore, the model chosen is

$$\rho = a_0 + (a_1 + a_2 T)H + a_3 U + a_4 T \quad , \tag{2.30}$$

ORNL–DWG 90–5045

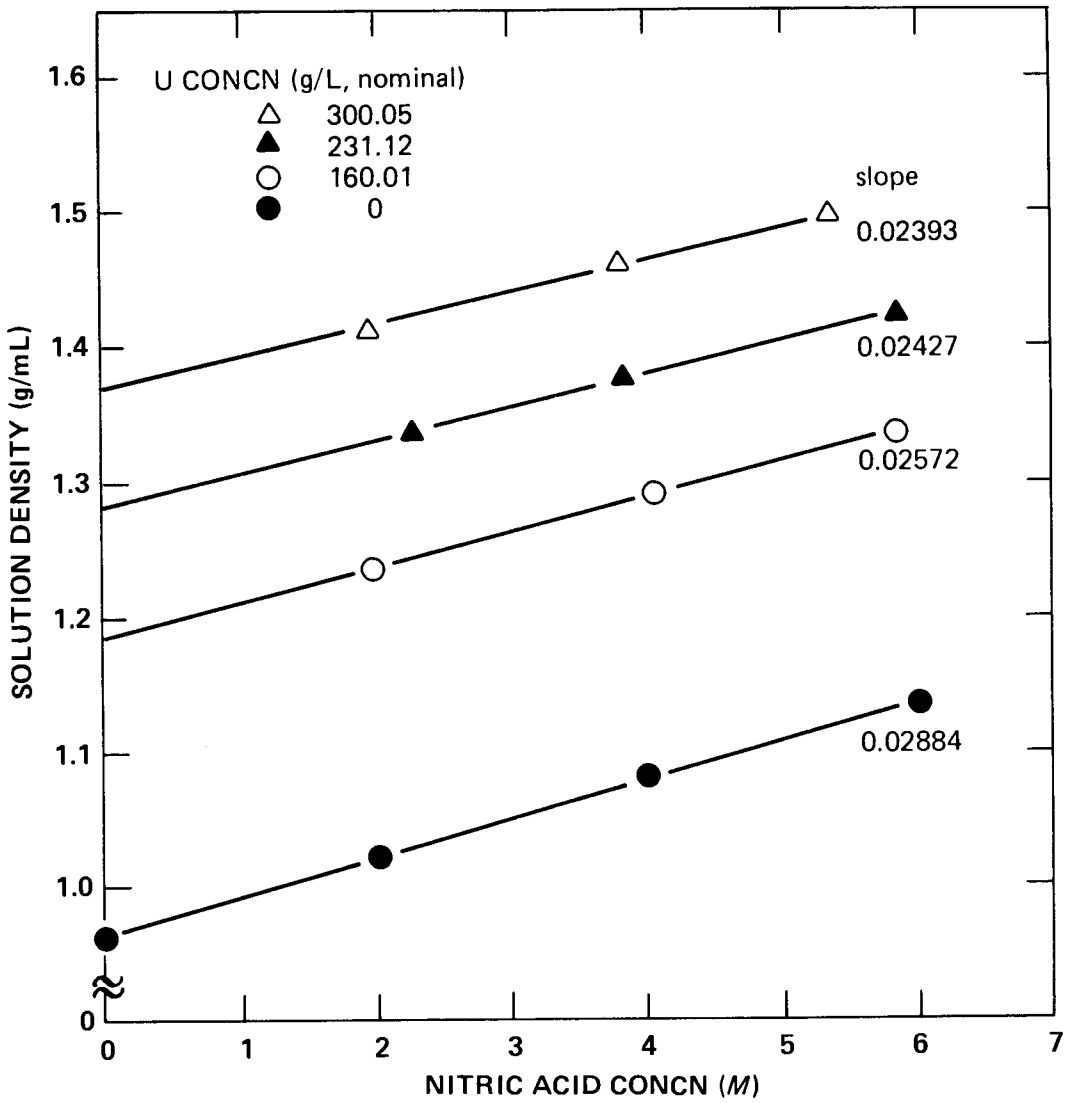

Fig. 2.10. Change in density with nitric acid concentration at various uranium concentrations at 95°C.

where

$a_0 = 1.022811$,

$a_1 = 2.935808 \times 10^{-2}$,

$a_2 = -3.475035 \times 10^{-5}$,

$a_3 = 1.312180 \times 10^{-3}$,

$a_4 = -4.680629 \times 10^{-4}$.

This equation correlates the data to within 0.66%. Table 2.12 compares the experimental value of density with the value computed from the correlation. The correlation is quite good for such a simple model.

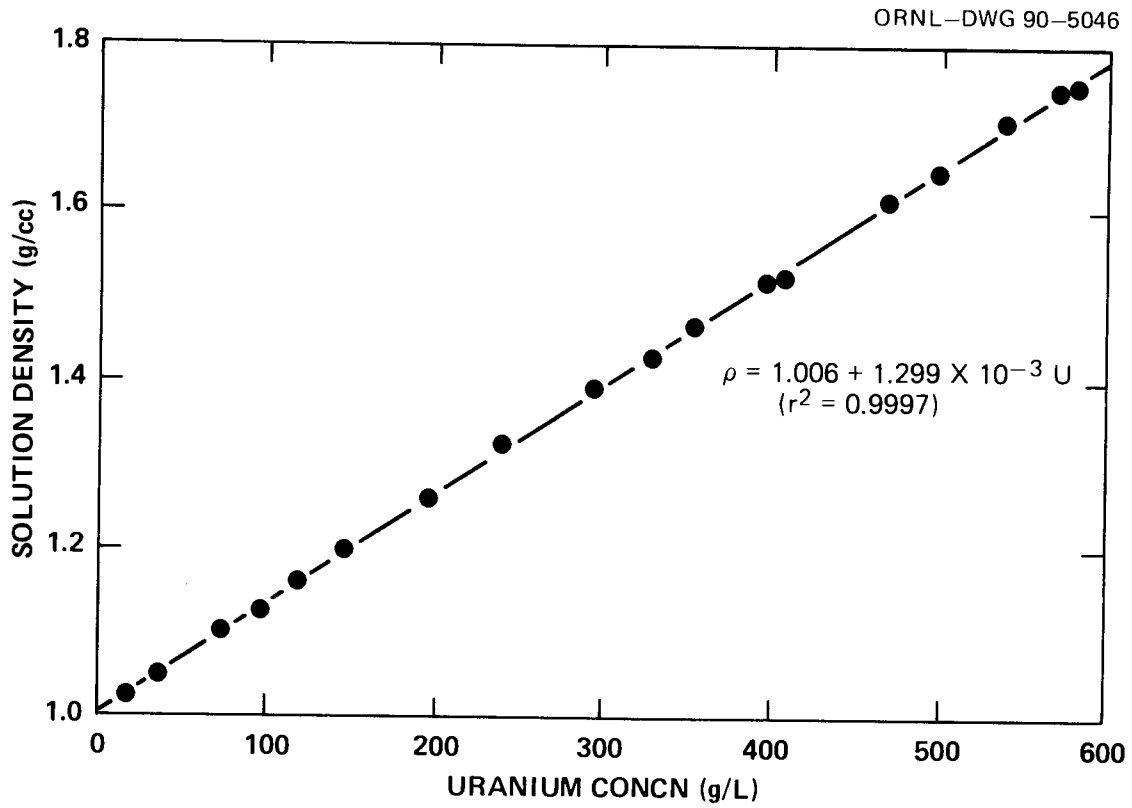

Fig. 2.11. Density of uranyl nitrate solutions at 17°C.

At a given temperature, Eq. (2.30) collapses to the form

$$\rho = a'_0 + a'_1 H + a'_2 U \quad , \tag{2.31}$$

which may be easily solved for one concentration in terms of the other, a convenience that will prove useful.

2.2.2 Conductivity

Data on the conductivity of the three-component system, H_2O-HNO_3-U, are available from an ORNL study.[15] There are a limited number of data points from this study covering a temperature range of 25 to 95°C, an acid concentration range of 1.9 to 6.3 *M*, and a uranium concentration range of 160 to 300 g/L. Of the 58 data points, 27 are repeated measurements made in order to estimate the experimental error. (See Appendix C for a summary of the data.)

Conductivities of H_2O-HNO_3-U solutions are plotted in Fig. 2.14 as a function of nitric acid concentration, with uranium concentration and temperature as parameters. Along with the resulting family of curves, the conductivity of pure aqueous nitric acid is plotted for comparison. Increasing temperature has the expected effect of increasing the conductivity. The addition of uranium attenuates the conductivity values within the experimental range. The general shape of the curves appears to be the same as for the pure acid. Because there are no data on the conductivity of uranium solutions at very low or zero concentrations of acid, the behavior of the system is unknown in that region.

ORNL–DWG 90–5047

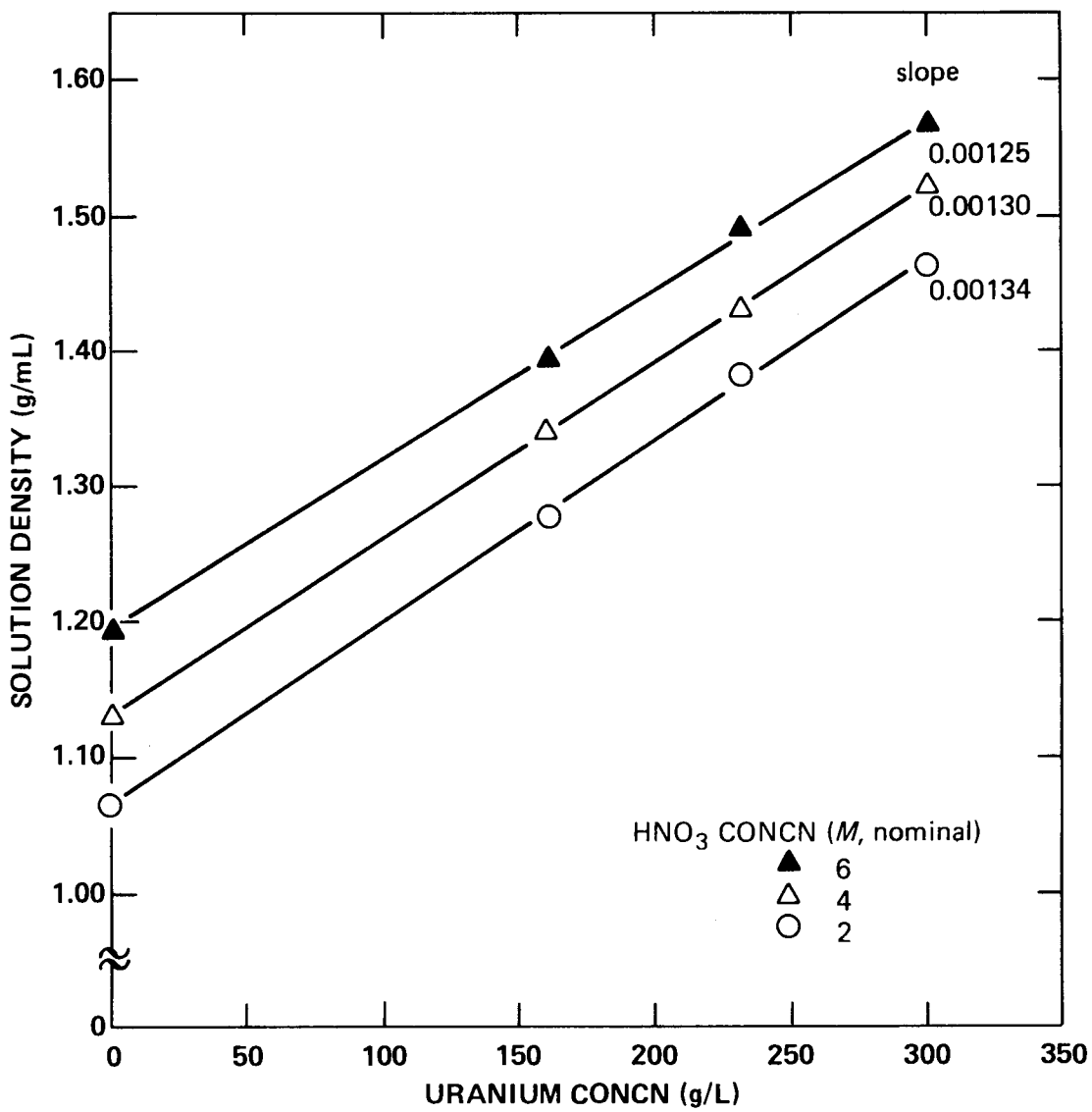

Fig. 2.12. Change in density with uranium concentration at various nitric acid concentrations at 25°C.

Specific criteria may be imposed on the conductivity correlation, in addition to those described earlier in Sect. 1.2. The equation should extrapolate to known states in the limit: (1) when the uranium concentration goes to zero, the equation should fit the pure acid case; (2) when the acid goes to zero, it should fit the pure uranium case; and (3) when both go to zero, the equation should go to zero. Since, as yet, there is no indication of how the conductivity of uranium solutions without acid behaves, satisfying the second point is difficult. It is likely that the condition of "no acid in uranium solutions" is well beyond the range of application. The most promising form for the conductivity equation, which does not satisfy the criterion at "no acid" but which apparently meets all other requirements, is

$$c = f(H,T)\,[1 - g(H,U,T)] \quad , \tag{2.32}$$

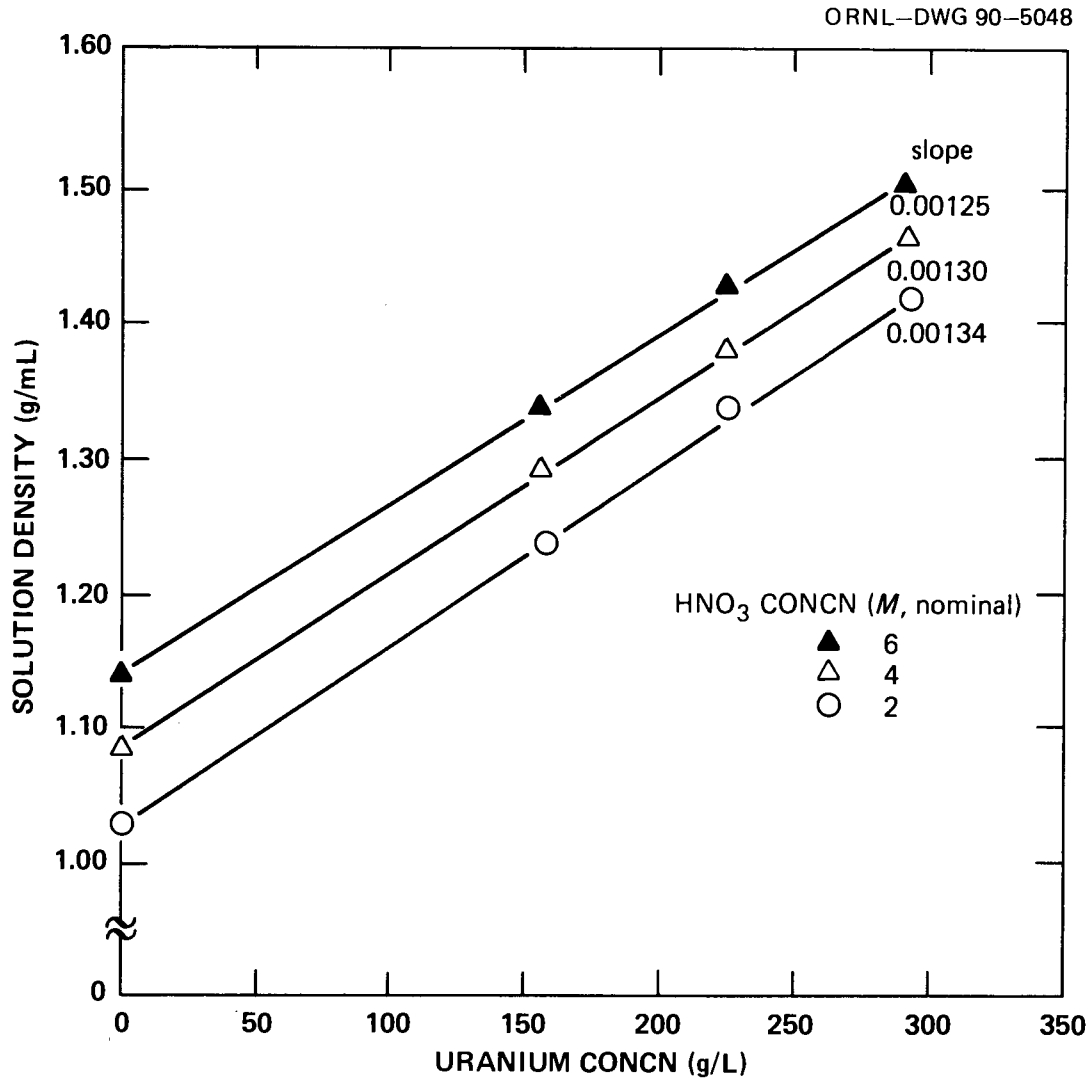

Fig. 2.13. Change in density with uranium concentration at various nitric acid concentrations at 95°C.

where f(H,T) is an expression describing "acid only" and g(H,U,T) is an expression describing the effect of adding uranium to the solution. It is necessary that U be a factor of g so that no artifact of its effect remains when U is absent. The function f contains H as a factor (see Sect. 2.1.2), which drives the conductivity to zero when acid is absent. The conductivity of pure water is truly negligible when compared to the large values of conductivity characterizing solutions of interest, but this form may be substantially in error for macro concentrations of uranium at very low acidities.

The function f has already been established and may be formed by replacing C in Eq. (2.18) with H. Equation (2.32) can be rearranged to solve for g as

$$g\,(H,U,T) = 1 - \frac{c}{f(H,T)} \quad . \tag{2.33}$$

Table 2.11. Regression models for density of aqueous nitric acid-uranium solutions

Number of variables in model	r^2	C(p)	Independent variables			
1	0.08240989	204818.0	H			
1	0.26468143	164120.0	TU			
1	0.78373354	48225.0	U^2			
1	0.78876441	47102.0	HU			
1	0.87608116	27606.0	U			
2	0.89707349	22921.0	U	T		
2	0.92883061	15830.0	HU	U^2		
2	0.95829889	9250.1	U	HU		
2	0.97984974	4438.2	U	H^2		
2	0.98195441	3968.3	U	H		
3	0.99652544	716.8	U	H^2	T^2	
3	0.99672434	672.4	U	H^2	T	
3	0.99817188	349.2	U	H	TH	
3	0.99911208	139.3	U	H	T^2	
3	0.99939141	76.9	U	H	T	
4	0.99941347	74.0	U	H	T	T^2
4	0.99942510	71.4	U	H	T	H^2
4	0.99943332	69.5	U	H	T^2	TH
4	0.99949889	54.9	U	H	T	HU
4[a]	0.99952557	48.9	U	H	T	TH

Table 2.11. (continued)

Number of variables in model	r^2	C(p)	Independent variables								
5	0.99954466	46.7	U	H	T	HU	H^2				
5	0.99955108	45.2	U	H	T	TH	T^2				
5	0.99955381	44.6	U	H	T^2	TH	HU				
5	0.99957389	40.1	U	H	T	TH	H^2				
5	0.99964222	24.9	U	H	T	TH	HU				
6	0.99961601	32.7	U	H	T^2	TH	HU	H^2			
6	0.99964944	25.3	U	H	T	TH	HU	U^2			
6	0.99965091	24.9	U	H	T	TH	HU	TU			
6	0.99966826	21.1	U	H	T	TH	HU	T^2			
6	0.99970626	12.6	U	H	T	TH	HU	H^2			
7	0.99967440	21.7	U	H	T	TH	HU	T^2	U^2		
7	0.99967652	21.2	U	H	T	TH	HU	T^2	TU		
7	0.99971409	12.8	U	H	T	TH	HU	H^2	TU		
7	0.99971554	12.5	U	H	T	TH	HU	H^2	U^2		
7	0.99972990	9.3	U	H	T	TH	HU	H^2	T^2		
8	0.99962296	35.2	U	H	T^2	TH	HU	H^2	U^2	TU	
8	0.99968203	22.0	U	H	T	TH	HU	T^2	TU	U^2	
8	0.99972258	12.9	U	H	T	TH	HU	H^2	U^2	TU	
8	0.99973735	9.6	U	H	T	TH	HU	H^2	T^2	TU	
8	0.99973798	9.5	U	H	T	TH	HU	H^2	T^2	U^2	
9	0.99974472	10.0	U	H	T	TH	HU	H^2	T^2	U^2	TU

[a]Chosen model.

Table 2.12. Comparison of density data with predictions from correlation

T (°C)	HNO_3 (*M*)	U (g/L)	Experimental ρ	Calculated ρ	% error
25.0	1.99	160.83	1.2770	1.2788	-0.14
25.0	2.01	160.28	1.2765	1.2787	-0.17
25.0	3.99	160.50	1.3403	1.3354	0.37
25.0	4.17	160.21	1.3386	1.3401	-0.11
25.0	6.00	160.80	1.3957	1.3930	0.19
25.0	6.30	160.36	1.3936	1.4010	-0.53
25.0	2.35	232.59	1.3823	1.3833	-0.07
25.0	2.38	231.66	1.3811	1.3829	-0.13
25.0	4.00	231.60	1.4299	1.4290	0.07
25.0	3.95	231.80	1.4295	1.4278	0.12
25.0	6.09	233.76	1.4897	1.4913	-0.11
25.0	6.04	233.04	1.4877	1.4890	-0.09
25.0	2.02	300.89	1.4641	1.4635	0.04
25.0	2.00	301.24	1.4625	1.4634	-0.06
25.0	3.89	301.74	1.5205	1.5179	0.17
25.0	3.94	301.38	1.5184	1.5188	-0.03
25.0	5.64	303.80	1.5649	1.5704	-0.35
25.0	5.63	301.42	1.5645	1.5670	-0.16
60.0	1.97	158.03	1.2569	1.2558	0.09
60.0	1.98	158.32	1.2572	1.2565	0.06
60.0	4.12	157.30	1.3148	1.3135	0.10
60.0	4.15	158.61	1.3149	1.3160	-0.09
60.0	6.02	157.35	1.3632	1.3654	-0.16
60.0	6.04	156.76	1.3627	1.3652	-0.18
60.0	2.32	227.68	1.3576	1.3568	0.06
60.0	2.33	227.79	1.3583	1.3572	0.08
60.0	3.90	227.15	1.4058	1.3992	0.47
60.0	3.95	227.32	1.4040	1.4007	0.23
60.0	5.96	226.34	1.4569	1.4543	0.18
60.0	5.93	226.80	1.4549	1.4541	0.06
60.0	2.00	295.84	1.4397	1.4375	0.15
60.0	2.03	295.93	1.4400	1.4384	0.11
60.0	3.82	294.82	1.4870	1.4858	0.08
60.0	3.92	294.12	1.4899	1.4876	0.16
60.0	5.53	294.24	1.5320	1.5316	0.02
60.0	5.52	296.38	1.5281	1.5342	-0.40
95.0	1.96	157.10	1.2351	1.2356	-0.04
95.0	1.94	157.57	1.2353	1.2357	-0.03
95.0	4.06	155.99	1.2871	1.2888	-0.13
95.0	4.07	157.19	1.2912	1.2907	0.04
95.0	5.73	155.65	1.3353	1.3319	0.26
95.0	5.96	155.41	1.3353	1.3376	-0.17
95.0	2.28	226.78	1.3386	1.3353	0.24
95.0	2.26	226.88	1.3343	1.3349	-0.05
95.0	3.82	224.90	1.3743	1.3730	0.10
95.0	3.82	225.79	1.3782	1.3742	0.29

Table 2.12. (continued)

T (°C)	HNO_3 (*M*)	U (g/L)	Experimental ρ	Calculated ρ	Percent error
95.0	5.88	222.86	1.4255	1.4240	0.11
95.0	5.82	224.52	1.4224	1.4246	-0.16
95.0	1.97	294.44	1.4151	1.4160	-0.07
95.0	1.98	293.13	1.4139	1.4146	-0.05
95.0	3.81	292.14	1.4606	1.4610	-0.02
95.0	3.86	291.86	1.4615	1.4619	-0.03
95.0	5.38	290.98	1.4985	1.5003	-0.12
95.0	5.35	288.99	1.4923	1.4970	-0.31
35.0	4.81	266.07	1.4927	1.4909	0.12
50.0	3.17	198.18	1.3478	1.3470	0.06
75.0	4.96	188.57	1.3691	1.3678	0.09
90.0	3.06	256.01	1.3972	1.3969	0.02
25.0	2.00	0.00	1.0631	1.0681	-0.47
25.0	4.00	0.00	1.1270	1.1251	0.17
25.0	6.00	0.00	1.1884	1.1820	0.53
60.0	2.00	0.00	1.0458	1.0493	-0.33
60.0	4.00	0.00	1.1058	1.1038	0.18
60.0	6.00	0.00	1.1632	1.1584	0.42
95.0	2.00	0.00	1.0237	1.0305	-0.66
95.0	4.00	0.00	1.0811	1.0826	-0.14
95.0	6.00	0.00	1.1348	1.1347	0.01

A forward selection analysis was performed by using SAS to determine the form g ought to have. The analysis was restricted to a regression in which the constant term (or intercept) was precluded. Several functional forms were tested and the results are given in Table 2.13. The results indicate that the greatest contribution to fitting the data comes from the uranium term, indicating that the function g is dominated by the factor U (essentially, $g = a_0U$). The use of only the one-term function for g did not provide an adequate fit to the data, but the high correlation coefficient did bolster confidence that U should be a factor of g, so that $g = 0$ when uranium is absent, as already mentioned. The U term may be forced to be a factor of g using the following further rearrangement to

$$g'(H,U,T) = \frac{(1 - c / f(H,T))}{U} \quad . \tag{2.34}$$

This equation gives pseudo-experimental values of g′, which may also be correlated by linear regression techniques. A constant term must now be included so that a coefficient for U will appear when Eq. (2.34) is expanded. All possible combinations of the terms thought to make up g′ were tested by using SAS. The results are given in Table 2.14. A six-coefficient equation (5 parameters) appears to be necessary to fit the data. The best equation for g′ is

$$g' = a_0 + a_1H + a_2T + a_3TU + a_4UH + a_5H^2 \tag{2.35}$$

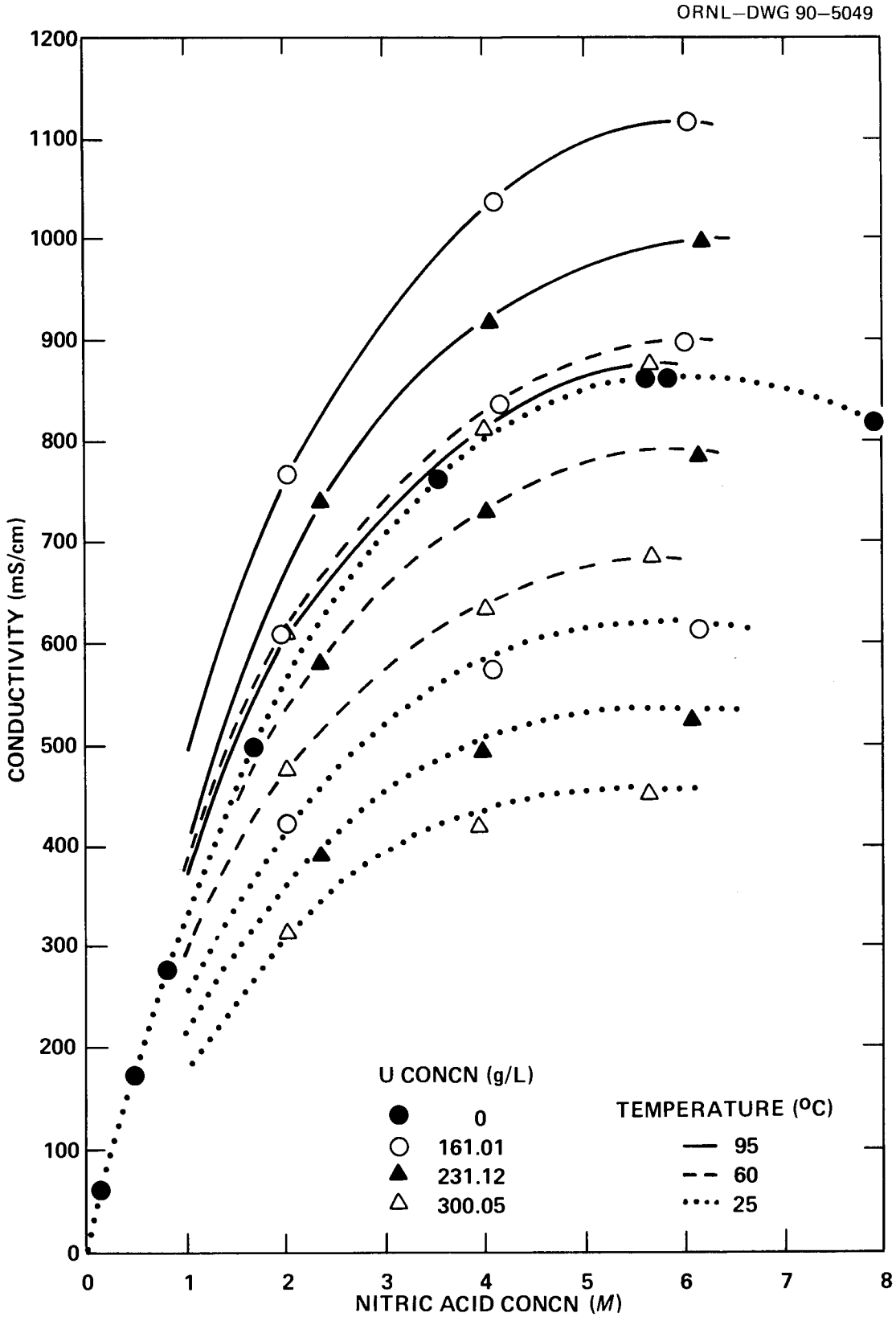

Fig. 2.14. Conductivity of aqueous nitric acid-uranium solutions at various temperatures.

Table 2.13. Summary of forward selection procedure for dependent variable g with constant term excluded

Step	Variable entered	Number in model	Partial r^2	Model r^2	C(p)
1	U	1	0.9886	0.9886	2508.2
2	H	2	0.0055	0.9941	1270.7
3	TU	3	0.0053	0.9994	93.1
4	T	4	0.0001	0.9994	79.6
5	H^2	5	0.0002	0.9996	37.4
6	TH	6	0.0001	0.9997	20.6
7	UH	7	0.0000	0.9997	13.1
8	T^2	8	0.0000	0.9998	11.7
9	T^2H^2U	9	0.0000	0.9998	10.5
10	U^2	10	0.0000	0.9998	10.0

where

$a_0 = 1.258519 \times 10^{-3}$,

$a_1 = 2.976994 \times 10^{-4}$,

$a_2 = -6.529605 \times 10^{-6}$,

$a_3 = 1.065403 \times 10^{-8}$,

$a_4 = -4.487609 \times 10^{-7}$

$a_5 = -1.575492 \times 10^{-5}$.

The complete equation for conductivity of aqueous nitric acid-uranium solutions can now be obtained by substituting Eq. (2.35) into Eq. (2.34) and then rearranging the result into the form of Eq. (2.32). The correlation fits the data to within 2.75%. Table 2.15 compares the experimental values of electrical conductivity with those values computed from the correlation. Graphical comparisons are shown in Figs. 2.15 through 2.17, indicating that the correlation is quite good.

2.2.3 Equations for Process Use

The objective is to extract nitric acid and uranium concentration from measurements of solution temperature, density, and electrical conductivity. This goal may be accomplished by solving Eq. (2.30) and Eqs. (2.34)—(2.35) simultaneously for the unknown terms H and U. These equations are nonlinear, and the terms H and U cannot be solved for explicitly by using analytic techniques. Therefore, a numerical method must be used to solve the equations iteratively.

A simple Newton algorithm may be used to perform the iteration. Newton methods require an initial guess, so to test the technique using the data in Table 2.15, an initial guess of H = 2 was tried. [Corresponding values of U are then immediately available through Eq. (2.30).] The iteration converged to values of H to within 10^{-4} in six iterations or less. Because there is a real need for speed in the calculation, a method to obtain a better initial guess was devised.

Table 2.14. Regression models for dependent variable g′ where an intercept is required

Number of variables in model	r^2	C(p)	Independent variables				
1	0.39132671	1210.7	T^2				
1	0.40179394	1189.0	T				
1	0.41513310	1161.3	H^2				
1	0.43132042	1127.6	H				
1	0.48412447	1017.9	TU				
2	0.77571153	414.0	H^2	T			
2	0.78620639	392.2	H	T^2			
2	0.79700396	369.8	H	T			
2	0.82394346	313.8	TU	H^2			
2	0.85044046	258.8	TU	H			
3	0.87937152	200.6	H	T^2	U		
3	0.89153300	175.4	H	T	U^2		
3	0.89278548	172.8	H	T	U		
3	0.92055975	115.1	H	T^2	UH		
3	0.93447042	86.2	H	T	UH		
4	0.94167756	73.2	H	T	UH	TH	
4	0.94321669	70.0	H	T	UH	U^2	
4	0.94397921	68.4	H	T	UH	U	
4	0.94647305	63.2	TU	H	UH	T	
4	0.95503641	45.4	H	T	UH	H^2	
5	0.95965349	37.8	H	T	UH	H^2	TH
5	0.95977544	37.6	H	T	UH	H^2	T^2H^2U
5	0.96722730	22.1	H	T	UH	H^2	U^2
5	0.96742467	21.7	H	T	UH	H^2	U
5[a]	0.96907770	18.3	TU	H	H^2	UH	T

Table 2.14. (continued)

Number of variables in model	r^2	C(p)	Independent variables									
6	0.97164412	14.9	TU	H	H^2	UH	T	T^2H^2U				
6	0.97172693	14.7	TU	H	H^2	UH	T	U^2				
6	0.97285708	12.4	H	T	UH	H^2	U^2	T^2H^2U				
6	0.97297083	12.2	H	T	UH	H^2	U	T^2H^2U				
6	0.97414543	9.7	TU	H	H^2	UH	T	TH				
7	0.97494058	10.1	TU	H	H^2	UH	T	TH	T^2H^2U			
7	0.97511482	9.7	TU	H	H^2	UH	T	T^2H^2U	U			
7	0.97545321	9.0	TU	H	H^2	UH	T	U^2	T^2H^2U			
7	0.97594644	8.0	TU	H	H^2	UH	T	TH	U			
7	0.97625217	7.3	TU	H	H^2	UH	T	TH	U^2			
8	0.97626095	9.3	TU	H	H^2	UH	T	TH	U^2	T^2H^2U		
8	0.97628044	9.3	TU	H	H^2	UH	T	TH	U^2	U		
8	0.97651034	8.8	TU	H	H^2	UH	T	TH	U	T^2		
8	0.97679065	8.2	TU	H	H^2	UH	T	TH	U^2	T^2		
8	0.97692135	7.9	TU	H	H^2	UH	T	TH	T^2H^2U	T^2		
9	0.97552696	12.9	TU	H	H^2	UH	T	U^2	T^2H^2U	T^2	U	
9	0.97629740	11.3	TU	H	H^2	UH	T	TH	U^2	U	T^2H^2U	
9	0.97681216	10.2	TU	H	H^2	UH	T	TH	U^2	T^2	U	
9	0.97710567	9.6	TU	H	H^2	UH	T	TH	U	T^2	T^2H^2U	
9	0.97727878	9.2	TU	H	H^2	UH	T	TH	U^2	T^2	T^2H^2U	
10	0.97738036	11.0	TU	H	H^2	UH	T	TH	U^2	T^2	T^2H^2U	U

[a]Chosen model.

Table 2.15. Comparison of conductivity data with calculations made from correlation

T (°C)	HNO_3 (*M*)	U (g/L)	Experimental c	Calculated c	Percent error
25.0	1.99	160.83	422.50	420.05	0.58
25.0	2.01	160.28	422.50	423.03	-0.13
25.0	3.99	160.50	575.00	574.66	0.06
25.0	4.17	160.21	575.00	581.45	-1.12
25.0	6.00	160.80	610.00	606.00	0.66
25.0	6.30	160.36	615.00	605.60	1.53
25.0	2.35	232.59	390.00	399.92	-2.54
25.0	2.38	231.66	392.50	403.31	-2.75
25.0	4.00	231.60	492.50	492.77	-0.05
25.0	3.95	231.80	495.00	490.98	0.81
25.0	6.09	233.76	530.00	519.31	2.02
25.0	6.04	233.04	525.00	519.95	0.96
25.0	2.02	300.89	312.50	318.61	-1.95
25.0	2.00	301.24	312.50	316.58	-1.30
25.0	3.89	301.74	420.00	420.57	-0.13
25.0	3.94	301.38	420.00	422.39	-0.57
25.0	5.64	303.80	452.50	453.03	-0.12
25.0	5.63	301.42	450.00	454.79	-1.06
60.0	1.97	158.03	610.00	604.02	0.98
60.0	1.98	158.32	610.00	605.55	0.73
60.0	4.12	157.30	835.00	840.35	-0.64
60.0	4.15	158.61	840.00	839.92	0.01
60.0	6.02	157.35	895.00	904.44	-1.05
60.0	6.04	156.76	900.00	905.80	-0.64
60.0	2.32	227.68	585.00	584.41	0.10
60.0	2.33	227.79	580.00	585.57	-0.96
60.0	3.90	227.15	725.00	721.55	0.48
60.0	3.95	227.32	735.00	723.98	1.50
60.0	5.96	226.34	785.00	791.37	-0.81
60.0	5.93	226.80	790.00	790.14	-0.02
60.0	2.00	295.84	475.00	472.37	0.55
60.0	2.03	295.93	477.50	476.20	0.27
60.0	3.82	294.82	635.00	626.90	1.28
60.0	3.92	294.12	635.00	632.81	0.34
60.0	5.53	294.24	685.00	692.62	-1.11
60.0	5.52	296.38	685.00	689.83	-0.71
95.0	1.96	157.10	770.00	765.39	0.60
95.0	1.94	157.57	765.00	760.33	0.61
95.0	4.06	155.99	1035.00	1046.48	-1.11
95.0	4.07	157.19	1040.00	1045.00	-0.48
95.0	5.73	155.65	1120.00	1121.51	-0.13
95.0	5.96	155.41	1115.00	1127.07	-1.08
95.0	2.28	226.78	735.00	743.07	-1.10
95.0	2.26	226.88	745.00	739.68	0.71
95.0	3.82	224.90	915.00	911.84	0.35
95.0	3.82	225.79	920.00	910.39	1.04

Table 2.15. (continued)

T (°C)	HNO_3 (*M*)	U (g/L)	Experimental c	Calculated c	Percent error
95.0	5.88	222.86	995.00	1001.52	-0.66
95.0	5.82	224.52	1000.00	997.29	0.27
95.0	1.97	294.44	605.00	609.46	-0.74
95.0	1.98	293.13	610.00	612.67	-0.44
95.0	3.81	292.14	810.00	805.83	0.52
95.0	3.86	291.86	815.00	809.33	0.70
95.0	5.38	290.98	875.00	881.40	-0.73
95.0	5.35	288.99	875.00	883.13	-0.93
35.0	4.81	266.07	552.50	544.72	1.41
50.0	3.17	198.18	657.50	651.70	0.88
75.0	4.96	188.57	940.00	922.10	1.90
90.0	3.06	256.01	785.00	778.48	0.83

The conductivities of aqueous nitric acid-uranium solutions were fit, using regression methods, to

$$\begin{aligned} c = {} & 2.5369\times10^{1} + 7.3978\times10^{0}T + 1.9137\times10^{2}H - 4.1789\times10^{-1}U \\ & -1.8311\times10^{-2}T^{2} - 1.6424\times10^{1}H^{2} + 1.2147\times10^{-4}U^{2} \\ & +5.1495\times10^{-1}\,HT - 6.3251\times10^{-3}\,TU - 1.3184\times10^{-1}HU \ , \end{aligned} \tag{2.36}$$

which fits the data with a relative maximum error of 3.0%. This result seems to be a close competitor to Eq. (2.35); however, it has ten adjustable constants compared to the six in Eq. (2.35) and does not extrapolate as well. Equation (2.36) does have an advantage in being easily solved. It also can be simultaneously solved analytically with Eq. (2.30), to provide close first approximations to H and U for the iteration of Eq. (2.35). A computer program that solves all of the equations is given in Table 2.16. The convergence of H to within an error of 10^{-4} again takes up to six iterations in rare cases but the use of the first approximation from Eq. (2.36) usually permits convergence in three iterations or less. Results of the calculation of concentration from measured physical properties are provided in Table 2.17 and compare quite well to the known values. The largest errors occur near concentrations of 6 *M* nitric acid because the conductivity curve is near the maximum there, as previously discussed. Uranium concentration is estimated more precisely than the nitric acid concentration. The nitric acid concentration is calculated to within 6.6% and the uranium concentration to within 4.7%. When the nitric acid concentration is <5 *M*, the calculations are considerably more accurate. The calculation of both concentrations is sufficiently accurate for an application to process control.

ORNL–DWG 90–5050

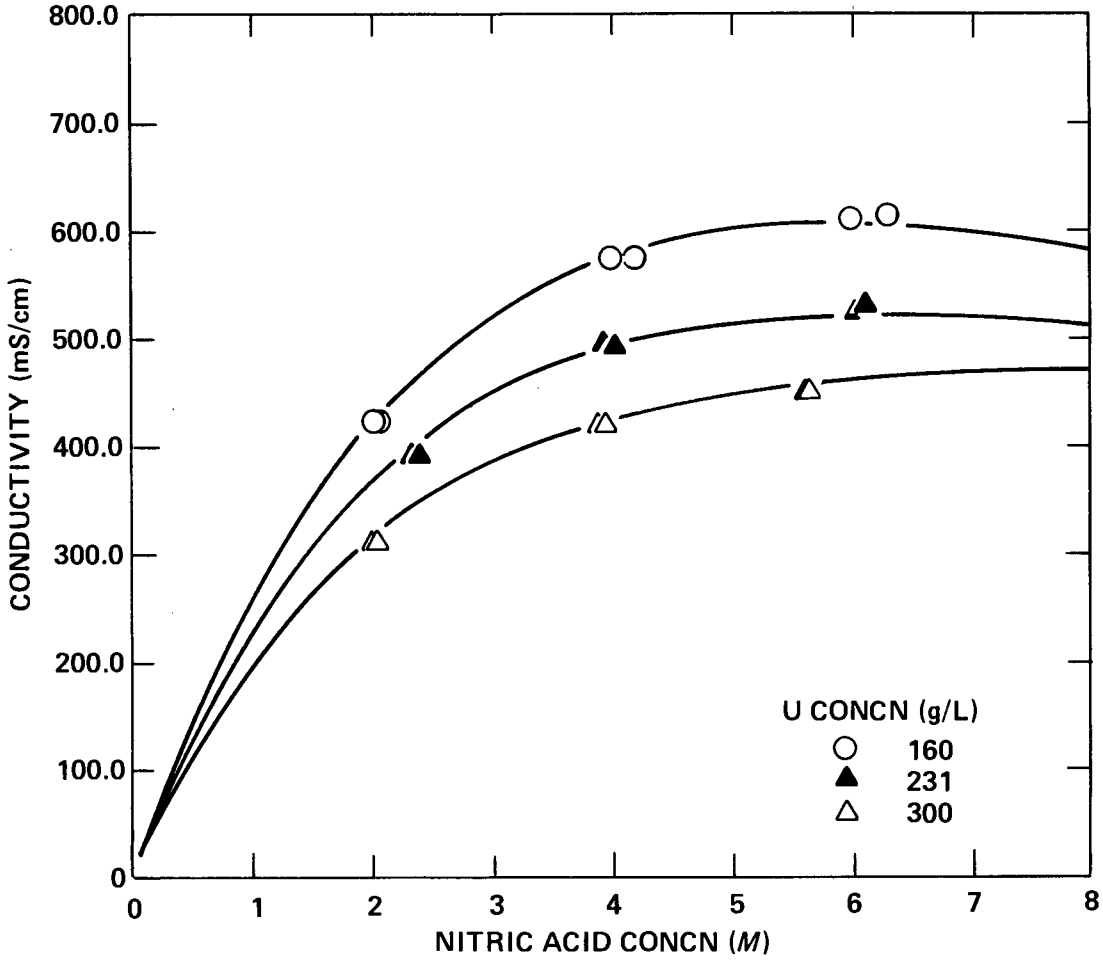

Fig. 2.15. Comparison of experimental electrical conductivity of aqueous nitric acid-uranium solutions at 25° to correlation.

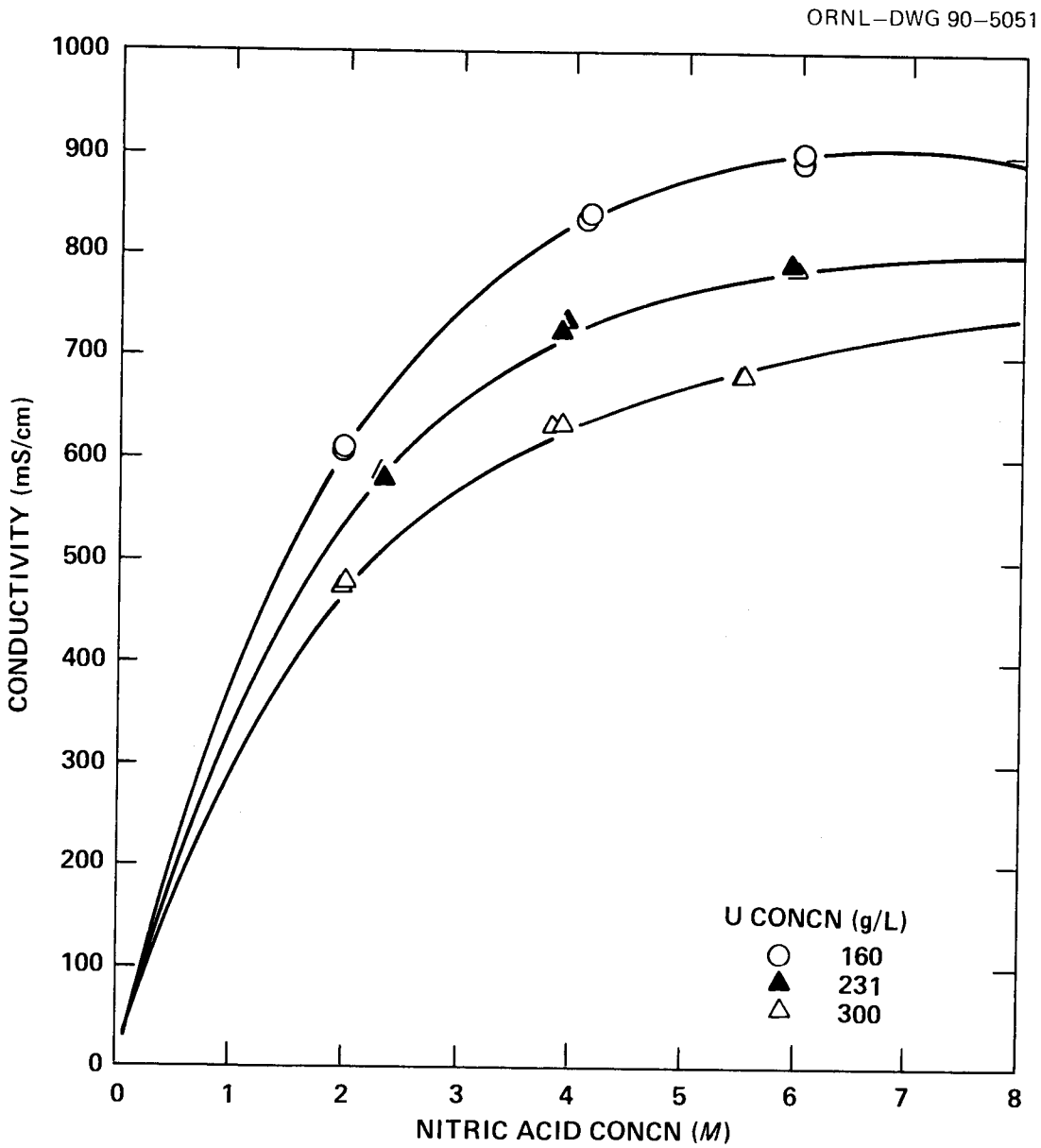

Fig. 2.16. Comparison of experimental electrical conductivity of aqueous nitric acid-uranium solutions at 60° to correlation.

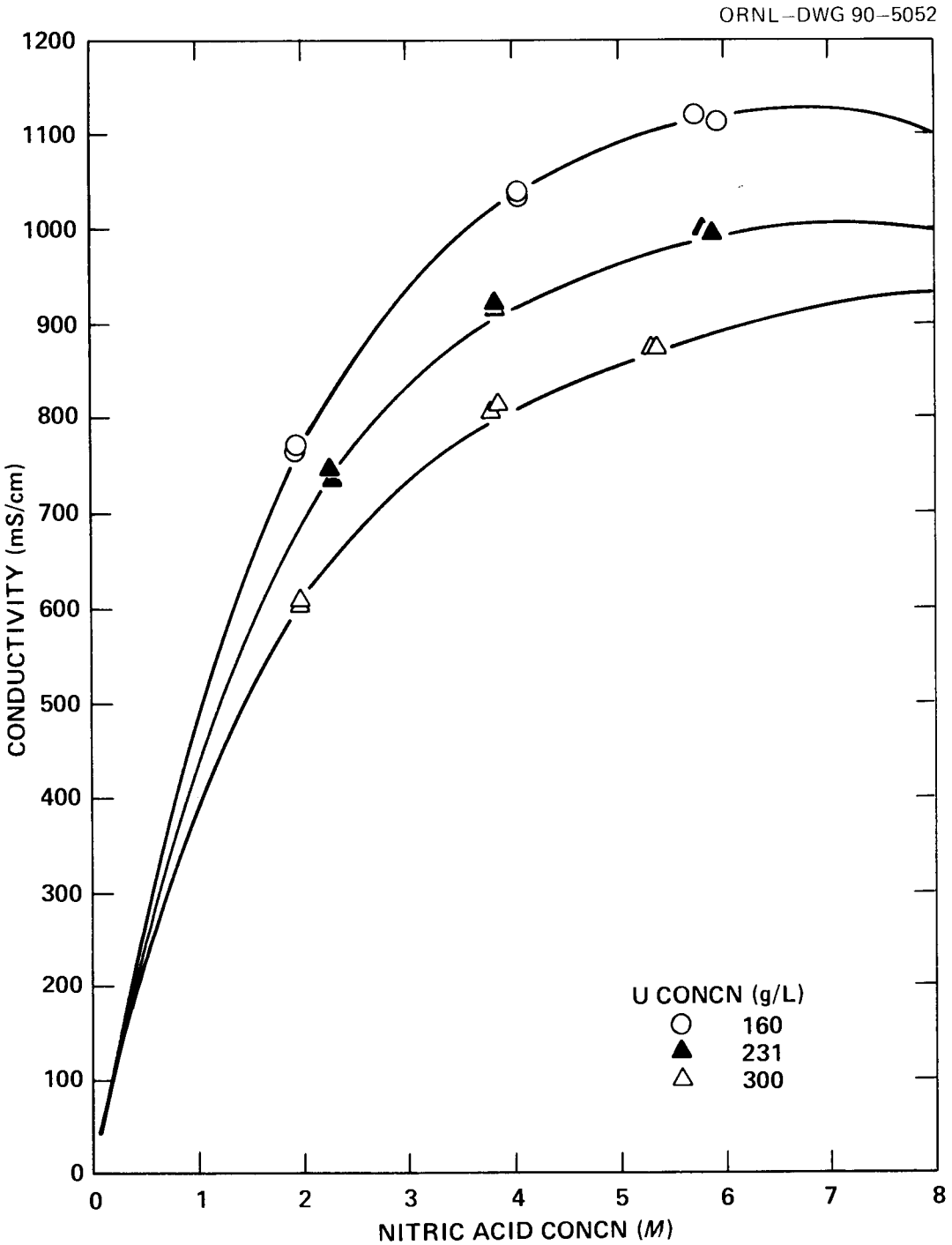

Fig. 2.17. Comparison of experimental electrical conductivity of aqueous nitric acid-uranium solutions at 95° to correlation.

Table 2.16. FORTRAN program for calculating nitric acid and uranium concentrations from electrical conductivity, density, and temperature

```
      SUBROUTINE ARCUH2(T,RHO,C,H,U,NITER)
      IMPLICIT REAL*8(A-H,K,O-Z)
C-----written by B. B. Spencer    version 9-22-89
C-----Calculates acid and uranium concentration
C-----  from measured temperature, density, and electrical conductivity
C        T = temperature, °C
C      RHO = density, gm/cc
C        C = conductivity, mS/cm
C        H = nitric acid concentration, M
C        U = uranium concentration, gm/L
C    NITER = number of iterations to converge
      DIMENSION A(3),B(4),G(5)
      DIMENSION FCO(8),GCO(6),DCO(5),R(8)
      DATA FCO/ 255.7921D0, 5.446796D0,-8.496950D-3, -36.42003D0,
     2         -1.043629D0, 1.437531D0, 1.310446D-1, -6.48670D-3/
      DATA GCO/ 1.258519D-3, 2.976994D-4, -6.529605D-6,
     2          1.065403D-8,-4.487609D-7, -1.575492D-5/
      DATA DCO/ 1.022811D0 , 2.935808D-2,-3.475035D-5,
     2          1.312180D-3,-4.680629D-4/
C
C-----Solve combined conductivity & density equation using
C      Newton Method
C
C-----first, incorporate temperature into coefficients
      A(1)=DCO(1)+DCO(5)*T
      A(2)=DCO(2)+DCO(3)*T
      A(3)=DCO(4)
      B(1)=FCO(1)+FCO(2)*T + FCO(3)*T*T
      B(2)=FCO(4)+FCO(5)*T
      B(3)=FCO(6)+FCO(7)*T
      B(4)=FCO(8)*T
      G(1)=GCO(1)+GCO(3)*T
      G(2)=GCO(2)
      G(3)=GCO(4)*T
      G(4)=GCO(5)
      G(5)=GCO(6)
      TT1=(RHO-A(1))/A(3)
      TT2=-A(2)/A(3)
C-----Then estimate acid and uranium concentrations using simple
C      correlation
      R(1)= 2.5369D1+7.3978D0*T-1.8311D-2*T*T
      R(2)= 1.9137D2
      R(3)=-4.1789D-1
      R(4)=-1.6424D1
      R(5)= 1.2147D-4
      R(6)= 5.1495D-1*T
      R(7)=-6.3251D-3*T
      R(8)=-1.3184D-1
      ALPHA=R(4)+R(5)*TT2*TT2+R(8)*TT2
      BETA=R(2)+R(3)*TT2+R(5)*2.D0*TT2*TT1+R(6)+R(7)*TT2+R(8)*TT1
      GAMMA=-C+R(1)+R(3)*TT1+R(5)*TT1*TT1+R(7)*TT1
      RAD=BETA*BETA-4.D0*ALPHA*GAMMA
```

Table 2.16. (continued)

```
      IF(RAD.LT.0.D0)GO TO 8
      H=(DSQRT(RAD)-BETA)/2.D0/ALPHA
      IF(H.GE.0.D0 .AND. H.LE.6.D0)GO TO 9
      WRITE(*,200)
 200  FORMAT(' ARCUH2:guessing formula failed, will use default')
   8  H=2.D0
   9  CONTINUE
C-----Now, do Newton iteration
      DO 1 I=1,10
      NITER=I
      TTH2=H*H
      TTH3=H*TTH2
      U=TT1+TT2*H
      F=B(1)+B(2)*H+B(3)*TTH2+B(4)*TTH3
      F=H*F
      FPRIME=B(1)+2.D0*B(2)*H+3.D0*B(3)*TTH2+4.D0*B(4)*TTH3
      BRAC=G(1)+G(2)*H+G(3)*U+G(4)*U*H+G(5)*TTH2
      GX=U*BRAC
      GPRIME=G(2)+G(3)*TT2+G(4)*TT1+2.D0*G(4)*TT2*H+2.D0*G(5)*H
      GPRIME=U*GPRIME+BRAC*TT2
      E=C-F*(1.D0-GX)
      EPRIME=F*GPRIME-(1.D0-GX)*FPRIME
      IF(DABS(E).LE.1.D-4)GO TO 2
      H=H-E/EPRIME
   1  CONTINUE
      WRITE(*,100)
 100  FORMAT(' ARCUH2:did not converge in 10 iterations')
   2  RETURN
      END
```

Table 2.17. Comparison of acid and uranium concentrations inferred from conductivity, density, and temperature with data

T (°C)	σ (g/cc)	c (mS/cm)	HNO_3 (M)	calc H	error %	U (g/L)	calc U	error %
25.	1.2770	422.50	1.99	2.00	.46	160.83	159.23	-1.01
25.	1.2765	422.50	2.01	2.00	-.64	160.28	158.89	-.87
25.	1.3403	575.00	3.99	4.07	1.92	160.50	162.55	1.26
25.	1.3386	575.00	4.17	4.04	-3.15	160.21	161.81	.99
25.	1.3957	610.00	6.00	6.26	4.10	160.80	157.25	-2.26
25.	1.3936	615.00	6.30	6.37	1.17	160.36	153.10	-4.74
25.	1.3823	390.00	2.35	2.25	-4.33	232.59	233.98	.59
25.	1.3811	392.50	2.38	2.27	-4.92	231.66	232.72	.45
25.	1.4299	492.50	4.00	4.01	.23	231.60	232.11	.22
25.	1.4295	495.00	3.95	4.05	2.46	231.80	230.93	-.38
25.	1.4897	530.00	6.09	6.52	6.59	233.76	223.17	-4.74
25.	1.4877	525.00	6.04	6.21	2.74	233.04	228.37	-2.05
25.	1.4641	312.50	2.02	1.97	-2.80	300.89	302.56	.55
25.	1.4625	312.50	2.00	1.96	-2.19	301.24	301.51	.09
25.	1.5205	420.00	3.89	3.91	.63	301.74	303.21	.48
25.	1.5184	420.00	3.94	3.89	-1.39	301.38	302.23	.28
25.	1.5649	452.50	5.64	5.51	-2.37	303.80	302.42	-.46
25.	1.5645	450.00	5.63	5.42	-3.88	301.42	304.07	.87
60.	1.2569	610.00	1.97	2.00	1.68	158.03	158.15	.08
60.	1.2572	610.00	1.98	2.00	1.24	158.32	158.36	.02
60.	1.3148	835.00	4.12	4.08	-1.00	157.30	159.14	1.15
60.	1.3149	840.00	4.15	4.14	-.36	158.61	158.05	-.35
60.	1.3632	895.00	6.02	5.79	-3.95	157.35	160.44	1.93
60.	1.3627	900.00	6.04	5.87	-2.91	156.76	158.44	1.06
60.	1.3576	585.00	2.32	2.33	.37	227.68	228.14	.20
60.	1.3583	580.00	2.33	2.30	-1.32	227.79	229.28	.65
60.	1.4058	725.00	3.90	4.03	3.23	227.15	229.51	1.03
60.	1.4040	735.00	3.95	4.13	4.40	227.32	226.03	-.57
60.	1.4569	785.00	5.96	5.89	-1.20	226.34	229.82	1.51
60.	1.4549	790.00	5.93	5.95	.27	226.80	227.11	.13
60.	1.4397	475.00	2.00	2.03	1.40	295.84	296.95	.37
60.	1.4400	477.50	2.03	2.05	.81	295.93	296.80	.29
60.	1.4870	635.00	3.82	3.94	3.09	294.82	293.23	-.54
60.	1.4899	635.00	3.92	3.98	1.49	294.12	294.66	.18
60.	1.5320	685.00	5.53	5.40	-2.49	294.24	297.31	1.03
60.	1.5281	685.00	5.52	5.33	-3.53	296.38	295.66	-.24
95.	1.2351	770.00	1.96	1.98	.86	157.10	156.41	-.44
95.	1.2353	765.00	1.94	1.96	.90	157.57	156.95	-.39
95.	1.2871	1035.00	4.06	3.93	-3.27	155.99	157.23	.79
95.	1.2912	1040.00	4.07	4.03	-1.00	157.19	158.40	.77
95.	1.3353	1120.00	5.73	5.79	1.00	155.65	157.10	.92
95.	1.3353	1115.00	5.96	5.71	-4.39	155.41	158.66	2.05
95.	1.3386	735.00	2.28	2.25	-1.16	226.78	229.79	1.31

Table 2.17. (continued)

95.	1.3343	745.00	2.26	2.28	1.09	226.88	225.90	-.44
95.	1.3743	915.00	3.82	3.87	1.25	224.90	224.94	.02
95.	1.3782	920.00	3.82	3.97	3.79	225.79	225.88	.04
95.	1.4255	995.00	5.88	5.80	-1.38	222.86	225.60	1.21
95.	1.4224	1000.00	5.82	5.82	-.03	224.52	222.88	-.74
95.	1.4151	605.00	1.97	1.94	-1.41	294.44	294.27	-.06
95.	1.4139	610.00	1.98	1.96	-.87	293.13	292.95	-.06
95.	1.4606	810.00	3.81	3.85	1.06	292.14	291.05	-.37
95.	1.4615	815.00	3.86	3.92	1.48	291.86	290.41	-.50
95.	1.4985	875.00	5.38	5.25	-2.43	290.98	292.10	.38
95.	1.4923	875.00	5.35	5.15	-3.87	288.99	289.40	.14
35.	1.4927	552.50	4.81	5.02	4.14	266.07	262.97	-1.18
50.	1.3478	657.50	3.17	3.23	1.92	198.18	197.48	-.36
75.	1.3691	940.00	4.96	5.24	5.34	188.57	183.83	-2.58
90.	1.3972	785.00	3.06	3.12	1.79	256.01	255.14	-.34

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Electrical conductivity and density of both aqueous nitric acid and aqueous nitric acid-uranium solutions have been correlated as functions of composition and temperature. The following correlations resulted from this study.

1. The density of aqueous nitric acid solutions at 25°C is well-represented by

$$\frac{1}{\rho_{25}} = a_0 + a_1 C + a_2 C^2 + a_3 C^3 \quad , \tag{3.1}$$

where the coefficients are

$a_0 = 1.003124,$

$a_1 = -3.364529 \times 10^{-2},$

$a_2 = 1.219254 \times 10^{-3},$

$a_3 = -1.681279 \times 10^{-5}.$

This equation covers the range from 0 to 21.2 *M* (from 0 to 90 wt %) and deviates a maximum of 0.05% from the data. The density at other temperatures may be obtained from

$$\frac{1}{\rho} = \left(\frac{1}{\rho_{25}}\right)[1 + (a_0 + a_1\rho_{25} + a_2 T)(T - 25)] \quad , \tag{3.2}$$

where

$a_0 = -1.647365 \times 10^{-3},$

$a_1 = 1.897063 \times 10^{-3},$

$a_2 = 2.017796 \times 10^{-6},$

Again, this equation covers the range of concentration from 0 to ~22 *M* (from 0 to 90 wt %), a temperature range of 0 to 100°C, and deviates a maximum of 0.6% from the data. Extrapolations up to 100% acid are considered good.

2. The electrical conductivity of aqueous nitric acid solutions were correlated by

$$c = C\,[b_{0,1} + b_{1,1}T + b_{2,1}T^2 + (b_{0,2} + b_{1,2}T)C + (b_{0,3} + b_{1,3}T)C^2 + b_{1,4}TC^3] \tag{3.3}$$

where the coefficients are

$b_{0,1} = 255.7921,$

$b_{1,1} = 5.446796,$

$b_{2,1} = -8.49695 \times 10^{-3}$,

$b_{0,2} = -36.42003$,

$b_{1,2} = -1.043629$,

$b_{0,3} = 1.437531$,

$b_{1,3} = 1.310446 \times 10^{-1}$,

$b_{1,4} = -6.48670 \times 10^{-3}$.

This equation correlates the data within a maximum error of 4.6% over a concentration range of 0.1 to 10.0 *M* and a temperature range of 0 to 100°C. Extrapolations to quite low acid concentrations (0.001 *M*) are expected to be good.

3. The density of aqueous nitric acid-uranium solutions was found to be well-correlated by the simple linear equation

$$\rho = a_0 + (a_1 + a_2 T)H + a_3 U + a_4 T \quad , \tag{3.4}$$

where the coefficients are

$a_0 = 1.022811$,

$a_1 = 2.935808 \times 10^{-2}$,

$a_2 = -3.475035 \times 10^{-5}$,

$a_3 = 1.312180 \times 10^{-3}$,

$a_4 = -4.680629 \times 10^{-4}$.

This equation was developed from data covering a temperature range of 25 to 95°C, an acid concentration range of 2 to 6 *M*, and a uranium concentration range of 0 to 300 g/L, and correlates the data to within 0.66%. Extrapolations down to ~15°C, down to 0 *M* acid, up to 7 *M* acid, and up to 450 g/L uranium are expected to be good.

4. The electrical conductivity of aqueous nitric acid-uranium solutions was correlated by

$$c = f(H,T)\,[(1 - g(H,U,T)] \quad , \tag{3.5}$$

where f(H,T) is equal to the right-hand side of Eq. (3.3) when C is replaced by H. The function g(H,U,T) is given by

$$g = U\,[a_0 + a_1 H + a_2 T + a_3 TU + a_4 UH + a_5 H^2] \quad , \tag{3.6}$$

where

$a_0 = 1.258519 \times 10^{-3}$,

$a_1 = 2.976994 \times 10^{-4}$,

$a_2 = -6.529605 \times 10^{-6}$,

$a_3 = 1.065403 \times 10^{-8}$,

$a^4 = -4.487609 \times 10^{-7}$,

$a^5 = -1.575492 \times 10^{-5}$.

This equation covers a temperature range of 25 to 95°C, an acid concentration range of 2 to 6 *M*, and a uranium concentration range of 160 to 300 g/L, and correlates the data to within 2.75%. Extrapolations down to perhaps 0.5 *M* acid may be expected to be good, but extrapolations to either high acid, temperatures, or uranium concentrations outside this range are judged risky.

In process control applications, extraction of solution concentration from measurements of the physical properties requires an inversion of the correlating equations. Analytic inversion of the rather complex equations is both difficult and numerically unstable, but numerical methods have been shown to be adequate. (Algorithms for obtaining acid and uranium concentrations from temperature, density, and conductivity measurements are described in Sect. 2 of this report.)

For aqueous nitric acid solutions with no uranium, a choice of using either electrical conductivity or density, in conjunction with temperature, to find the acid concentration is possible. Because conductivity reaches a maximum at around 6 *M*, there can be quite different concentrations having the same conductivity. Generally, conductivity should be used for solutions having concentrations of 6 *M* or less, and concentration can be estimated to very low acid values. Density continually increases as concentration increases and can be used throughout the range. But densities below ~0.8 *M* acid change little with concentration, and this method should not be used in that range.

The estimation of solution concentration for the aqueous nitric acid-uranium system requires density and conductivity measurements (in conjunction with temperature). Both uranium and acid concentration are determined simultaneously. The range must be kept within ranges for which both correlations are valid.

Several gaps in the existing data need to be filled. The behavior of uranium solution conductivity at zero and low acid should be measured. Additional data at higher acid concentrations are required to locate the true maximum in conductivity, which is important in determining the useful range. Data for low uranium concentration (from 25 to 100 g/L) throughout the acid concentration range are also needed.

An instrument could be designed that utilizes a single sensing head to measure temperature, electrical conductivity, and density. Algorithms, such as those presented in this report, could be programmed as part of the amplifier unit to provide concentration readings directly. This would reduce the computation load on the process control computer and preclude programming errors and costs associated with installing the algorithm in many different control systems. The economics of such an approach should be investigated.

REFERENCES

1. B. B. Spencer, *Summary and Results of the Automation Demonstrations in the Integrated Equipment Test Facility*, ORNL/TM-10808, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., August 1988.

2. B. B. Spencer et al., *Technical Description of the Automation of the Solvent Extraction and Supporting Processing Systems*, ORNL/TM-11190, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., May 1989.

3. A. A. Ray, *SAS User's Guide Statistics, 1982 Edition*, SAS Institute, Inc., Raleigh, NC, 1982.

4. R. H. Perry, ed., *Chemical Engineer's Handbook*, 5th ed., McGraw-Hill, New York, 1973, pp. 3-76 to 3-77.

5. R. C. Weast, ed., *CRC Handbook of Chemistry and Physics*, 57th ed., CRC Press, Boca Raton, Fla., 1976, pp. D-218 and D-238.

6. J. A. Dean, ed., *Lange's Handbook of Chemistry*, 11th ed., McGraw-Hill, New York, 1973, pp. 6-32 to 6-33 and pp. 10-100 to 10-102.

7. E. W. Washburn, ed., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. III*, National Research Council, McGraw-Hill, New York, 1928, pp.51-59.

8. K. Gieck, *Engineering Formulas*, 3rd ed., McGraw-Hill, New York, 1979.

9. E. W. Washburn, ed., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. VI*, National Research Council, McGraw-Hill, New York, 1929, pp. 229-230 and 241-242.

10. *Handling of Nitric Acid*, Foxboro Technical Information Bul. TI 5-75a, The Foxboro Co., Foxboro, Mass., 1954.

11. *Theory and Application of Electrical Conductivity*, Foxboro Technical Information Bul. TI 612-112, The Foxboro Co., Foxboro, Mass., 1980.

12. P. W. Pair, unpublished data, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn.

13. E. W. Washburn, ed., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. VII*, National Research Council, McGraw-Hill, New York, 1930, pp. 64-65 and 71.

14. Allied General Nuclear Services, *Separations Plant Data Manual*, p. 3-2, September 3, 1975.

15. C. K. Bayne, Computing and Telecommunications Division, Oak Ridge Natl. Lab., letter to D. A. Costanzo, Oak Ridge Natl. Lab., Feb. 2, 1979.

NOMENCLATURE

a_i	adjustable coefficients, where i = 0, 1, 2 . . .
b	coefficients
c	conductivity, mS/cm
C	concentration, *M*
C(p)	Mallow statistic, defined in Eq. (2.2)
f	a function
g	another function
H	nitric acid concentration, *M*
m	number of independent variables
n	number of observations
p	number of coefficients
r^2	correlation coefficient, defined in Eq. (2.1)
s^2	mean square error, defined in Eq. (2.2)
T	temperature, °C
T_0	reference temperature
U	uranium metal concentration, g/L
V	volume, cm^3
w	concentration, weight percent
y_i	ith observation of dependent variable
$\hat{y}_i$	value of dependent variable calculated from model
$\bar{y}$	average of all observed y values
β	volumetric coefficient of thermal expansion, $°C^{-1}$
ρ	density, g/cm^3
ρ_0	density at reference temperature, g/cm^3

APPENDIX A
DENSITY OF AQUEOUS NITRIC ACID SOLUTIONS

The literature contains data on the density of aqueous nitric acid solutions covering a concentration range of 0 to 100 wt % and 0 to 100°C. Common references include the Chemical Engineer's Handbook (ref. 4), the CRC Handbook (ref. 5), and Lange's Handbook of Chemistry (ref. 6). Most of the data quoted in these standard references are from the International Critical Tables (ref. 7). Table A.1 presents the density data as found in the Critical Tables. Because it is often convenient to use concentration in molar units, Table A.2 was prepared to give the molar concentration at each value of wt % and temperature for which the density was given in Table A.1.

Table A.1. Density of aqueous nitric acid solution at various weight percent acid and temperatures

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
0	0.99987	0.99999	0.99973	0.99913	0.99823	0.99708	0.99568	0.99225	0.98807	0.98324	0.97183	0.95838
1	1.0058	1.00572	1.00534	1.00464	1.00364	1.00241	1.0009	0.9973	0.9931	0.9882	0.9767	0.9632
2	1.0117	1.01149	1.01099	1.01018	1.00909	1.00778	1.0061	1.0025	0.9982	0.9932	0.9816	0.9681
3	1.0176	1.01730	1.01668	1.01576	1.01457	1.01318	1.0114	1.0077	1.0033	0.9982	0.9865	0.9730
4	1.0236	1.02315	1.02240	1.02137	1.02008	1.01861	1.0168	1.0129	1.0084	1.0033	0.9915	0.9779
5	1.0296	1.02904	1.02816	1.02702	1.02563	1.02408	1.0222	1.0182	1.0136	1.0084	0.9965	0.9829
6	1.0357	1.03497	1.03397	1.03272	1.03122	1.02958	1.0277	1.0235	1.0188	1.0136	1.0015	0.9879
7	1.0418	1.0410	1.0399	1.0385	1.0369	1.0352	1.0333	1.0289	1.0241	1.0188	1.0066	0.9929
8	1.0480	1.0471	1.0458	1.0443	1.0427	1.0409	1.0389	1.0344	1.0295	1.0241	1.0117	0.9980
9	1.0543	1.0532	1.0518	1.0502	1.0485	1.0466	1.0446	1.0399	1.0349	1.0294	1.0169	1.0032
10	1.0606	1.0594	1.0578	1.0561	1.0543	1.0523	1.0503	1.0455	1.0403	1.0347	1.0221	1.0083
11	1.0669	1.0656	1.0639	1.0621	1.0602	1.0581	1.0560	1.0511	1.0458	1.0401	1.0273	1.0134
12	1.0733	1.0718	1.0700	1.0681	1.0661	1.0640	1.0618	1.0567	1.0513	1.0455	1.0326	1.0186
13	1.0797	1.0781	1.0762	1.0742	1.0721	1.0699	1.0676	1.0624	1.0568	1.0509	1.0379	1.0238
14	1.0862	1.0845	1.0824	1.0803	1.0781	1.0758	1.0735	1.0681	1.0624	1.0564	1.0432	1.0289
15	1.0927	1.0909	1.0887	1.0865	1.0842	1.0818	1.0794	1.0739	1.0680	1.0619	1.0485	1.0341
16	1.0992	1.0973	1.0950	1.0927	1.0903	1.0879	1.0854	1.0797	1.0737	1.0675	1.0538	1.0393
17	1.1057	1.1038	1.1014	1.0989	1.0964	1.0940	1.0914	1.0855	1.0794	1.0731	1.0592	1.0444
18	1.1123	1.1103	1.1078	1.1052	1.1026	1.1001	1.0974	1.0913	1.0851	1.0787	1.0646	1.0496
19	1.1189	1.1168	1.1142	1.1115	1.1088	1.1062	1.1034	1.0972	1.0908	1.0843	1.0700	1.0547
20	1.1255	1.1234	1.1206	1.1178	1.1150	1.1123	1.1094	1.1031	1.0966	1.0899	1.0754	1.0598
21	1.1322	1.1300	1.1271	1.1242	1.1213	1.1185	1.1155	1.1090	1.1024	1.0956	1.0808	1.0650
22	1.1389	1.1366	1.1336	1.1306	1.1276	1.1247	1.1217	1.1150	1.1083	1.1013	1.0862	1.0701
23	1.1457	1.1433	1.1402	1.1371	1.1340	1.1310	1.1280	1.1210	1.1142	1.1070	1.0917	1.0753
24	1.1525	1.1501	1.1469	1.1437	1.1404	1.1374	1.1343	1.1271	1.1201	1.1127	1.0972	1.0805
25	1.1594	1.1569	1.1536	1.1503	1.1469	1.1438	1.1406	1.1332	1.1260	1.1185	1.1027	1.0857
26	1.1663	1.1638	1.1603	1.1569	1.1534	1.1502	1.1469	1.1394	1.1320	1.1244	1.1083	1.0910
27	1.1733	1.1707	1.1670	1.1635	1.1600	1.1566	1.1533	1.1456	1.1381	1.1303	1.1139	1.0963
28	1.1803	1.1777	1.1738	1.1702	1.1666	1.1631	1.1597	1.1519	1.1442	1.1362	1.1195	1.1016
29	1.1874	1.1847	1.1807	1.1770	1.1733	1.1697	1.1662	1.1582	1.1503	1.1422	1.1251	1.1069
30	1.1945	1.1917	1.1876	1.1838	1.1800	1.1763	1.1727	1.1645	1.1564	1.1482	1.1307	1.1122
31	1.2016	1.1988	1.1945	1.1906	1.1867	1.1829	1.1792	1.1708	1.1625	1.1542	1.1363	1.1175
32	1.2088	1.2059	1.2014	1.1974	1.1934	1.1896	1.1857	1.1772	1.1687	1.1602	1.1419	1.1228
33	1.2160	1.2131	1.2084	1.2043	1.2002	1.1963	1.1922	1.1836	1.1749	1.1662	1.1476	1.1281

Table A.1. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
34	1.2233	1.2203	1.2155	1.2113	1.2071	1.2030	1.1988	1.1901	1.1812	1.1723	1.1533	1.1335
35	1.2306	1.2275	1.2227	1.2183	1.2140	1.2098	1.2055	1.1966	1.1876	1.1784	1.1591	1.1390
36	1.2375	1.2344	1.2294	1.2249	1.2205	1.2163	1.2119	1.2028	1.1936	1.1842	1.1645	1.1440
37	1.2444	1.2412	1.2361	1.2315	1.2270	1.2227	1.2182	1.2089	1.1995	1.1899	1.1699	1.1490
38	1.2513	1.2479	1.2428	1.2381	1.2335	1.2291	1.2245	1.2150	1.2054	1.1956	1.1752	1.1540
39	1.2581	1.2546	1.2494	1.2446	1.2399	1.2354	1.2308	1.2210	1.2112	1.2013	1.1805	1.1589
40	1.2649	1.2613	1.2560	1.2511	1.2463	1.2417	1.2370	1.2270	1.2170	1.2069	1.1858	1.1638
41	1.2717	1.2680	1.2626	1.2576	1.2527	1.2480	1.2432	1.2330	1.2229	1.2126	1.1911	1.1687
42	1.2786	1.2747	1.2692	1.2641	1.2591	1.2543	1.2494	1.2390	1.2287	1.2182	1.1963	1.1735
43	1.2854	1.2814	1.2758	1.2706	1.2655	1.2606	1.2556	1.2450	1.2345	1.2238	1.2015	1.1783
44	1.2922	1.2880	1.2824	1.2771	1.2719	1.2669	1.2618	1.2510	1.2403	1.2294	1.2067	1.1831
45	1.2990	1.2947	1.2890	1.2836	1.2783	1.2732	1.2680	1.2570	1.2461	1.2350	1.2119	1.1879
46	1.3058	1.3014	1.2955	1.2901	1.2847	1.2795	1.2742	1.2630	1.2519	1.2406	1.2171	1.1927
47	1.3126	1.3080	1.3021	1.2966	1.2911	1.2858	1.2804	1.2690	1.2577	1.2462	1.2223	1.1976
48	1.3194	1.3147	1.3087	1.3031	1.2975	1.2921	1.2867	1.2750	1.2635	1.2518	1.2275	1.2024
49	1.3263	1.3214	1.3153	1.3096	1.3040	1.2984	1.2929	1.2811	1.2693	1.2575	1.2328	1.2073
50	1.3327	1.3277	1.3215	1.3157	1.3100	1.3043	1.2987	1.2867	1.2748	1.2628	1.2377	1.2118
51	1.3391	1.3339	1.3277	1.3218	1.3160	1.3102	1.3045	1.2923	1.2802	1.2680	1.2425	1.2163
52	1.3454	1.3401	1.3338	1.3278	1.3219	1.3160	1.3102	1.2978	1.2856	1.2731	1.2473	1.2208
53	1.3517	1.3462	1.3399	1.3338	1.3278	1.3218	1.3159	1.3033	1.2909	1.2782	1.2521	1.2252
54	1.3579	1.3523	1.3459	1.3397	1.3336	1.3275	1.3215	1.3087	1.2961	1.2833	1.2568	1.2296
55	1.3640	1.3583	1.3518	1.3455	1.3393	1.3331	1.3270	1.3141	1.3013	1.2883	1.2615	1.2339
56	1.3700	1.3642	1.3576	1.3512	1.3449	1.3386	1.3324	1.3194	1.3064	1.2932	1.2661	1.2382
57	1.3759	1.3700	1.3634	1.3569	1.3505	1.3441	1.3377	1.3246	1.3114	1.2981	1.2706	1.2424
58	1.3818	1.3757	1.3691	1.3625	1.3560	1.3495	1.3430	1.3298	1.3164	1.3029	1.2751	1.2466
59	1.3875	1.3813	1.3747	1.3680	1.3614	1.3548	1.3482	1.3348	1.3213	1.3077	1.2795	1.2507
60	1.3931	1.3868	1.3801	1.3734	1.3667	1.3600	1.3533	1.3398	1.3261	1.3124	1.2839	1.2547
61	1.3986	1.3922	1.3855	1.3787	1.3719	1.3651	1.3583	1.3447	1.3308	1.3169	1.2881	1.2587
62	1.4039	1.3975	1.3907	1.3838	1.3769	1.3700	1.3632	1.3494	1.3354	1.3213	1.2922	1.2625
63	1.4091	1.4027	1.3958	1.3888	1.3818	1.3748	1.3679	1.3540	1.3398	1.3255	1.2962	1.2661
64		1.4078	1.4007	1.3936	1.3866	1.3795	1.3725					
65		1.4128	1.4055	1.3984	1.3913	1.3841	1.3770					
66		1.4177	1.4103	1.4031	1.3959	1.3887	1.3814					
67		1.4224	1.4150	1.4077	1.4004	1.3932	1.3857					

Table A.1. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
68		1.4271	1.4196	1.4122	1.4048	1.3976	1.3900					
69		1.4317	1.4241	1.4166	1.4091	1.4019	1.3942					
70		1.4362	1.4285	1.4210	1.4134	1.4061	1.3983					
71		1.4406	1.4328	1.4252	1.4176	1.4102	1.4023					
72		1.4449	1.4371	1.4294	1.4218	1.4142	1.4063					
73		1.4491	1.4413	1.4335	1.4258	1.4182	1.4103					
74		1.4532	1.4454	1.4376	1.4298	1.4221	1.4142					
75		1.4573	1.4494	1.4415	1.4337	1.4259	1.4180					
76		1.4613	1.4533	1.4454	1.4375	1.4296	1.4217					
77		1.4652	1.4572	1.4492	1.4413	1.4333	1.4253					
78		1.4690	1.4610	1.4529	1.4450	1.4369	1.4288					
79		1.4727	1.4647	1.4565	1.4486	1.4404	1.4323					
80		1.4764	1.4683	1.4601	1.4521	1.4439	1.4357					
81		1.4800	1.4718	1.4636	1.4555	1.4473	1.4391					
82		1.4835	1.4753	1.4670	1.4589	1.4507	1.4424					
83		1.4869	1.4787	1.4704	1.4622	1.4540	1.4456					
84		1.4903	1.4820	1.4737	1.4655	1.4572	1.4487					
85		1.4936	1.4852	1.4769	1.4686	1.4603	1.4518					
86		1.4968	1.4883	1.4799	1.4716	1.4633	1.4548					
87		1.4999	1.4913	1.4829	1.4745	1.4662	1.4577					
88		1.5029	1.4942	1.4858	1.4773	1.4690	1.4605					
89		1.5058	1.4970	1.4885	1.4800	1.4716	1.4631					
90		1.5085	1.4997	1.4911	1.4826	1.4741	1.4656					
91		1.5111	1.5023	1.4936	1.4850	1.4766	1.4681					
92		1.5136	1.5048	1.4960	1.4873	1.4789	1.4704					
93		1.5156	1.5068	1.4979	1.4892	1.4807	1.4722					
94		1.5177	1.5088	1.4999	1.4912	1.4826	1.4741					
95		1.5198	1.5109	1.5019	1.4932	1.4846	1.4761					
96		1.5220	1.5130	1.5040	1.4952	1.4867	1.4781					
97		1.5244	1.5152	1.5062	1.4974	1.4889	1.4802					
98		1.5278	1.5187	1.5096	1.5008	1.4922	1.4835					
99		1.5327	1.5235	1.5144	1.5056	1.4969	1.4881					
100		1.5402	1.5310	1.5217	1.5129	1.5040	1.4952					

Notes: Data for pure water from Ref. 5. All other data from Ref. 7.

Table A.2. Molarity of aqueous nitric acid solution at various weight percent acid and temperatures

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
0	0	0	0	0	0	0	0	0	0	0	0	0
1	0.1596	0.1596	0.1595	0.1594	0.1593	0.1591	0.1588	0.1583	0.1576	0.1568	0.1550	0.1528
2	0.3211	0.3210	0.3209	0.3206	0.3202	0.3198	0.3193	0.3182	0.3168	0.3152	0.3115	0.3072
3	0.4844	0.4843	0.4840	0.4836	0.4830	0.4823	0.4815	0.4797	0.4776	0.4752	0.4696	0.4632
4	0.6497	0.6494	0.6489	0.6483	0.6475	0.6465	0.6454	0.6429	0.6401	0.6368	0.6293	0.6207
5	0.8169	0.8164	0.8158	0.8148	0.8137	0.8125	0.8110	0.8078	0.8042	0.8001	0.7906	0.7798
6	0.9861	0.9854	0.9844	0.9832	0.9818	0.9803	0.9785	0.9745	0.9700	0.9650	0.9535	0.9406
7	1.1572	1.1563	1.1551	1.1535	1.1517	1.1499	1.1477	1.1429	1.1375	1.1316	1.1181	1.1029
8	1.3304	1.3292	1.3276	1.3257	1.3236	1.3214	1.3188	1.3131	1.3069	1.3000	1.2843	1.2669
9	1.5057	1.5041	1.5021	1.4998	1.4974	1.4947	1.4918	1.4851	1.4780	1.4701	1.4523	1.4327
10	1.6830	1.6811	1.6785	1.6758	1.6730	1.6698	1.6666	1.6590	1.6507	1.6419	1.6219	1.6000
11	1.8623	1.8600	1.8570	1.8539	1.8506	1.8469	1.8432	1.8347	1.8254	1.8155	1.7931	1.7689
12	2.0437	2.0409	2.0374	2.0338	2.0300	2.0260	2.0218	2.0121	2.0018	1.9908	1.9662	1.9396
13	2.2272	2.2239	2.2200	2.2159	2.2116	2.2070	2.2023	2.1916	2.1800	2.1678	2.1410	2.1119
14	2.4130	2.4092	2.4046	2.3999	2.3950	2.3899	2.3848	2.3728	2.3601	2.3468	2.3175	2.2857
15	2.6008	2.5966	2.5913	2.5861	2.5806	2.5749	2.5692	2.5561	2.5421	2.5275	2.4956	2.4614
16	2.7907	2.7859	2.7801	2.7742	2.7681	2.7620	2.7557	2.7412	2.7260	2.7103	2.6755	2.6387
17	2.9827	2.9776	2.9711	2.9643	2.9576	2.9511	2.9441	2.9282	2.9117	2.8947	2.8573	2.8173
18	3.1770	3.1713	3.1641	3.1567	3.1493	3.1421	3.1344	3.1170	3.0993	3.0810	3.0407	2.9979
19	3.3734	3.3671	3.3592	3.3511	3.3429	3.3351	3.3267	3.3080	3.2887	3.2691	3.2260	3.1798
20	3.5719	3.5652	3.5563	3.5474	3.5386	3.5300	3.5208	3.5008	3.4802	3.4589	3.4129	3.3634
21	3.7728	3.7655	3.7558	3.7461	3.7365	3.7271	3.7172	3.6955	3.6735	3.6508	3.6015	3.5489
22	3.9758	3.9678	3.9573	3.9469	3.9364	3.9263	3.9158	3.8924	3.8690	3.8446	3.7919	3.7357
23	4.1814	4.1726	4.1613	4.1500	4.1387	4.1277	4.1168	4.0912	4.0664	4.0401	3.9843	3.9245
24	4.3891	4.3799	4.3678	4.3556	4.3430	4.3316	4.3198	4.2924	4.2657	4.2375	4.1785	4.1149
25	4.5993	4.5894	4.5763	4.5632	4.5497	4.5374	4.5248	4.4954	4.4668	4.4371	4.3744	4.3070
26	4.8118	4.8015	4.7870	4.7730	4.7586	4.7454	4.7317	4.7008	4.6703	4.6389	4.5725	4.5011
27	5.0268	5.0157	4.9998	4.9848	4.9699	4.9553	4.9411	4.9082	4.8760	4.8426	4.7723	4.6969
28	5.2441	5.2326	5.2152	5.1992	5.1832	5.1677	5.1526	5.1179	5.0837	5.0482	4.9740	4.8944
29	5.4641	5.4517	5.4332	5.4162	5.3992	5.3826	5.3665	5.3297	5.2934	5.2561	5.1774	5.0936
30	5.6863	5.6730	5.6534	5.6354	5.6173	5.5997	5.5825	5.5435	5.5049	5.4659	5.3826	5.2945
31	5.9108	5.8970	5.8758	5.8566	5.8375	5.8188	5.8006	5.7593	5.7184	5.6776	5.5895	5.4971
32	6.1380	6.1233	6.1004	6.0801	6.0598	6.0405	6.0207	5.9775	5.9344	5.8912	5.7983	5.7013
33	6.3675	6.3523	6.3277	6.3062	6.2848	6.2643	6.2429	6.1978	6.1523	6.1067	6.0093	5.9072

Table A.2. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
34	6.5998	6.5837	6.5578	6.5351	6.5124	6.4903	6.4677	6.4207	6.3727	6.3247	6.2222	6.1154
35	6.8345	6.8173	6.7906	6.7662	6.7423	6.7190	6.6951	6.6457	6.5957	6.5446	6.4374	6.3258
36	7.0692	7.0515	7.0229	6.9972	6.9721	6.9481	6.9229	6.8710	6.8184	6.7647	6.6522	6.5351
37	7.3061	7.2873	7.2573	7.2303	7.2039	7.1787	7.1522	7.0976	7.0424	6.9861	6.8687	6.7460
38	7.5451	7.5246	7.4939	7.4655	7.4378	7.4113	7.3835	7.3262	7.2684	7.2093	7.0863	6.9584
39	7.7858	7.7641	7.7319	7.7022	7.6731	7.6453	7.6168	7.5562	7.4955	7.4343	7.3055	7.1719
40	8.0286	8.0057	7.9721	7.9410	7.9105	7.8813	7.8515	7.7880	7.7245	7.6604	7.5265	7.3869
41	8.2735	8.2494	8.2143	8.1818	8.1499	8.1193	8.0881	8.0217	7.9560	7.8890	7.7491	7.6034
42	8.5213	8.4953	8.4586	8.4247	8.3913	8.3593	8.3267	8.2574	8.1887	8.1188	7.9728	7.8208
43	8.7706	8.7433	8.7051	8.6696	8.6348	8.6014	8.5672	8.4949	8.4233	8.3503	8.1981	8.0398
44	9.0220	8.9927	8.9536	8.9166	8.8803	8.8454	8.8098	8.7344	8.6597	8.5836	8.4251	8.2603
45	9.2756	9.2449	9.2042	9.1657	9.1278	9.0914	9.0543	8.9757	8.8979	8.8186	8.6537	8.4823
46	9.5314	9.4993	9.4562	9.4168	9.3774	9.3394	9.3007	9.2190	9.1380	9.0555	8.8839	8.7058
47	9.7893	9.7550	9.7110	9.6700	9.6290	9.5894	9.5492	9.4641	9.3799	9.2941	9.1159	8.9316
48	10.0494	10.0136	9.9679	9.9252	9.8826	9.8414	9.8003	9.7112	9.6236	9.5345	9.3494	9.1582
49	10.3124	10.2743	10.2269	10.1825	10.1390	10.0955	10.0527	9.9609	9.8692	9.7775	9.5854	9.3871
50	10.5736	10.5340	10.4848	10.4388	10.3935	10.3483	10.3039	10.2087	10.1142	10.0190	9.8199	9.6144
51	10.8369	10.7948	10.7446	10.6969	10.6500	10.6030	10.5569	10.4582	10.3602	10.2615	10.0551	9.8431
52	11.1014	11.0576	11.0056	10.9561	10.9075	10.8588	10.8109	10.7086	10.6079	10.5048	10.2919	10.0732
53	11.3678	11.3216	11.2686	11.2173	11.1668	11.1164	11.0668	10.9608	10.8565	10.7497	10.5302	10.3040
54	11.6354	11.5875	11.5326	11.4795	11.4272	11.3750	11.3235	11.2139	11.1059	10.9962	10.7692	10.5361
55	11.9042	11.8544	11.7977	11.7427	11.6886	11.6345	11.5812	11.4687	11.3570	11.2435	11.0096	10.7687
56	12.1739	12.1224	12.0637	12.0069	11.9509	11.8949	11.8398	11.7243	11.6088	11.4915	11.2507	11.0027
57	12.4447	12.3913	12.3316	12.2728	12.2149	12.1570	12.0992	11.9807	11.8613	11.7410	11.4923	11.2372
58	12.7173	12.6612	12.6004	12.5397	12.4798	12.4200	12.3602	12.2387	12.1154	11.9911	11.7353	11.4730
59	12.9899	12.9319	12.8701	12.8074	12.7456	12.6838	12.6220	12.4965	12.3702	12.2428	11.9788	11.7092
60	13.2634	13.2034	13.1396	13.0758	13.0121	12.9483	12.8845	12.7559	12.6255	12.4951	12.2237	11.9457
61	13.5377	13.4758	13.4109	13.3451	13.2793	13.2134	13.1476	13.0160	12.8814	12.7469	12.4681	12.1835
62	13.8118	13.7488	13.6819	13.6140	13.5461	13.4783	13.4114	13.2756	13.1379	12.9991	12.7129	12.4207
63	14.0865	14.0225	13.9536	13.8836	13.8136	13.7436	13.6747	13.5357	13.3937	13.2508	12.9579	12.6570
64		14.2969	14.2248	14.1527	14.0816	14.0095	13.9384					
65		14.5719	14.4966	14.4234	14.3501	14.2759	14.2026					
66		14.8474	14.7699	14.6945	14.6191	14.5437	14.4672					
67		15.1223	15.0436	14.9660	14.8884	14.8119	14.7321					

Table A.2. (continued)

wt %	0°C	5°C	10°C	15°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
68		15.3987	15.3178	15.2380	15.1581	15.0804	14.9984					
69		15.6755	15.5923	15.5102	15.4281	15.3493	15.2650					
70		15.9527	15.8672	15.7839	15.6995	15.6184	15.5317					
71		16.2302	16.1423	16.0567	15.9711	15.8877	15.7987					
72		16.5079	16.4188	16.3308	16.2440	16.1572	16.0669					
73		16.7858	16.6955	16.6051	16.5159	16.4279	16.3364					
74		17.0639	16.9723	16.8807	16.7891	16.6987	16.6060					
75		17.3433	17.2493	17.1553	17.0624	16.9696	16.8756					
76		17.6228	17.5263	17.4310	17.3358	17.2405	17.1452					
77		17.9023	17.8046	17.7068	17.6103	17.5126	17.4148					
78		18.1818	18.0828	17.9826	17.8848	17.7845	17.6843					
79		18.4613	18.3610	18.2583	18.1592	18.0564	17.9549					
80		18.7420	18.6392	18.5351	18.4335	18.3294	18.2253					
81		19.0225	18.9171	18.8117	18.7076	18.6022	18.4968					
82		19.3029	19.1962	19.0882	18.9828	18.8761	18.7681					
83		19.5831	19.4751	19.3658	19.2578	19.1498	19.0392					
84		19.8644	19.7537	19.6431	19.5338	19.4232	19.3099					
85		20.1454	20.0321	19.9201	19.8082	19.6962	19.5816					
86		20.4260	20.3100	20.1954	20.0821	19.9689	19.8529					
87		20.7063	20.5876	20.4716	20.3557	20.2411	20.1238					
88		20.9862	20.8647	20.7474	20.6288	20.5129	20.3942					
89		21.2657	21.1414	21.0213	20.9013	20.7827	20.6626					
90		21.5432	21.4175	21.2947	21.1733	21.0519	20.9305					
91		21.8201	21.6930	21.5674	21.4432	21.3219	21.1992					
92		22.0963	21.9679	21.8394	21.7124	21.5898	21.4657					
93		22.3660	22.2362	22.1048	21.9765	21.8510	21.7256					
94		22.6379	22.5051	22.3724	22.2426	22.1143	21.9875					
95		22.9103	22.7762	22.6405	22.5094	22.3797	22.2516					
96		23.1850	23.0479	22.9108	22.7768	22.6473	22.5163					
97		23.4635	23.3219	23.1833	23.0479	22.9171	22.7831					
98		23.7582	23.6167	23.4752	23.3384	23.2046	23.0693					
99		24.0776	23.9331	23.7902	23.6519	23.5152	23.3770					
100		24.4399	24.2939	24.1463	24.0067	23.8654	23.7258					

Note: Molar concentrations calculated from density and wt% data given in Table A.1.

APPENDIX B
CONDUCTIVITY OF AQUEOUS NITRIC ACID SOLUTIONS

Electrical conductivity is that property of a material characterized by its ability to conduct an electric current. Conductivity is the reciprocal of electrical resistance. Conductivity can be extremely low, as in materials used for insulators, or very high, as in metal wires used to deliver electric power. Many liquid solutions are moderate electrical conductors and, in particular, their conductivity can change drastically with changes in the solute concentration. Such is the case with nitric acid solutions. This property provides the opportunity to nondestructively measure the concentration of nitric acid (the solute in this application) by inference.

The literature does not contain as large a body of data for electrical conductivity of aqueous nitric acid as it does for the density of this corrosive liquid. The International Critical Tables (ref. 9) contains conductivity data over a wide range of concentrations, at a temperature of 18°C, and over a wide range of temperatures for low concentrations as shown in Table B.1 and Tables B.2 and B.3, respectively. The data are presented in the International Critical Tables in the form of K vs concentration, where K is the ratio of specific conductivity to concentration. Specific conductivity has been extracted and listed separately in the tables presented in this appendix as convenient and useful information.

Foxboro (ref. 11) has published conductivity data for aqueous nitric acid at 25°C covering a wide range of concentrations. These data are summarized in Table B.4. (For completeness, the densities of the solutions from the Foxboro reference are also given, but the values are the same as those given in Appendix A at the same concentration and temperature.)

The CRC Handbook of Chemistry (ref. 5) provides some limited data on conductivity of dilute nitric acid at 20°C. These data are provided in Table B.5.

Because there seemed to be a gap in the conductivity data for concentrated nitric acid solutions, some measurements were made in the chemistry laboratory of the Fuel Recycle Division, Oak Ridge National Laboratory (ref. 12). These data are summarized in Table B.6. Also shown are the measurements of density made on the same solutions. The density data compare favorably in magnitude to other literature sources but show a distinct bias in being from 0.2 to 0.5% high. Therefore, these density data were not used in the density correlations. For conductivity, the few solutions having the same concentration and temperature in Table B.6 and in Table B.3 are reported to have a slightly lower conductivity in Table B.6, but for the most part Table B.6 represents new data for which there is no basis for eliminating specific points. The second column in Table B.6 gives the nominal nitric acid concentration and the last column (marked experimental) is the concentration determined experimentally for the solution tested, and is the more accurate value.

Table B.1. Conductivity of concentrated and dilute aqueous nitric acid solution at 18°C

HNO_3 concentration (*M*)	K (mS/cm/*M*)	Conductivity (mS/cm)
0.0005	373.3	0.1867
0.001	372.6	0.3726
0.002	370.6	0.7412
0.005	366.8	1.834
0.010	364.0	3.640
0.020	360.4	7.210
0.050	353.0	17.65
0.070	349.6	24.47
0.100	345.7	34.57
0.200	336.0	67.20
0.500	321.5	160.8
0.700	315.5	220.9
1.000	305.5	305.5
2.000	259.1	518.2
3.000	220.0	660.0
4.000	184.4	737.6
5.000	154.6	773.0
6.000	129.1	774.6
7.000	108.6	760.2
8.000	91.9	735.2
9.000	77.6	698.4
10.000	64.9	649.0
16.500	20.43	337.1
17.000	17.65	300.1
18.000	12.55	225.9
19.000	8.50	161.5
20.000	5.50	110.0
21.000	2.90	60.9
22.385	1.009	22.59
22.870	0.6690	15.30
23.660	0.8538	20.20
23.800	1.667	39.67
24.060	1.720	41.38

Source: Data from ref. 9.

Table B.2. K-values of dilute aqueous nitric acid solutions at different temperatures

concn.	temperature, °C										
M	0	25	25	35	50	75	100	128	156	218	306
0.0005			416.2		562.8	695.7	813.2	928.	1026.		
0.001			414.6		560.7	692.3	809.		1018.		
0.002			412.9		557.7	688.3	804.6	917.	1010.	1164.	1154.
0.005		411.2	409.0		552.	681.6	795.	904.	993.		
0.010	253.4	407.3	405.2	455.8	546.9	674.7	784.5	891.	976.		
0.020	251.7	402.4	400.8	450.4	540.	665.2	772.	872.	954.		
0.050	248.6	394.0	392.5	441.4	527.4	647.6	748.6	843.	915.		
0.070	247.1		388.7	437.4	521.9	639.6	737.7	830.	898.		482.
0.080										924.	453.
0.100	245.3	386.0	384.2	432.6	514.7	630.6	727.0	815.	878.		
0.200	241.3	376.1	374.4	419.0							
0.500		356.5	356.6								
0.700			347.0								
1.000		329.8	333.2								

data from ref. 9

Table B.3. Conductivity of dilute aqueous nitric acid solutions at different temperatures

concn.	temperature, °C										
M	0	25	25	35	50	75	100	128	156	218	306
0.0005			0.2081		0.2814	0.3479	0.4066	0.464	0.5130		
0.001			0.4146		0.5607	0.6923	0.809		1.018		
0.002			0.8258		1.115	1.377	1.609	1.834	2.020	2.328	2.308
0.005		2.056	2.045		2.76	3.408	3.975	4.52	4.97		
0.010	2.534	4.073	4.052	4.558	5.469	6.747	7.845	8.91	9.76		
0.020	5.030	8.050	8.020	9.010	10.80	13.30	15.44	17.4	19.1		
0.050	12.43	19.70	19.63	22.07	26.37	32.38	37.43	42.15	45.8		
0.070	17.30		27.21	30.62	36.53	44.77	51.64	58.1	62.9		33.7
0.080										73.9	36.2
0.100	24.53	38.60	38.42	43.26	51.47	63.06	72.70	81.5	87.8		
0.200	48.26	75.22	74.88	83.80							
0.500		178.3	178.3								
0.700			242.9								
1.000		329.8	333.2								

Note: Calculated from data given in Table B.2.

Table B.4. Conductivity of concentrated and dilute aqueous nitric acid solutions at 25°C

HNO_3 (Wt %)	Density (g/cc)	HNO_3 (*M*)	Conductivity (mS/cm)	Comments
0.0001	0.99708	1.582E-5	0.0068	[a]
0.0003	0.99708	4.747E-5	0.020	[a]
0.001	0.99709	1.582E-4	0.067	[a]
0.003	0.99710	4.747E-4	0.199	[a]
0.01	0.99713	1.582E-3	0.657	[a]
0.03	0.99724	4.747E-3	1.95	[a]
0.1	0.99761	1.583E-2	6.38	[a]
0.3	0.99868	4.754E-2	18.90	[a]
1.0	1.00241	0.1591	60.00	
3.0	1.01318	0.4823	172.00	
5.0	1.02408	0.8125	275.00	
10.0	1.05230	1.6698	498.00	
20.0	1.11230	3.5300	763.00	
30.0	1.17630	5.5997	861.00	
31.0	1.18290	5.8188	862.00	
40.0	1.24170	7.8813	820.00	
50.0	1.30430	10.3483	717.00	
75.0	1.42590	16.9696	340.00	
100.0	1.50400	23.8654	50.00	

Source: Data from ref. 11.

[a]Density values were obtained by the author from a linear interpolation between the density of pure water and the density of 1 wt % nitric acid solution.

Table B.5. Conductivity of dilute aqueous nitric acid solutions at 20°C

HNO_3 (*M*)	Conductivity (mS/cm)
0.079	28.4
0.159	56.1
0.240	84.7
0.320	108.0
0.401	138.0
0.483	160.0
0.565	184.0
0.648	213.0

Source: Data from ref. 5

Table B.6. Electrical conductivity of concentrated aqueous nitric acid solution at various temperatures

T (°C)	HNO_3 (*M*)	Conductivity (mS/cm)	Density (g/cc)	Experimental HNO_3 (*M*)
25.0	0.1000	37.60	0.99837	0.0973
60.0	0.1000	54.00	0.98957	0.1022
85.0	0.1000	64.55	0.97802	0.1009
25.0	0.2000	74.40	1.00210	0.2023
60.0	0.2000	105.50	0.99274	0.2038
85.0	0.2000	126.00	0.98064	0.2022
25.0	0.5000	172.00	1.01196	0.4921
60.0	0.5000	255.00	1.00166	0.5028
85.0	0.5000	295.50	0.99035	0.5160
25.0	1.0000	317.50	1.02767	0.9438
60.0	1.0000	440.00	1.01540	0.9808
85.0	1.0000	528.00	1.00573	1.0103
25.0	2.0000	560.00	1.06028	1.9806
60.0	2.0000	800.00	1.04818	2.0421
85.0	2.0000	925.00	1.03436	2.0600
25.0	3.0000	720.00	1.09330	3.0269
60.0	3.0000	1020.00	1.07637	3.0595
85.0	3.0000	1177.50	1.06581	3.1577
25.0	4.0000	812.50	1.12554	4.0150
60.0	4.0000	1145.00	1.10698	4.1097
85.0	4.0000	1332.50	1.09446	4.1235
25.0	5.0000	850.00	1.15684	5.0426
60.0	5.0000	1210.00	1.13672	5.1246
85.0	5.0000	1400.00	1.11838	5.1207
25.0	7.5000	835.00	1.22634	7.5209
60.0	7.5000	1205.00	1.18998	7.8107
85.0	7.5000	1415.00	1.17918	7.6733
25.0	9.0000	780.00	1.26458	9.0409
60.0	9.0000	1147.50	1.23509	9.1800
85.0	9.0000	1360.00	1.21349	9.0229

APPENDIX C
CONDUCTIVITY AND DENSITY OF AQUEOUS NITRIC ACID-URANIUM SOLUTIONS

Early data on the density of uranyl nitrate solution at 17°C are available in the International Critical Tables (ref. 13). Concentration was reported on the basis of anhydrous uranyl nitrate [$UO_2(NO_3)_2$]. In aqueous solution, the species probably exists in the form of uranyl nitrate hexahydrate (UNH); $UO_2(NO_3)_2 \cdot 6H_2O$. In keeping with the format of this report, the concentration is converted to grams of Uranium metal per liter, with the understanding that the uranium exists as part of the UNH complex. The data from the Critical Tables are summarized in Table C.1.

Data on the density of UNH-H_2O-HNO_3 solutions at 25°C are given in the Allied General Separations Plant Data Manual (ref. 14). The freezing point of the solution is also provided. These data are summarized in Table C.2. The same reference provides a chart for the estimation of the density at the boiling point for solutions containing 0 to 80 wt % uranyl nitrate and 0 to 60 wt % HNO_3. Because, in this work, the density will be used with conductivity measurements at temperatures substantially below the boiling point, that chart is not reproduced here.

A more recent study at the Oak Ridge National Laboratory (ref. 15), made to determine the feasibility of using density and electrical conductivity to infer both nitric acid and uranium concentration in aqueous solution, resulted in some good data covering a temperature range of 25 to 95°C, a uranium concentration range of 160 to 300 g/L, and an acid concentration range of 2 to 6 *M*. These data are summarized in Table C.3. The second and third columns of the table contain the nominal concentration of uranium and acid, respectively. The last two columns of the table give the concentration as measured for the particular sample at the temperature listed. The latter were therefore used in all correlations developed in this report.

Unfortunately, no data are available for the conductivity of uranyl nitrate solutions in the absence of nitric acid.

Table C.1. Density of uranyl nitrate solutions at 17°C

U concentration			
Wt %[a]	g/L[b]	s.g.[c]	ρ g/cm^3
2.80	17.33	1.0257	1.0244
5.73	36.33	1.0510	1.0497
10.92	72.70	1.1035	1.1021
14.26	97.11	1.1288	1.1274
16.96	118.95	1.1625	1.1611
20.05	144.95	1.1983	1.1968
25.58	194.44	1.2599	1.2584
29.77	237.93	1.3247	1.3231
34.88	293.33	1.3939	1.3922
37.85	326.43	1.4295	1.4277
39.73	351.61	1.4669	1.4651
43.11	395.44	1.5204	1.5185
44.02	405.67	1.5275	1.5256
47.94	467.25	1.6155	1.6135
49.92	497.12	1.6506	1.6486
52.04	537.45	1.7118	1.7097
53.91	568.53	1.7480	1.7458
54.77	579.45	1.7536	1.7514

[a]Wt % of anhydrous $UO_2(NO_3)_2$, from ref. 13.
[b]Equivalent concentration of U as metal.
[c]Specific gravity with respect to water at 17°C, also from ref. 13.

Table C.2. Density and freezing point data for UNH-H_2O-HNO_3 systems at 25°C

Density (g/cc)	UNH (g/L)	U (g/L)	HNO_3 (*M*)	Freezing point (°C)
1.8707	1317.4	624.46	1.0	33.8[a]
1.8481	1285.0	609.11	0.8	32.5[a]
1.8733	1461.2	692.63	0.0	32.5[a]
1.7658	1215.4	576.12	0.0	18.3
1.7680	1217.1	576.92	0.0	16.3
1.6988	1110.1	526.20	0.0	5.7
1.7491	1130.1	535.68	0.77	19.8
1.2357	369.48	175.14	0.0	-5.0
1.2659	367.97	174.42	0.92	-11.3
1.0669	107.85	51.122	0.0	-1.0
1.0994	107.2	50.81	0.99	-5.2
1.2579	107.54	50.975	2.81	-16.5
1.3287	393.6	186.57	2.84	-26.1
1.7644	1101.8	522.27	2.74	33.5[a]
1.8956	1351.6	640.68	2.23	44.5[a]
1.0758	107.52	50.966	0.29	-2.2
1.1493	370.5	175.6	0.28	-6.5
1.7092	1107.7	525.06	0.28	11.0
1.7903	1249.7	592.37	0.29	23.5
1.5789	912.26	432.42	0.0	-20.0
1.5477	849.84	402.84	0.24	-20.7
1.4699	689.04	326.61	0.96	-21.1
1.5317	693.69	328.82	3.04	1.6
1.3862	461.09	218.56	2.99	-22.5
1.5628	828.09	392.53	0.79	[b]
1.5621	806.2	382.2	1.05	-13.3

Source: Data from ref. 14.
[a]Determined at freezing point.
[b]Not determined.

Table C.3. Electrical conductivity and density of aqueous nitric acid-uranium solutions

T °C	U (g/L)	HNO_3 (*M*)	Conductivity (mS/cm)	Density (g/cc)	Experimental U (g/L)	Experimental HNO_3 (*M*)
25.0	160.01	2.0180	422.50	1.27700	160.83	1.9900
25.0	160.01	2.0180	422.50	1.27650	160.28	2.0100
25.0	160.01	4.0590	575.00	1.34030	160.50	3.9900
25.0	160.01	4.0590	575.00	1.33860	160.21	4.1700
25.0	160.01	6.0210	610.00	1.39570	160.80	6.0000
25.0	160.01	6.0210	615.00	1.39360	160.36	6.3000
25.0	231.12	2.3520	390.00	1.38230	232.59	2.3500
25.0	231.12	2.3520	392.50	1.38110	231.66	2.3800
25.0	231.12	4.0180	492.50	1.42990	231.60	4.0000
25.0	231.12	4.0180	495.00	1.42950	231.80	3.9500
25.0	231.12	6.1390	530.00	1.48970	233.76	6.0900
25.0	231.12	6.1390	525.00	1.48770	233.04	6.0400
25.0	300.05	2.0240	312.50	1.46410	300.89	2.0200
25.0	300.05	2.0240	312.50	1.46250	301.24	2.0000
25.0	300.05	3.9940	420.00	1.52050	301.74	3.8900
25.0	300.05	3.9940	420.00	1.51840	301.38	3.9400
25.0	300.05	5.6600	452.50	1.56490	303.80	5.6400
25.0	300.05	5.6600	450.00	1.56450	301.42	5.6300
60.0	160.01	2.0180	610.00	1.25690	158.03	1.9700
60.0	160.01	2.0180	610.00	1.25720	158.32	1.9800
60.0	160.01	4.0590	835.00	1.31480	157.30	4.1200
60.0	160.01	4.0590	840.00	1.31490	158.61	4.1500
60.0	160.01	6.0210	895.00	1.36320	157.35	6.0200
60.0	160.01	6.0210	900.00	1.36270	156.76	6.0400
60.0	231.12	2.3520	585.00	1.35760	227.68	2.3200
60.0	231.12	2.3520	580.00	1.35830	227.79	2.3300
60.0	231.12	4.0180	725.00	1.40580	227.15	3.9000
60.0	231.12	4.0180	735.00	1.40400	227.32	3.9500
60.0	231.12	6.1390	785.00	1.45690	226.34	5.9600
60.0	231.12	6.1390	790.00	1.45490	226.80	5.9300
60.0	300.05	2.0240	475.00	1.43970	295.84	2.0000
60.0	300.05	2.0240	477.50	1.44000	295.93	2.0300
60.0	300.05	3.9940	635.00	1.48700	294.82	3.8200
60.0	300.05	3.9940	635.00	1.48990	294.12	3.9200
60.0	300.05	5.6600	685.00	1.53200	294.24	5.5300
60.0	300.05	5.6600	685.00	1.52810	296.38	5.5200
95.0	160.01	2.0180	770.00	1.23510	157.10	1.9600
95.0	160.01	2.0180	765.00	1.23530	157.57	1.9400
95.0	160.01	4.0590	1035.00	1.28710	155.99	4.0600
95.0	160.01	4.0590	1040.00	1.29120	157.19	4.0700
95.0	160.01	6.0210	1120.00	1.33530	155.65	5.7300
95.0	160.01	6.0210	1115.00	1.33530	155.41	5.9600
95.0	231.12	2.3520	735.00	1.33860	226.78	2.2800
95.0	231.12	2.3520	745.00	1.33430	226.88	2.2600
95.0	231.12	4.0180	915.00	1.37430	224.90	3.8200
95.0	231.12	4.0180	920.00	1.37820	225.79	3.8200
95.0	231.12	6.1390	995.00	1.42550	222.86	5.8800

Table C.3. (continued)

T °C	U (g/L)	HNO_3 (*M*)	Conductivity (mS/cm)	Density (g/cc)	Experimental U (g/L)	Experimental HNO_3 (*M*)
95.0	231.12	6.1390	1000.00	1.42240	224.52	5.8200
95.0	300.05	2.0240	605.00	1.41510	294.44	1.9700
95.0	300.05	2.0240	610.00	1.41390	293.13	1.9800
95.0	300.05	3.9940	810.00	1.46060	292.14	3.8100
95.0	300.05	3.9940	815.00	1.46150	291.86	3.8600
95.0	300.05	5.6600	875.00	1.49850	290.98	5.3800
95.0	300.05	5.6600	875.00	1.49230	288.99	5.3500
35.0	264.91	4.8500	552.50	1.49270	266.07	4.8100
50.0	197.83	3.1400	657.50	1.34780	198.18	3.1700
75.0	187.99	4.9600	940.00	1.36910	188.57	4.9600
90.0	255.52	3.0300	785.00	1.39720	256.01	3.0600

Source: Data from ref. 15.

ORNL/TM-11365
Dist. Category UC-526T
(Applied)

INTERNAL DISTRIBUTION

1. D. E. Benker
2. J. F. Birdwell
3. D. A. Bostic
4. W. D. Burch
5. D. O. Campbell
6. J. L. Collins
7. M. H. Ehinger
8. R. E. Eversole
9. R. W. Glass
10. W. S. Groenier
11. W. R. Hamel
12. M. J. Haire
13. J. E. Hardy
14-16. T. Ichimura
17. R. T. Jubin
18. M. V. Keigan
19. L. N. Klatt
20. E. H. Krieg, Jr.
21. C. T. Kring
22. B. E. Lewis
23. J. C. Mailen
24-26. S. A. Meacham
27. D. R. Moser
28. R. E. Norman
29. K. E. Plummer
30. S. L. Schrock
31. J. H. Shaffer
32. B. H. Singletary
33. G. R. Smolen
34. J. W. Snider
35-39. B. B. Spencer
40-41. J. G. Stradley
42. H. R. Yook
43. Laboratory Records
44-45. Laboratory Records,
46. ORNL-RC
47-48. RPSD Publications Office
49. ORNL Patent Section
50. Central Research Library
51. Document Reference Section

EXTERNAL DISTRIBUTION

52. D. E. Bailey, Director, Division of Fuels and Reprocessing, Office of Facilities, Fuel Cycle, and Test Programs, NE-471, Department of Energy, Washington, D.C. 20545.
53. F. P. Baranowski, 657 Fairfax Way, Williamsburg, VA 23185.
54. J. E. Dunn, Jr., ORNL/CFRP On-Site Representative, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.
55. H. Kashihara, Director, Nuclear Fuel Cycle Development Division, Power Reactor and Nuclear Fuel Development Corporation, 9-13, 1-Chome, Akasaka, Minato-ku, Tokyo, Japan.
56. T. Kawata, Technical Coordinator, USDOE/PNC Collaboration Program, General Manager, Components and Material Development Section, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.
57. Y. Kishimoto, Director, Technology Development Coordination Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.

58. T. Matsumoto, Technical Correspondent, Design Optimization of Facility, USDOE/PNC Collaboration Program, Senior Staff, Engineering and Design Section, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.
59. W. H. McVey, Manager, LMR Reprocessing Projects, Division of Fuels and Reprocessing, Office of Facilities, Fuel Cycle, and Test Programs, NE-471, Department of Energy, Washington, D.C. 20545.
60. M. J. Ohanian, Associate Dean for Research, College of Engineering, 300 Weil Hall, University of Florida, Gainesville, FL 32611.
61. M. Ozawa, Technical Correspondent, Chemical Process Technology, USDOE/PNC Collaboration Program, Components and Material Development Section, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.
62. M. J. Rohr, Branch Chief, Fusion and Nuclear Technology Branch, Energy Programs Division, Department of Energy, P.O. Box 2008, Oak Ridge, TN 37831-6269.
63. J. H. Saling, ORNL/CFRP On-Site Representative, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.
64. J. L. Scott, USDOE Representative, Power Reactor and Nuclear Fuel Development Corporation, 9-13, 1-Chome, Akasaka, Minato-ku, Tokyo, Japan.
65. H. Takeda, Technical Correspondent, Continuous Head-End Process Technology, USDOE/PNC Collaboration Program, General Manager, Engineering and Design Section, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.

66-75. Y. Tanaka, Deputy General Manager, Reprocessing Technology Development Section, Nuclear Fuel Cycle Development Division, Power Reactor and Nuclear Fuel Development Corporation, 9-13, 1-Chome, Akasaka, Minato-ku, Tokyo, Japan.

76. T. Yagi, Director, Power Reactor and Nuclear Fuel Development Corporation, Washington Office, Suite 715, 2600 Virginia Avenue, N.W., Washington, D.C. 20037.

77-78. T. Yamaguchi, General Manager, International Cooperation Office, Power Reactor and Nuclear Fuel Development Corporation, 9-13, 1-Chome, Akasaka, Minato-ku, Tokyo, Japan.

79. R. Yamamoto, Technical Correspondent, Advanced Remote Technology, USDOE/PNC Collaboration Program, Manager, Remote Maintenance Development Group, Components and Material Development Section, Reprocessing Technology Development Division, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan Post No. 319-11.
80. Office of Assistant Manager for Energy Research and Development, Oak Ridge Operations Office, Department of Energy, P.O. Box 2001, Oak Ridge, TN 37831.

81-122. Given distribution as shown in DOE/OSTI-4500 under UC-526T, Consolidated Fuel Reprocessing Category.