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PROGRESS REPORT NO. 11

CONTROL INDICES AND ANALYTICAL PROCEDURES

By

PHILIP J. ELVING

ANNA GRIFFIN

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SUMMARY

The present work covers work done since Progress Report No. 8, September, 1953, on one phase of the assigned objectives as described under "Control Index Studies. I. Determination of the Relationship of Specific Gravity to Zirconium Concentration." Specifically, tabular and graphical data are presented for the densities at 25, 40, and 60°C of samples of originally 7.4, 8, and 9M hydrofluoric acid solutions, to which have been added varying amounts of zirconium to give zirconium concentrations varying from 0.00 to 1.50M by increments of 0.25 or 0.50. Data were not obtained at 80°C due to the difficulty of obtaining satisfactory measurements.

Data for all concentrations of zirconium over the complete temperature range are not available for every hydrofluoric acid concentration, but sufficient information is now available to set up a system of control based on density measurement. Since a change in zirconium concentration of 0.0008 molar unit corresponds to 0.0001 density unit, a density-indicating device accurate to ±0.0002 density unit will permit the estimation of zirconium content with a probable maximum error of 0.0016 molarity in the range of 0 to 1.5M or higher zirconium concentration for a given original hydrofluoric acid concentration.

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SUMMARY OF RESULTS

CONTROL INDEX STUDIES. I. DETERMINATION OF THE RELATIONSHIP

OF DENSITY TO ZIRCONIUM CONCENTRATION

A. Objective and Implementation

Objective. The objective of the present study is to supplement and extend data given in Progress Report No. 8, September, 1953, on the relation-ship between density and zirconium concentration in hydrofluoric acid solu-tions at various temperatures. The results are presented graphically with density as a function of zirconium concentration. The ultimate objective of the work is its possible usefulness as the basis for a control method for de-termining the composition of zirconium- hydrofluoric acid solutions. The specific concentrations and temperatures for which data were obtained were determined on the basis of discussion with Mr. William L. Ginkel of the Idaho Operations Office of the Atomic Energy Commission on November 18, 1953, and a letter dated December 23, 1953, from Mr. J. Bion Philipson of the same office.

Preliminary Work. Much of the detail of the experimental procedure has been explained in Progress Report No. 1, June, 1953, which covers the de-termination of the relationship of stainless-steel concentration in sulfuirc acid solution using the specific-gravity balance and in Progress Report No. 2, August, 1953, which includes a complete description of the measurement of density by a direct weighing method using an analytical balance. The possi-ble errors inherent in the method for determining densities by the specific-gravity balance, which led to the direct weighing method, are discussed in Progress Report No. 2.

Data relating concentration and densities determined by both meth-ods at various temperatures, of a considerable range of zirconium- hydro-fluoric acid solutions are presented in tables and graphs in Progress Report

No. 8. Errors introduced by the adherence of gas bubbles to the surface of the polyethylene plummet are also discussed in the latter report. In general, the present report should be read in conjunction with Progress Report No. 8.

B. Experimental Procedure

Preparation of Hydrofluoric Acid Solutions. The solutions in originally 7.4 and 8M hydrofluoric acid were those for which some data were presented in Progress Report No. 8; fresh solutions were prepared of the zirconium in 9M hydrofluoric acid. Polyethylene containers were used for preparation and storage of the solutions. The molarity of the hydrofluoric acid itself was determined to three decimal places (total of four significant figures) by reference to a table and graph relating molarity and density which were compiled after discrepancies were noted in available tables (for complete details see Progress Report No. 3, August, 1953).

The solution of 1.75M zirconium in originally 7.4M hydrofluoric acid produced a voluminous white precipitate on standing, which largely, but not completely, disappeared on heating the solution. This solution could therefore not be measured; lack of time, as well as lack of prepared 7.4M acid and satisfactory zirconium, prevented preparation of a new solution of this composition.

Zirconium Samples. The zirconium was supplied during the summer of 1953 by the resident representative of the American Cyanamid Company. Sample sizes used were 1/4 by 1/4 by 1/2 inch, 1/8 by 1/8 by 1/2 inch, 1/8-inch cubes, and shavings. Rough edges and adhering material left by the bandsaw used in preparing the material were removed with wire cutters and an abrasive stone. The pieces were then cleaned with acetone and dried. Further details on preparation of the zirconium are given on pages 2 and 3 of Progress Report No. 8.

Dissolution of the Zirconium. The hydrofluoric acid solutions were weighed out in 200-ml portions into polyethylene bottles on a Harvard trip balance. Loosely fitting polyethylene stoppers were used to allow the hydrogen evolved on adding the zirconium to escape without mechanical loss of solution. The bottles and their contents were cooled in a dry-ice- acetone bath. Even with the 9M acid the rate of dissolution could thus be controlled when two-thirds of the acid was kept in the solid state while the first 7 grams of zirconium were added in pieces of 1 gram or less at a time. For a more detailed description and an illustration of the arrangement for the dissolution process, reference can be made to pages 3, 4, and 5 of Progress Report No. 8.

Constant-Temperature System. This system is described in Progress Report No. 1, June, 1953.

Measurements of Density Using the Analytical Balance. This method
is explained in detail in Progress Report No. 2.

Density measurements were made in the same polyethylene bottles in
which the solutions were prepared in order to avoid solution loss in trans-
fer. The polyethylene bottles were kept at constant temperature in the sam-
ple bath described in Progress Report No. 1. The water line supplying the
sample bath was tapped to give a continuous supply of constant-temperature
water for the copper "condenser" which fitted on the top of the bottle (Fig.
1 of Progress Report No. 8). In this way the temperature of the solution re-
mained at its proper value; the use of cold water in the condenser permitted
the temperature to fall below that desired. A split polyethylene plug with a
1/8-inch hole through which the platinum wire passed was inserted in the bot-
tle opening to limit loss of solution due to evaporation. This arrangement
is illustrated on page 4 and a more detailed description is given on page 5
of Progress Report No. 8.

Since polyethylene does not wet readily and the polyethylene plum-
met is not perfectly smooth, the collection and adherence of gas bubbles to
it, especially at the higher temperatures of 60 and 80°C, presented a signif-
icant source of error. Heating the sample solutions to remove dissolved
gases would probably change their composition. A slight modification in the
temperature equilibration procedure was made in an effort to minimize this
source of error. The zirconium -hydrofluoric acid solutions and the plummet
were preheated to temperatures higher than those at which measurements were
made; the solution was then agitated to remove gas bubbles formed during
heating. The subsequent cooling of the solution and plummet would tend to
result in dissolution of gas bubbles present at the plummet surface due to
the increase of gas solubility in the solution with decrease in temperature.

Each sample was heated to a temperature 15°C higher than the tem-
perature at which its density was to be measured. After stirring it was
placed in the sample bath and allowed to cool to bath temperature before the
plummet was introduced.

For measurements at 25°C the plummet was preheated in water at 45°C
and then allowed to cool to about 35°C. At 35°C the plummet was removed,
dried with warm acetone, waved several times in air to permit the acetone to
evaporate, and immediately placed in the sample solution.

For 40°C measurements the plummet was preheated to 65°C, allowed to
cool to 55°C, dried with hot acetone, waved, and immediately placed in the
sample solution.

For 60°C measurements the plummet was preheated to about 70°C in
water, allowed to cool to 65°C, dried with hot acetone, waved, and placed in
the sample solution. When the plummet was preheated to temperatures between

80 and 85°C, in boiled distilled water, the readings obtained were inconsistent with each other and with those obtained when the plummet was preheated to only 70°C; consistent readings were obtained when the plummet was preheated to 70°C.

The balance reading for a 1.5M zirconium solution, originally 7.4M in hydrofluoric acid, dropped at 80°C from 18.8930 to 18.8156 over a period of two hours without reaching an apparent levelling-off point. When inconsistent results were still obtainend at 80°C on preboiled distilled water after contact between the solution and plummet for three hours, which included intermittent stirring, the measurements at 80°C were discontinued.

The method suggested in Progress Report No. 8 of starting at 90°C and allowing the solution to drop to 80, 60, 40, and 25°C was not followed due to the longer time required to reach equilibrium at the higher temperatures and the possibility of change in the composition of the solutions due to evaporation.

The possible errors of density measurement at various temperatures due to the gas-bubble effect were roughly estimated in Progress Report No. 8 (page 6) as being 0.4 part per 1000 at 25°C, 1 part at 40°C, 2 parts at 60°C, and 25 parts at 80°C. The present measurements at 25, 40, and 60°C are believed to be safely within these limits of error.

Improvement of the Plummet. The fabrication of a plummet from a material more readily wetted by hydrofluoric acid solutions was discussed on page 13 of Progress Report No. 8. In this respect, note should be made of the availability of data and directions for rhodium plating from Baker and Company, Inc., 113 Astor Street, Newark 5, New Jersey.

Use of a plummet method for density measurement in process control would necessitate a properly wetted plummet.

C. Calculation and Treatment of Data

The methods of handling the experimental data are described in detail in Progress Reports Nos. 1 and 2. The latter report contains corrections on the methods of calculation given in the former report.

D. Data Obtained and Interpretation

The data, which were all obtained by the analytical balance method, are given in Tables I, II, and III, and are presented graphically in Figs. 1, 2, and 3.

TABLE I

DENSITIES OF SOLUTIONS OF ZIRCONIUM
ORIGINALLY IN 7.358M HYDROFLUORIC ACID AT VARIOUS TEMPERATURES
(Determined Using Analytical Balance)

| Concentration of Zirconium, moles/liter	Density, gm/cc		
	at 25°C	at 40°C	at 60°C
0.00	1.0437	1.0347	1.0213
0.25	1.0712	1.0615	1.0484
0.50	1.0983	1.0904	1.0780
0.75	1.1277	1.1196	1.1080
1.00	1.1577	1.1498	1.1383
1.25	1.1940	1.1858	1.1739
1.50	1.2360	1.2270	1.2141

TABLE II

DENSITIES OF SOLUTIONS OF ZIRCONIUM
ORIGINALLY IN 8.074M HYDROFLUORIC ACID AT VARIOUS TEMPERATURES
(Determined Using Analytical Balance)

Concentration of Zirconium, moles/liter	Density, gm/cc		
	at 25°C	at 40°C	at 60°C
0.00	1.0478	1.0389	1.0247
0.50	1.1003	1.0914	1.0789
1.00	1.1648	1.1567	1.1451
1.50	1.2344	1.2255	1.2139

TABLE III

DENSITIES OF SOLUTIONS OF ZIRCONIUM
ORIGINALLY IN 9.015M HYDROFLUORIC ACID AT 25 AND 40°C
(Determined Using Analytical Balance)

Concentration of Zirconium, moles/liter	Density, gm/cc	
	at 25°C	at 40°C
0.00	1.0536	1.0439
0.50	1.1087	1.0989
1.00	1.1660	1.1571
1.50	1.2328	1.2238

FIG I. DENSITIES OF SOLUTIONS OF ZIRCONIUM IN 7.358 M
HYDROFLUORIC ACID (DATA TAKEN FROM TABLE I)
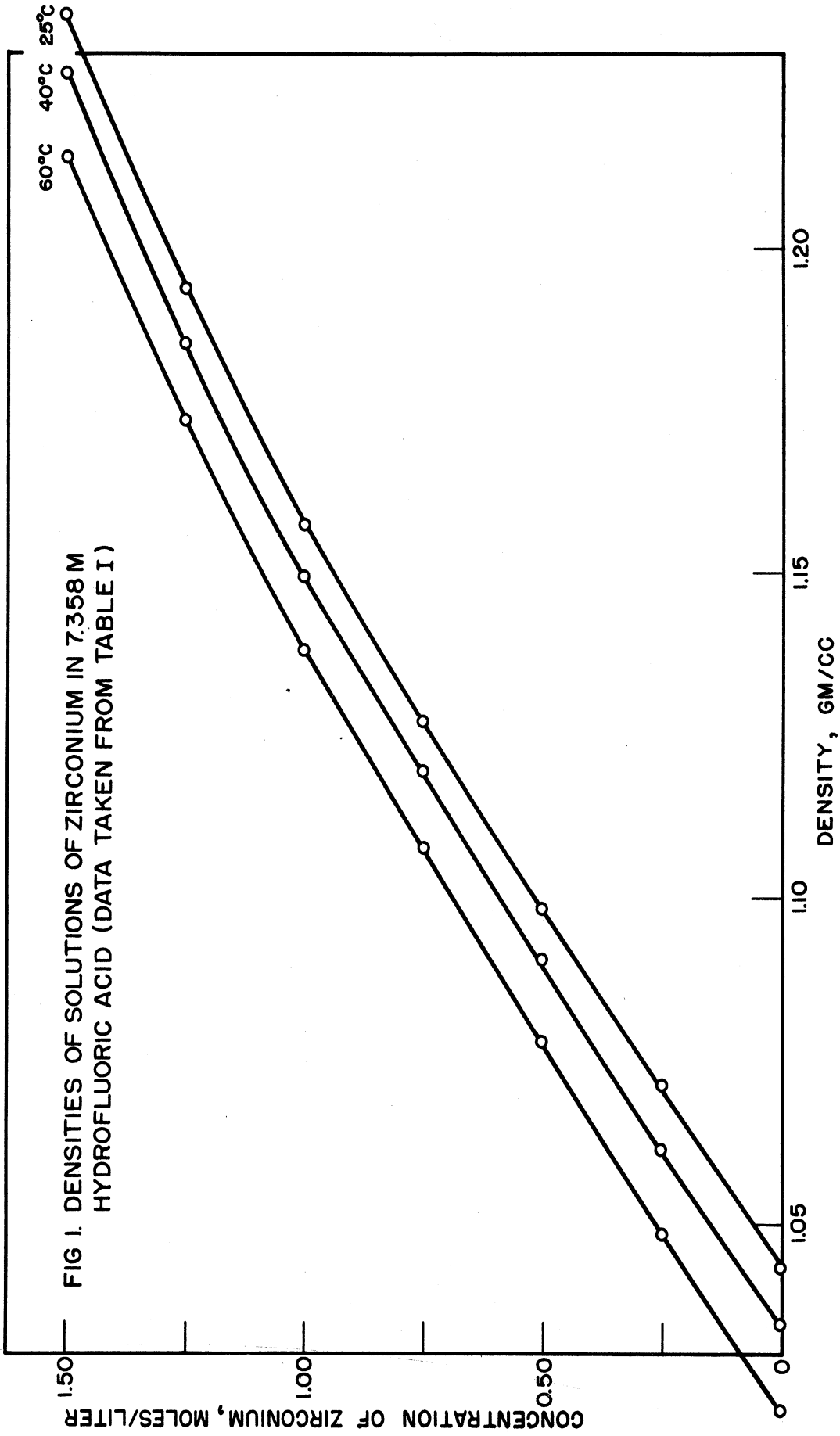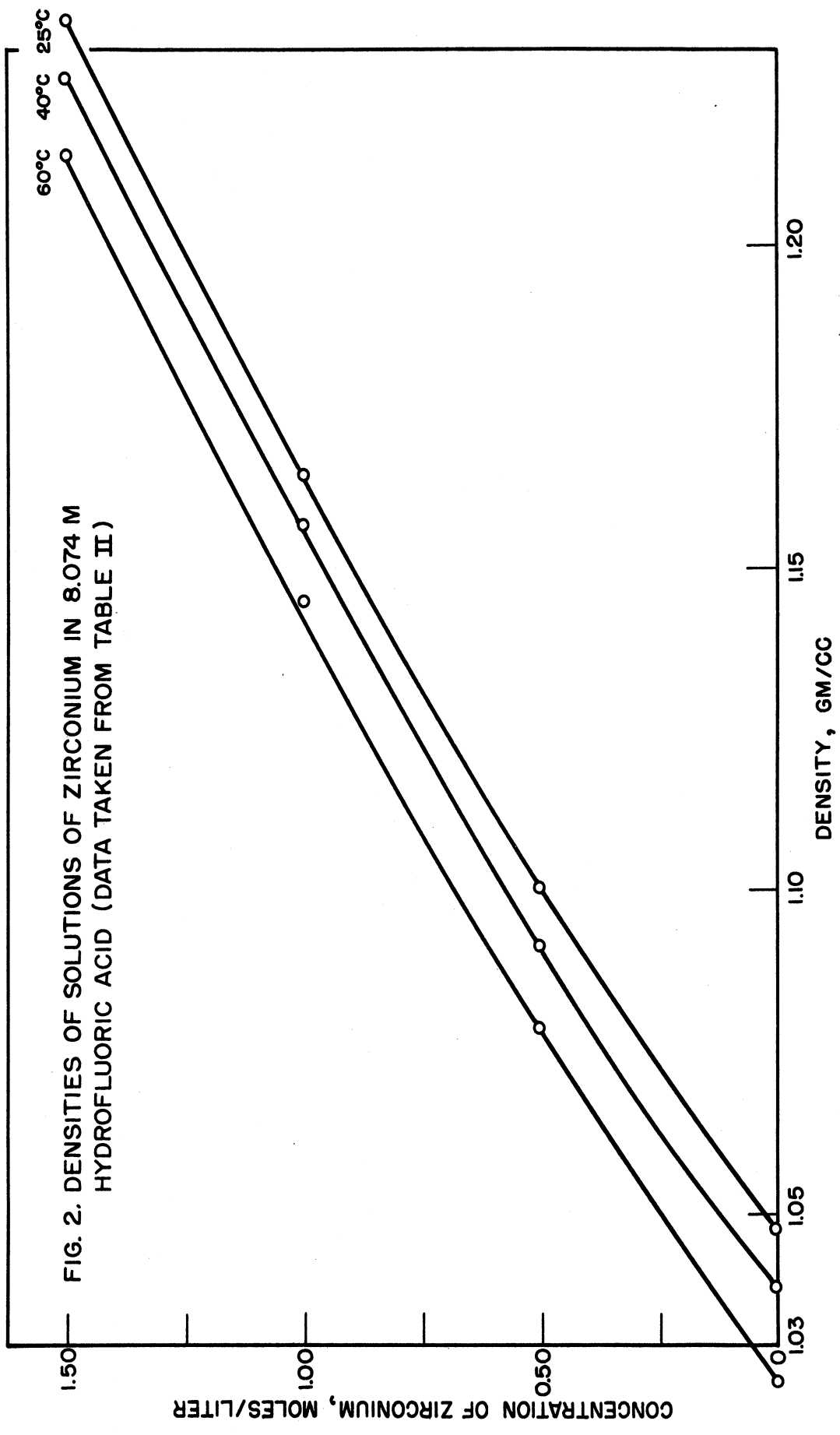
FIG. 2. DENSITIES OF SOLUTIONS OF ZIRCONIUM IN 8.074 M
HYDROFLUORIC ACID (DATA TAKEN FROM TABLE II)

FIG. 3. DENSITIES OF SOLUTIONS OF ZIRCONIUM IN 9.015 M HYDROFLUORIC ACID (DATA TAKEN FROM TABLE III)
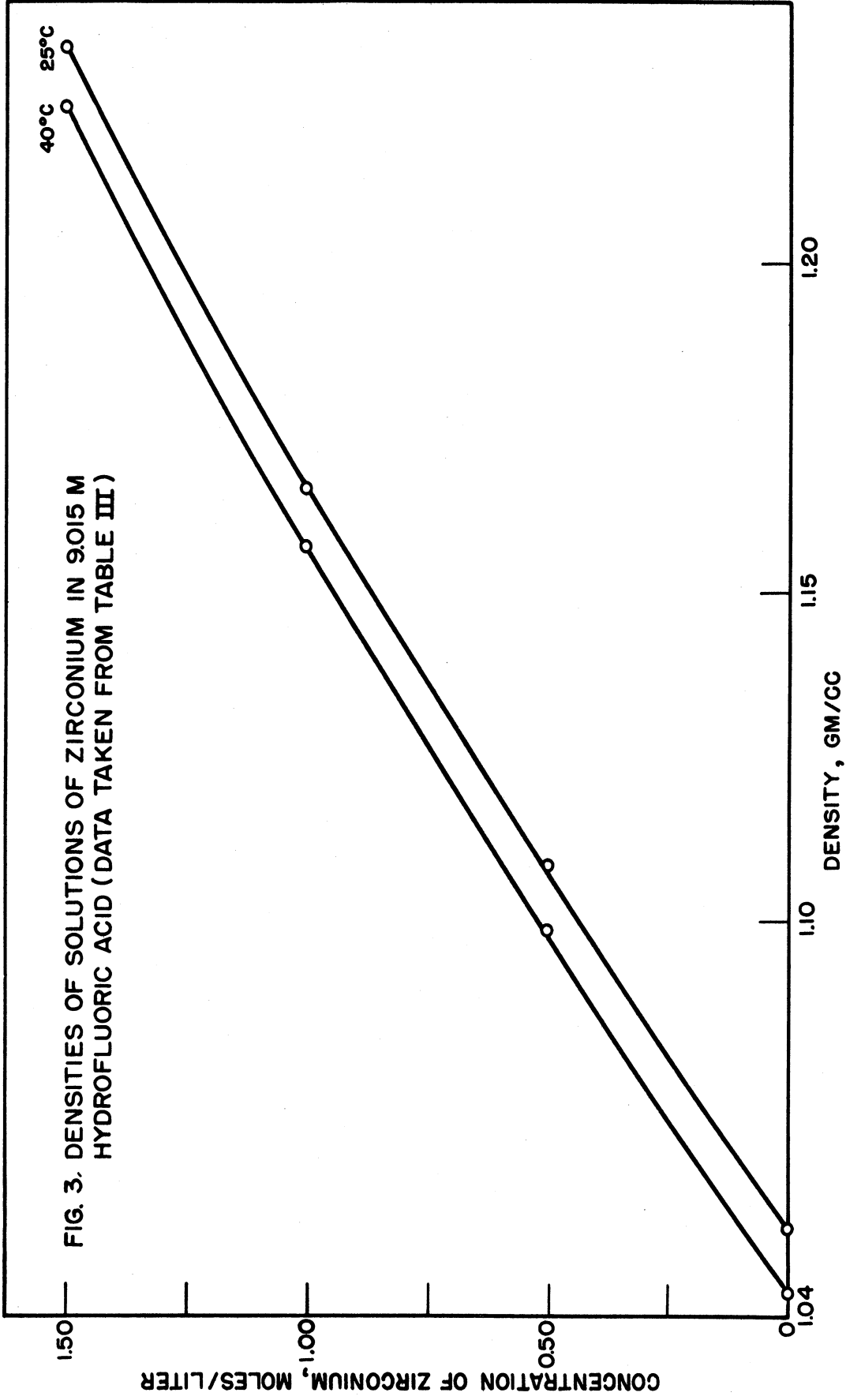
The solutions of originally 7.4 and 8M hydrofluoric acid, whose densities are given in Tables I and II, are the same as those for which data are presented in Tables IVC and VC of Progress Report No. 8. Densities were remeasured at 25°C in order to note any significant changes that might have occurred after standing for four months. The results obtained were very close to those previously found, indicating no significant changes. Densities at 40 and 60°C appear for the first time.

Densities at 25 and 40°C of samples of originally 9M hydrofluoric acid solutions to which have been added various weights of zirconium, are presented in Table III.

Although precautions were taken to minimize the error due to gas bubbles, the validity of data at 60°C should still be considered as open to some doubt (see the previous discussion of possible magnitude of this source of error).

Equation Derived from the Data. In Progress Report No. 1, it was pointed out that the straight-line relation between specific gravity or density and the dissolved steel concentration for each particular original acid concentration and temperature permitted the derivation of simple linear equations involving a constant characteristic of the experimental conditions. An attempt was made to obtain similar equations of the following for the data of Figs. 1, 2, and 3:

$$D \text{ of Soln} = D \text{ of Acid} + K (Zr \text{ concn}) ,$$

where

D of Soln = density of the solution at the temperature of measurement,

D of Acid = density at the temperature of measurement of the original acid solution before any zirconium was dissolved in it,

K = constant characteristic of the original acid concentration and of the temperature of measurement, and

Zr concn = concentration of dissolved zirconium in moles per liter of original acid solution.

The values of K given in Table IV are calculated by such an equation for each set of experimental conditions. The error introduced by using an average value for K can be readily approximated for any concentration range. Extrapolation of these K values will permit the use of measurements made at temperatures and original concentrations of hydrofluoric acid other than those specified in the present report.

TABLE IV

DENSITIES AND EQUATION CONSTANTS
FOR VARIOUS INITIAL ACID CONCENTRATIONS AND TEMPERATURES

Original HF Concn.,M	Temp., °C	D of Acid	Values of K for Various Zirconium Molarities					
			0.25	0.50	0.75	1.00	1.25	1.50
4.981	25*	1.0280		0.1104		0.1244		
6.019	25*	1.0345		0.1098		0.1175	0.1265	
7.075	25*	1.0411	0.1072		0.1112		0.1208	0.1279
7.358	25*	1.0437	0.1088	0.1100	0.1117	0.1138	0.1192	0.1276
	25	1.0437	.0.1100	0.1092	0.1120	0.1140	0.1202	0.1282
	40	1.0347	0.1072	0.1114	0.1121	0.1151	0.1209	0.1282
	60	1.0213	0.1084	0.1134	0.1156	0.1170	0.1221	0.1285
8.074	25*	1.0477		0.1050		0.1168		0.1238
	25	1.0478		0.1050		0.1170		0.1244
	40	1.0389		0.1050		0.1178		0.1244
	60	1.0247		0.1084		0.1204		0.1261
9.015	25	1.0536		0.1102		0.1124		0.1195
	40	1.0439		0.1100		0.1132		0.1199

Note: The data in this table were obtained by the analytical balance method; data marked by an asterisk opposite the temperature is taken from Progress Report No. 8 (Tables IC to VC).

The deviations from straight lines of the data of Tables I, II, and III as plotted in Figs. 1, 2, and 3 are readily seen from the individual calculated values of K (Table IV). The "bowed" nature of the relation between density and zirconium concentration may be due to a variety of effects, e.g., the lowering of the hydrogen fluoride concentration as the zirconium concentration is increased, the presence of complex zirconium fluoride species, etc.

Possible Precision of Control. The average ranges of density change from 0.0 to 1.5M zirconium concentration are about 0.192, 0.193, 0.187, and 0.180 for the originally 5, 6, 7, 7.4, 8, and 9M hydrofluoric acid solutions. A change in zirconium concentration of 0.0008 molar unit accordingly corresponds to 0.0001 density unit. Consequently, use of a density-measuring device accurate to ±0.0002 density unit, which is the probable error of an individual reading on a good density-measuring device, will permit estimation of the zirconium concentration for a given original hydrofluoric acid concentration with a probable maximum error of 0.0016 molar unit.

Coefficients of Cubical Expansion. The temperature coefficients of temperature change for the zirconium - hydrofluoric acid solutions described in this report and in Progress Report No. 8 have not been evaluated due to lack of time. The coefficients can be readily calculated; the necessary procedure is indicated in detail on pages 20 to 22 of Progress Report No. 1.