Conductivity of Hydrofluoric Acid Solutions and the Effect of the Impurities, Sulfurous and Hydrofluosilicic Acids

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IN THE MANUFACTURE of uranium tetrafluoride, uranium dioxide is converted to the fluoride by hydrofluoric acid. The excess acid is drawn off and made a part of a recovery system. The acid of 20 to 25% concentration is pumped to Karbate condensers and thence to distillation pots, where it is concentrated to the azeotrope (38% acid). At present, platinum electrodes are installed in various parts of the system to measure the acid concentration. These electrodes are troublesome because corrosion products cause errors of as much as 5% in the readings. A more accurate knowledge of the acid concentration could result in better operation of the uranium tetrafluoride salt production. An electrodeless instrument has recently been developed and its substitution would undoubtedly eliminate the shortcomings of the platinum electrodes.

Hill and Sirkar (*2*) determined the conductivity of hydrofluoric acid solutions and found a linear relation to exist up to 60% acid. Beyond this point the conductivity increase is not linear and the slope changes abruptly at 75% with the conductively approaching zero at 100% acid. Hill and Sirkar maintain that at concentrations below 7.7% HF the temperature coefficient is practically constant and equal to 12.5×10^{-3}. Because the Hill and Sirkar (*2*) data and the Mooney (*4, 5*) compilations are incomplete, conductivity data were obtained in the laboratory under conditions simulating those existing in special locations in the plant.

The principle of operation of the electrodeless conductivity system (Industrial Instruments, Inc., Type RS) is that the liquid to be measured is constrained in a closed loop. Nonmagnetic and nonconductive piping must be used for the loop or pipe, and two single-winding toroidal coils are mounted on the piping. One coil is connected to the transmitting unit, which supplies a source of stable voltage in a high audiofrequency range. The second is connected to the receiving unit, which is a sensitive device for measuring the output voltage from this winding.

Before the electrodeless instrument could be designed, laboratory data with platinum electrodes under conditions simulating those existing in plant practice were necessary, especially at locations where the acid concentration was to be determined. It is claimed that an electrodeless instrument can be designed to duplicate the laboratory data. One location at an HF plant had the following conditions: Reactor offgas condensate, acid concentration 10 to 50% HF, temperature 100° to 200° F. Impurities, intermittently entrained UF_4, solid corrosion products of Monel and silver piping, small amounts of entrained noncondensables, sulfur as H_2S and or H_2SO_3, about 400 p.p.m. of sulfur, silicon about 1000 p.p.m. probably as H_2SiF_6.

Other locations may have different temperatures and impurity concentrations from those mentioned.

The maximum pressure expected at any point in the system is 6 p.s.i.g. at the feed line sampling point; in the other parts, not higher than 1 p.s.i.g.

APPARATUS AND MATERIAL

Platinum electrode in epoxy resin. Cell constant 50. Cell, grade A nickel (Ni 99+%), 4⅞ inches high, 2 inches in diameter, and 122-ml. capacity.

Platinum electrode in epoxy resin. Cell constant 30. Cell, grade A nickel (Ni 99+%), 6½ inches long, 2 inches in outside diameter, and 0.100 inch in wall thickness. Threaded cap with threaded hole in center for electrode. Capacity 195 ml.

HF, aqueous, Baker's analyzed reagent, 49%.

Hydrofluosilicic acid, H_2SiF_6. Baker's analyzed, assay 31% H_2SiF_6.

The conductivity bridge (Model R C 1B, Industrial Instruments, Inc.) is simply a Wheatstone bridge arrangement with an electron ray eye null indicator for noting when the bridge is in balance. The electronic indicating device replaces the delicate galvanometer usually associated with bridge measurements and provides adequate sensitivity for all adjustments. The bridge current is of 1000 cps., which makes for a sharper shadow image in the null indicator eye than the ordinary current line frequency.

EXPERIMENTAL PROCEDURE

The conductivity data were obtained by means of a platinum electrode which simply measures with a conductivity bridge the resistance of the solution between two metal plates serving as electrodes. The procedure followed was to measure the requisite amount of HF into the nickel cell by using a plastic buret. The distilled water for dilution to the proper concentration was measured in a glass buret. The impurity addition as hydrofluosilicic acid was measured in a plastic buret and the sulfurous acid in a glass pipet. A particular requirement for reproducible measurements was to ensure that the liquid in the cell was about ½ inch above the top hole in the electrode. The cell containing the well-mixed acid and electrode was placed in a constant temperature bath for a definite length of time predetermined for each temperature and readings were made on the bridge. The reading in ohms of resistance, divided by the cell constant, is the specific resistance, and the reciprocal is the specific conductance.

A series of conductivity measurements was made on solutions varying from 9 to 48% HF and at temperatures of 37.7° and 93.3° C. in the 122-ml. cell with the platinum electrode of 50 cell constant. The sequence of operations for one concentration of acid was to measure the plain acid solution, add 2.5 ml. of hydrofluosilicic and 1.7 ml. of sulfurous acids, place the cell in the water bath, and take another reading. Each concentration of acid was handled in this order.

The results of the measurements are shown graphically in Figures 1, 2, and 3. Figure 1 compares the conductivities at 37.8° and 93.3° C., replotted from the values found for the pure solutions from Figures 2 and 3. Figures 2 and 3 show the effect of added impurities on the specific conductivities at those temperatures. The added impurities, totaling 4.2 ml. of liquid, dilute the HF solution by 3.4%, so a correction was applied to HF concentrations containing the impurities. In Figure 4 is shown the effect of the impurity additions at 93.3° C. in the range 1 to 9% acid. The 25° C. diagram was included to note the small difference in the temperature coefficient with the 93.3° C. diagram in this acid range.

For the higher temperature measurements of 93.3° to 115° C. and 1 to 15% acid, simulating certain plant conditions, a closed pressure-tight cell was necessary. A larger cell of 195-ml. capacity was more convenient to accommodate the longer electrode of 30 cell constant. The results of these experiments are shown in Figure 7.

Preliminary experimentation had indicated that the conductance was lower at 115° C. As this was contrary to normal behavior, a series of test runs was made to verify

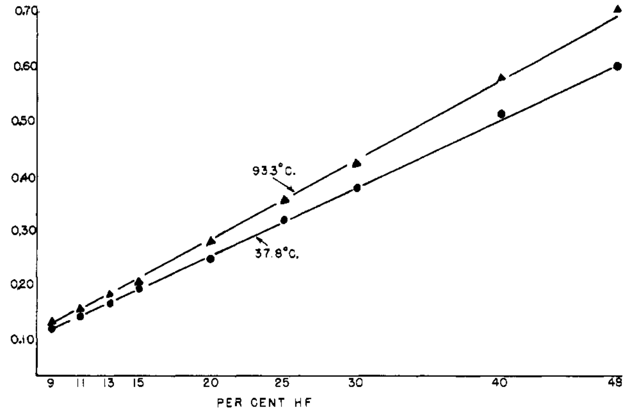

Figure 1. Conductivity of hydrofluoric acid solutions (9 to 48%) at 37.8° and 93.3° C.

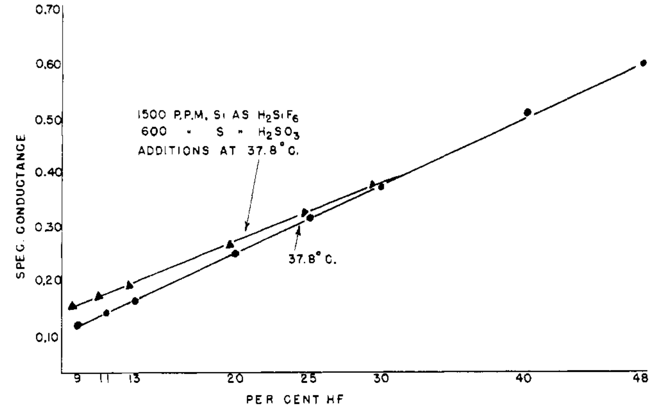

Figure 2. Effect of impurities (H_2SiF_6 and H_2SO_3) on conductivity of hydrofluoric acid solutions (9 to 48%) at 37.8° C.

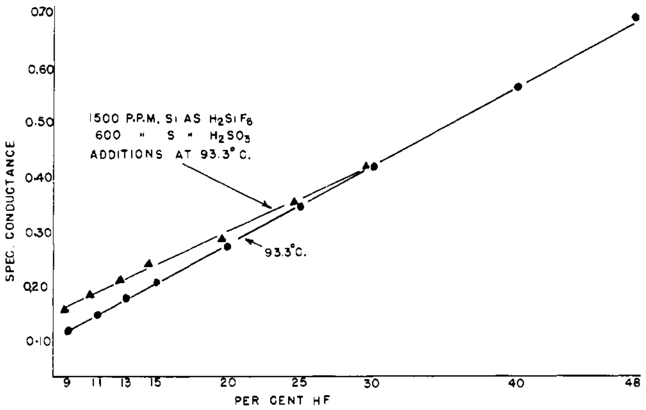

Figure 3. Effect of impurities (H_2SiF_6 and H_2SO_3) on conductivity of hydrofluoric acid solutions (9 to 48%) at 93.3° C.

this observation. Instead of one reading at 115.5° C., readings were taken every minute for 15 minutes, from the time the solution was first placed in the oil bath, maintained at 115.5° C. This length of time was more than sufficient for the temperature of the solution to reach 115.5° C., for pretrials with water had indicated that 115.5° C. would be reached in about 5 minutes. Time instead of temperature was used to follow the conductivity changes, because it was inadvisable to build a thermocouple well in the conductivity cell. The results of these runs are graphically shown in Figures 5 and 6. Some of the plots showed irregularities after 10 minutes and this is probably due to some leakage from the cell at the high pressures. The diagrams all have the same form, in that conductance increases with temperature to a maximum. Figure 7 shows the specific conductance at 115.5° C. *vs.* the acid concentration with and without added impurities, as well as the data obtained at 93.3° C.

DISCUSSION

The conductivity of aqueous hydrofluoric acid solutions is a straight-line function of the concentration in the range 1 to 48% acid (Figure 1). In Figure 1 it is seen that the slope at the higher temperature (93.3° C.) and higher concentrations is slightly greater than at 37.8° C., indicating a larger temperature coefficient. At 1% acid (Figure 4), the difference in the temperature coefficient becomes small, as the curves are almost the same. Hill and Sirkar (*2*) found that below 7.7% acid, between 0° and 18° C., the temperature coefficient is practically constant.

Impurities. Hydrofluosilicic [hexafluorosilicic acid (*3*)] and sulfurous acids are always present in commercial grade

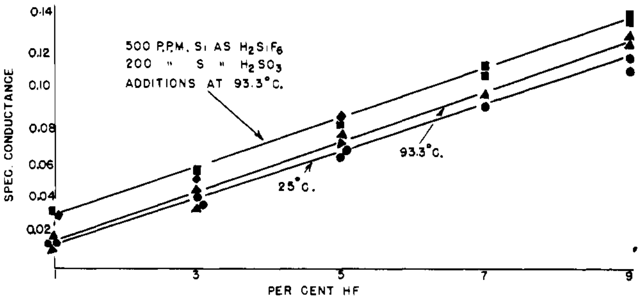

Figure 4. Conductivity of hydrofluoric acid solutions (1 to 9%) at 25° and 93.3° C.

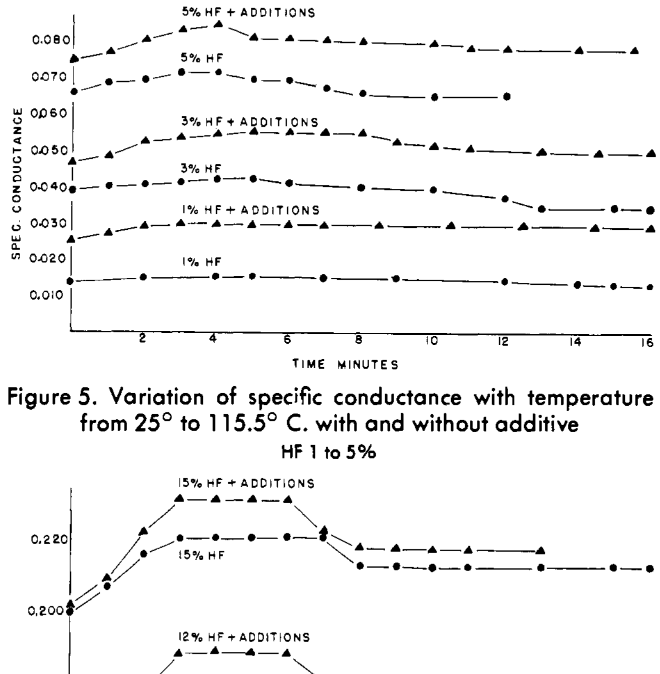

Figure 5. Variation of specific conductance with temperature from 25° to 115.5° C. with and without additive

HF 1 to 5%

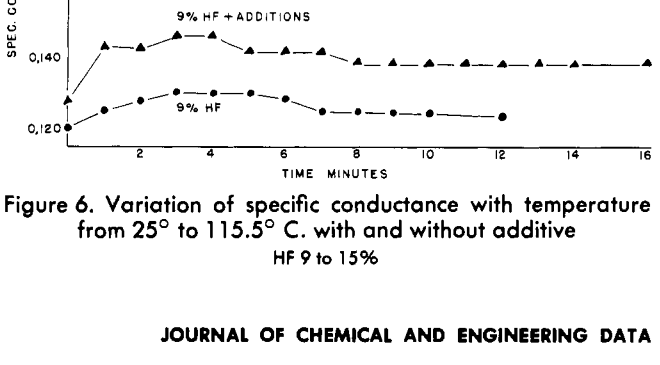

Figure 6. Variation of specific conductance with temperature from 25° to 115.5° C. with and without additive

HF 9 to 15%

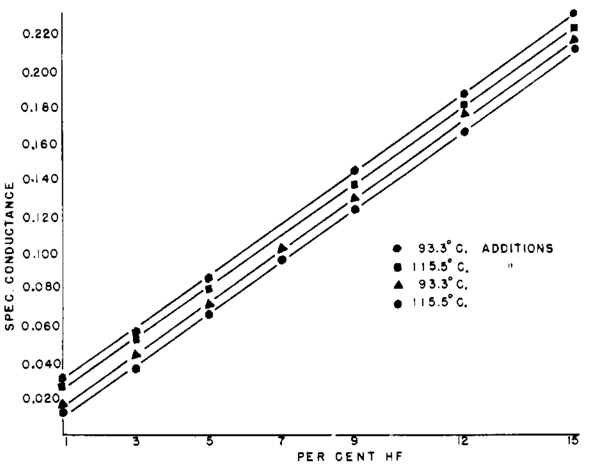

Figure 7. Effect of temperature of 93.3° and 115.5° C. on specific conductance of HF solutions (1 to 15%) with and without additive

Additive. 500 p.p.m. Si as H_2SiF_6 and 200 p.p.m. Si as H_3SO_3

hydrofluoric acid, so it is necessary to know the effect of these constituents on the conductivities. Figures 2 and 3 clearly show the effect of one concentration of impurities [2100 p.p.m. total (1500 p.p.m. of Si as H_2SiF_6 and 600 p.p.m. of S as H_2SO_3)]. The effect is greatest at the lower concentration (9%) acid and at about 30% acid it is essentially negligible. The pattern is the same at 93.3° and at 37.8° C.

The effect of the impurities is explained on the basis of the ionic behavior. Davies and Huddleston (*1*) in determining transport numbers in hydrofluoric acid solutions confirmed what earlier investigators had found, that the complex ion (HF_2^-) is formed by the reaction $HF + F^- = HF_2^-$. Roth (*6*) determined the equilibrium constants of hydrofluoric acid on the assumption that only H^+, F^-, HF_2^-, and HF are present. Thus the following are considered.

1. $HF \rightleftarrows H^+ + F^-$ and $HF + F^- \rightleftarrows HF_2$ 11% ionized
2. $H_2SO_3 \rightleftarrows 2H^+ + SO_3^{-2}$
In concentration used possibly moderately ionized
$H_2SiF_6 \rightleftarrows 2H^+ + SiF_6$ Weak

The conductance of a solution depends on the product of the number of ions, the charge carried by each ion, and the velocity with which the ions move. An accurate calculation of the ions present in the solutions based on the primary and secondary ionization constants does not seem warranted because of the unknown changes that probably occur in the mixtures. Instead, simple calculations indicate that the number of H ions in solution in the 1% hydrofluoric acid are of the same order of magnitude as those produced in the ionization of 200 p.p.m. of S (as H_2SO_3) and of 500 p.p.m. of Si (as H_2SiF_6). The negative ions as F^- in the HF are also of the same order of magnitude as the sum of the SO_3^{-2} and SiF_6^{-2} ions. The mobilities of the negative ions are all about the same. The hydrogen ions, on the other hand, are many times faster than the negative ions. So the effect of the impurities in producing a specific conductance of 0.016 (Figure 4) is explained on the basis of simple ionic abundance.

As the concentration of the hydrofluoric acid increases to about 30%, the effect of the added impurities decreases and finally disappears (Figures 2 and 3). The cause of this decrease has not been determined.

Conductivity at 115.5° C. Since hydrofluoric acid is a weak acid and only about 11% ionized, the dissociation in solution may be considered as

$$HF \rightleftarrows H^+ + F^- \qquad \text{and} \qquad K(\text{T.P.}) = \frac{a_{H^+} a_{F^-}}{a_{HF}}$$

The K is constant only at constant temperature and pressure. In the experiment under discussion (data plotted in Figures 5 and 6) the temperature was raised from room temperature to 115.5° C. by placing the closed nickel cell in an oil bath at 115.5° C. The conductivity of the HF solution was being continuously measured as the temperature increased from room temperature to 115.5° C. as indicated by the time designation in minutes (abscissa, Figures 5 and 6). Time was used instead of temperature because the cell contained no thermocouple.

Of interest in the figures are the maximum specific conductance and its falling off to a lower level. To explain this behavior an experiment was performed in which a 15% hydrofluoric acid solution was contained in a closed glass bulb and heated above the boiling point of the mixture—that is, up to 115° C. At 105° to 110° C., a fine string of bubbles was seen continuously passing up the length of the bulb. These bubbles were small and regular. As the temperature was increased, the bubbles formed were larger but still regular and continuous. In further trials with different acid concentrations bubbles were always formed but in some cases they were very small, appearing throughout the solution. On the basis of these experiments the explanation advanced for the changes occurring in the diagram (Figures 5 and 6) is that, initially, the specific conductance increases with temperature to the maximum, which is probably the closed system boiling point, slightly above 100° C., depending on the hydrofluoric acid concentration. The specific conductance remains constant for a few minutes during the heat of vaporization period. As the temperature again rises, hydrofluoric acid and water vaporize and the air space above the liquid in the cell is saturated with hydrogen fluoride. In a closed system the vapor concentration will be about the same as that of the liquid. This is assuming that the liquids water and hydrofluoric acid form the solubility-type curve, concave upward liquid and concave downward vapor, between 100° and 120° C. Any changes in liquid concentration are considered small and therefore negligible.

It is the hydrogen fluoride–water bubbles in the liquid that cause the decrease of the specific conductance from the maximum. At the stable state conditions of maximum temperature (115.5° C.) vaporization and condensation are taking place simultaneously, producing an agitated solution of stable liquid bubble composition which accounts for the constant specific conductance values after about 7 or 8 minutes. The influence of hydrogen fluoride gas seems to be greater than that of water vapor, since the higher hydrofluoric acid concentrations (Figure 6) show the larger specific conductance change.

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