Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Conductivity of Sodium Sulfate Solutions Containing Sodium Hydroxide or Sulfuric Acid

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The conductivity of solutions of sodium sulfate mixed with sodium hydroxide or sulfuric acid was investigated by the Bureau of Mines in conjunction with the preparation of sulfuric acid and sodium hydroxide by the electrolysis of sodium sulfate solutions. The sulfuric acid was used to leach manganese from its low-grade ores; the sodium hydroxide was used for the precipitation of manganese from solution. The electrolysis of sodium sulfate in a three-compartment cell produces three solutions of different compositions, each of which contributes to the total conductivity of the cell. Conductivity data were obtained for solutions of sodium sulfate, sodium sulfate mixed with sodium hydroxide, and sodium sulfate mixed with sulfuric acid at three levels of concentration and at three temperatures for each.

PREVIOUS WORK

The literature reports the conductivity of sodium sulfate solutions at several concentrations and temperatures, but no data were found for mixtures of sodium sulfate with sulfuric acid or with sodium hydroxide. Mellor (*3*) reports the equivalent conductivity of a 1.0*N* solution of sodium sulfate to be 50.80 ohms^{-1} per liter or 0.05080 ohm^{-1}cm.$^{-1}$ at 18°C. The International Critical Tables (*2*) give a value of 0.0503 ohm^{-1} cm.$^{-1}$ for the same temperature. Stender and Seerak (*4*) report specific conductivity for sodium sulfate solutions over a considerable range of concentration at 35°C. These data are plotted in Figures 4 and 5 for comparison with the data reported in this paper.

MATERIALS AND EQUIPMENT

Analytical reagent-grade chemicals were used to prepare stock solutions. Three stock solutions of each of the three reagents—sodium hydroxide, sodium sulfate, and sulfuric acid—were prepared to normalities of 1.0, 2.0, and 2.8. The sodium hydroxide contained a maximum of 1.2% of sodium carbonate and the sodium sulfate contained an

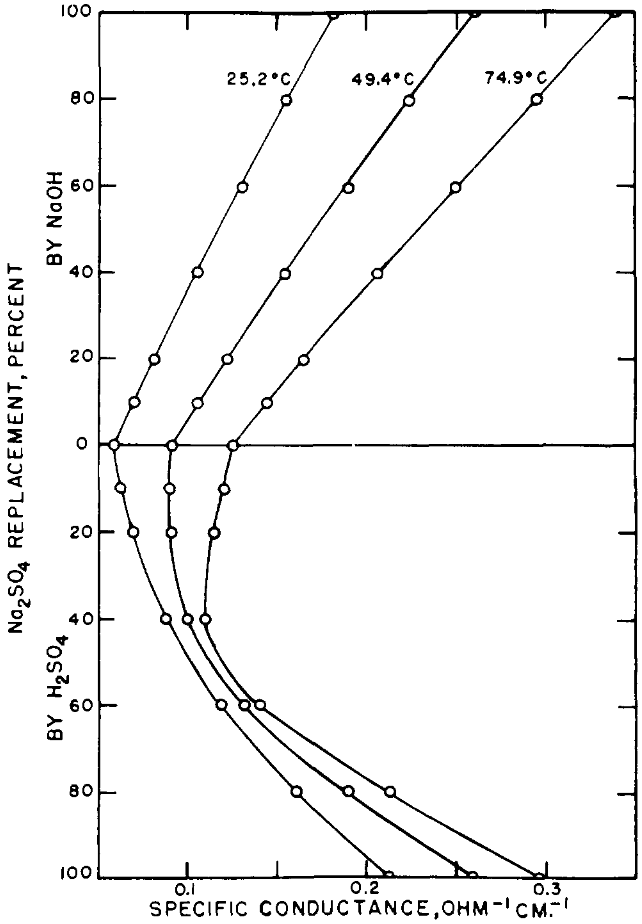

Figure 1. Specific conductance vs. sodium sulfate replacements for 1*N* solutions

Table I. Specific Conductivity of Sodium Sulfate Solutions

Na_2SO_4 Replaced, %	Solution Volumes, Ml.			Specific Conductance, Ohm^{-1} $Cm.^{-1}$								
				1.0*N* Solutions			2.0*N* Solutions			2.8*N* Solutions		
	Na_2SO_4	NaOH	H_2SO_4	25.2°C.	49.4°C.	74.9°C.	25.2°C.	49.4°C.	74.9°C.	25.2°C.	49.4°C.	74.9°C.
100.0	0	250.0	...	0.1815	0.2603	0.3398	...	...	...	...	...	...
80.0	50.0	200.0	...	0.1559	0.2244	0.2950	...	...	...	...	...	...
75.0	62.5	187.5	...	...	...	...	0.2435	0.3582	0.4760	...	...	...
60.0	100.0	150.0	...	0.1308	0.1898	0.2499	...	...	...	...	...	...
53.5	116.1	133.9	...	...	...	...	...	...	...	0.2395	0.3631	0.4916
50.0	125.0	125.0	...	...	...	...	0.1925	0.2858	0.3792	...	...	...
40.0	150.0	100.0	...	0.1062	0.1557	0.2071	0.1716	0.2569	0.3431	...	...	...
35.8	160.7	89.3	...	...	...	...	...	...	...	0.1948	0.2990	0.4060
30.0	175.0	75.0	...	...	...	...	0.1514	0.2280	0.3059	...	...	...
28.6	178.6	71.4	...	...	...	...	...	...	...	0.1779	0.2738	0.3733
21.4	196.4	53.6	...	...	...	...	...	...	...	0.1604	0.2478	0.3409
20.0	200.0	50.0	...	0.0821	0.1225	0.1648	0.1314	0.1999	0.2695	...	...	...
14.3	214.3	35.7	...	...	...	...	...	...	...	0.1441	0.2242	0.3085
10.0	225.0	25.0	...	0.0705	0.1064	0.1446	0.1123	0.1732	0.2351	...	...	...
7.15	232.1	17.9	...	...	...	...	...	...	...	0.1283	0.2058	0.2856
5.0	237.5	12.5	...	...	...	...	0.1028	0.1599	0.2179	...	...	...
3.57	241.1	8.9	...	...	...	...	...	...	...	0.1199	0.1899	0.2640
0.0	250.0	0	0	0.0598	0.0925	0.1264	0.0949	0.1485	0.2040	0.1128	0.1802	0.2523
3.57	241.1	...	8.9	...	...	...	...	...	...	0.1175	0.1822	0.2511
5.0	237.5	...	12.5	...	...	...	0.0998	0.1502	0.2021	...	...	...
7.15	232.1	...	17.9	...	...	...	...	...	...	0.1227	0.1850	0.2501
10.0	225.0	...	25.0	0.0644	0.0909	0.1206	0.1046	0.1514	0.1982	...	...	...
14.3	214.3	...	35.7	...	...	...	...	...	...	0.1334	0.1901	0.2480
20.0	200.0	...	50.0	0.0699	0.0917	0.1150	0.1168	0.1562	0.1930	...	...	...
21.4	196.4	...	53.6	...	...	...	...	...	...	0.1469	0.1969	0.2468
28.6	178.6	...	71.4	...	...	...	...	...	...	0.1611	0.2039	0.2438
30.0	175.0	...	75.0	...	...	...	0.1315	0.1623	0.1900	...	...	...
35.8	160.7	...	89.3	...	...	...	...	...	...	0.1800	0.2153	0.2443
40.0	150.0	...	100.0	0.0874	0.1005	0.1103	0.1518	0.1754	0.1910	...	...	...
50.0	125.0	...	125.0	...	...	...	0.1790	0.2013	0.2103	...	...	...
53.5	116.1	...	133.9	...	...	...	...	...	...	0.2470	0.2812	0.2967
60.0	100.0	...	150.0	0.1180	0.1327	0.1417	...	...	...	...	...	...
75.0	62.5	...	187.5	...	...	...	0.2783	0.3311	0.3689	...	...	...
80.0	50.0	...	200.0	0.1615	0.1908	0.2142	...	...	...	...	...	...
100.0	0	...	250.0	0.2126	0.2594	0.2960	...	...	...	...	...	...

undetermined small quantity of sodium bisulfate. Ordinary distilled water was redistilled in borosilicate glass and boiled just before use as the solvent. The conductivity of the water was considered insignificant for this work.

The Kohlrausch alternating current bridge method was used for the conductivity measurements. The components of the apparatus were: a Kohlrausch slide-wire, a resistance box wound for a minimum of capacitance and inductance, a microphone hummer having a stable 1000-cycle frequency output, a simple amplifier unit, earphones, a Washburn high conductivity cell, and a constant temperature bath controlled to ± 0.03°C. All component parts, except the slide-wire, were well shielded.

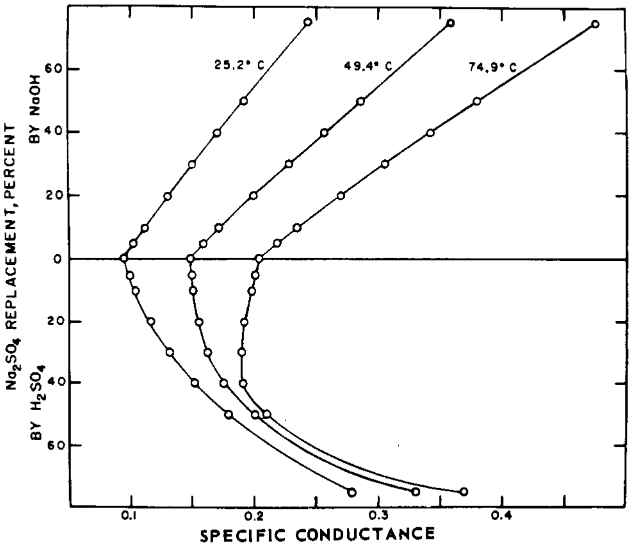

Figure 2. Specific conductance vs. sodium sulfate replacement for 2*N* solutions

PROCEDURE AND EXPERIMENTAL RESULTS

The equation $L = K/R$ relates the specific conductivity L, expressed in ohm^{-1} $cm.^{-1}$, and R, the measured resistance in ohms of the solution in the conductivity cell. K is the cell constant expressed by the unit $cm.^{-1}$ and corrects the geometry of the actual conductivity cell to that of a standard cell.

To determine the value of the cell constant, K, a 1.0000*N* solution of special grade chemically pure potassium chloride was used. The specific conductivity of the solution was given as 0.11219 ohm^{-1} $cm.^{-1}$ at 25.2°C. (*1*) and from this value the cell constant, K, was determined to be 33.961 ± 0.0145 cm^{-1}. This value was used in all subsequent calculations to derive the specific conductance of the stock solutions and mixtures.

This study was on the products formed when a solution of sodium sulfate is fed continuously to a compartmented electrolytic cell. Two product solutions are recovered from such a cell, one rich in sodium hydroxide and the other rich in sulfuric acid. Each of these solutions contributes to the total conductivity of the cell. To evaluate individual contributions, appropriate volumes of stock solutions of equal normalities were mixed. For example, on mixing equinormal solutions of sodium sulfate and sodium hydroxide, the entire range of replacement of the sulfate ion by equivalent hydroxyl ions could be studied without changing the concentration of the sodium ion. Similarly, sodium ions were replaced by equivalent hydrogen ions on the acidic

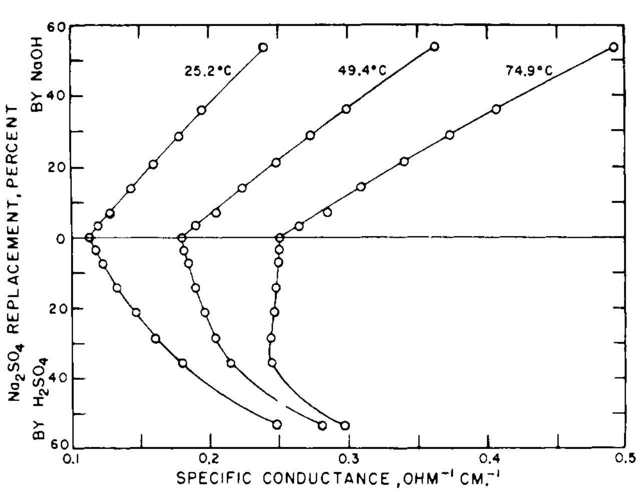

Figure 3. Specific conductance vs. sodium sulfate replacement for 2.8N solutions

side by mixing equinormal solutions of sodium sulfate and sulfuric acid for a constant sulfate ion concentration.

Each solution mixture was placed in the conductivity cell and resistance was measured at the temperature indicated. Each value for the specific conductance reported is an average of five individual determinations. The maximum standard deviation did not exceed ± 0.00024 for any set of five values. Further, the majority of sets showed a deviation less than ± 0.00010.

Table I records the specific conductivities of sodium sulfate solutions mixed with sodium hydroxide or sulfuric acid at three levels of concentration and at three temperatures for each. The first column shows the fraction of sodium sulfate, expressed as a percentage number, that was replaced by sodium hydroxide on the caustic side or by sulfuric acid on the acidic side. The next three columns under "solution volumes" show the volumes of solutions used for each fractional replacement. The remainder of the table records the specific conductivity of each solution mixture at three different temperatures.

The curves in Figures 1, 2, and 3 show graphically the specific conductivity variance with temperature, with salt concentrations, and with changes in ion replacements for both the caustic and acidic sides of neutral sodium sulfate.

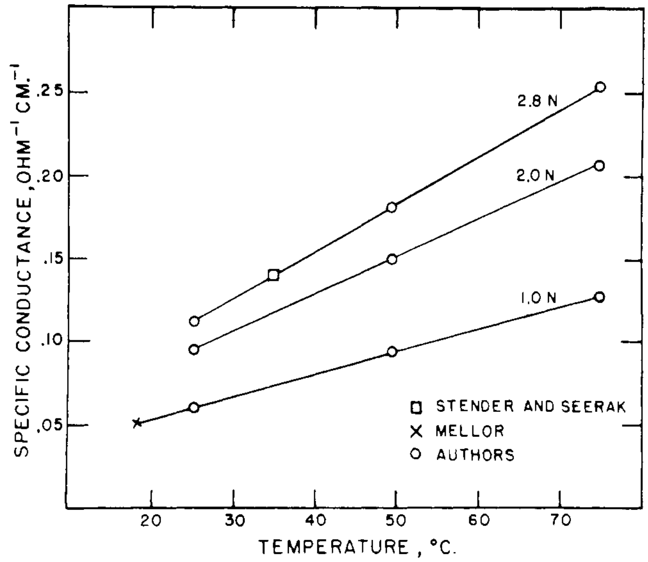

Figure 4. Temperature vs. specific conductance for sodium sulfate solution

The variations of conductivity as illustrated by these curves are consistent with what might be expected. In the caustic replacement series the conductivity change is nearly a linear function of the sodium hydroxide replacement. As the sodium hydroxide concentration is increased, the sulfate ions are replaced by hydroxyl ions, which have a much greater ionic mobility, thus increasing the conductivity of the solution.

The conductivity changes due to the sulfuric acid replacement are not straight lines, because the formation of bisulfate ions contributes to the total effect. The bisulfate ion partly ionizes to hydrogen and sulfate ions, but with the excess sulfate ions present the equilibrium is shifted and the bisulfate ions tend to remain as such. Consequently the total number of ions in solution are actually decreased, and thus the conductivity is decreased. This decrease is partly offset by the presence of hydrogen ions which have a very high mobility. The interaction of hydrogen and sulfate ions is greater at the higher temperatures. After all of the sulfate ions have been converted to bisulfate ions, the conductivity increases rapidly as the hydrogen ions increase.

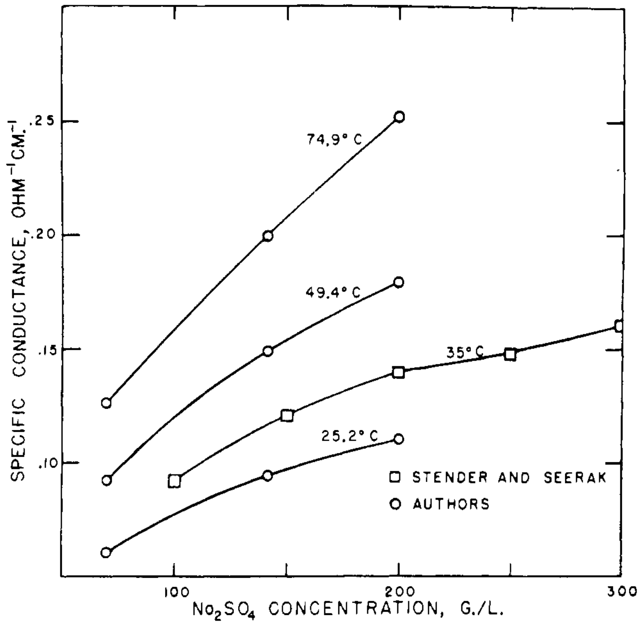

Figure 5. Concentration vs. specific conductance for sodium sulfate solutions

Figure 4 shows the plot of specific conductivity vs. temperature for pure sodium sulfate solutions. Similar curves may be drawn for any other particular ion replacement. Another family of curves may be drawn by plotting specific conductivity against concentration. Figure 5 shows one member of this family, that for pure sodium sulfate solutions.

SUMMARY

The conductivities of mixtures of pure solutions of sodium sulfate, sodium hydroxide, and sulfuric acid were determined at three levels of salt concentrations and at three temperatures for each concentration. The replacement of sulfate ions by equivalent hydroxide ions increased the specific conductivity with increasing replacement. At room temperature the equivalent replacement of sodium ions with hydrogen ions appeared to increase the specific conductivity, but at higher temperatures a tendency was noted for the specific conductivity to remain constant or to decrease slightly as the composition of the solution approached that of sodium bisulfate. After that composition

was passed the specific conductivity increased again with increasing hydrogen ion concentration.

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Solubility of Acrylonitrile in Aqueous Bases and Alkali Salts

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During a study of the reaction in which cotton cellulose was cyanoethylated with acrylonitrile using aqueous alkali bases as catalysts, the solubility of acrylonitrile in aqueous systems was required. Since the liquid phase associated most intimately with the cotton cellulose during the reaction is a dilute aqueous solution of sodium hydroxide or other base, the solubility of the acrylonitrile in this phase was believed to be a determining factor in both the rate of the reaction and the extent of cyanoethylation at equilibrium. The solubility of acrylonitrile in water has been reported for various temperatures (*1*), but no solubility data for acrylonitrile in various alkali and saline solutions could be found.

MATERIALS USED

The acrylonitrile was of commercial grade, containing 0.8% of water. In order to facilitate reading of the interface with aqueous layers the acrylonitrile was colored with 0.005% Celliton Fast Red GGA Ex. Conc. (Pr. 236). (Pr. 236 refers to the prototype dye number listed in the AATCC Yearbook for 1955.) All alkali hydroxides and salts were of reagent grade, except Naxonate G, a commercially available mixture of xylene sulfonates.

PROCEDURE

Because acrylonitrile reacts with water in the presence of bases, it was necessary to use a solubility determination procedure not based on equilibrium measurements. The measurements were carried out at 25° ±1° C. in an air bath. The techniques employed are essentially those reported by Booth and Everson (*2*) in their study of hydrotropic salts. In the procedure adopted, 45 ml. of various concentrations of alkali bases were weighed into stoppered, graduated sulfonation bottles (ASTM D 875-46T); a measured volume of acrylonitrile was then added rapidly, and the bottles were sealed and tumbled end over end. Thirty minutes after the addition of acrylonitrile the tumbling was stopped and the volume remaining was read on the graduated scale of the bottle. Thereafter readings were taken every 15 minutes until the residual acrylonitrile was less than 1.0 ml.

The change in the volume of acrylonitrile was due to two causes. The first, a rapid change complete in less than 30 minutes, was due to the solution of the acrylonitrile in the aqueous phase. The second, and slower change, was due to the hydration of acrylonitrile to ethylene cyanohydrin. As the aqueous phase was saturated with respect to acrylonitrile during the entire measurement period, and the base concentration remained essentially unchanged, the rate of acrylonitrile hydration was evidently zero order. A plot of the volume of acrylonitrile remaining *vs.* time was found to be linear. Extrapolation of this plot to zero time permitted a correction to be made for the loss of acrylonitrile due to reaction, and yielded the volume of acrylonitrile dissolved in the aqueous phase. Use of the density of the acrylonitrile and the known weight of water in the flask allowed calculation of the molality of acrylonitrile in the aqueous phase.

When both alkali bases and salts were present simultaneously, the same procedure was followed. The aqueous base was weighed into the flasks, and weights of the salt calculated to give a constant molality of salt solution were added.

When the solubility of acrylonitrile was determined in salt solutions alone, the previous method was not necessary. Weighed amounts of salt solutions were placed in the flasks and increments of acrylonitrile were added until a second phase persisted. The solutions were tumbled for 30 minutes between additions of acrylonitrile.