A plot of ($\log[Nb(OH)_2Cl_4^-] - \log$ [II]) *versus* log (apparent chloride activity) also yields a good straight line with a slope of 0.95. The loss of one chloride is thus indicated. One would expect that $Nb(OH)_2Cl_3$ would be the species formed. This could be considered a hydrate of $NbOCl_3$ and as such would be expected to show an absorption curve similar to that of $NbOCl_3$. Comparison of these 260 mμ peaks to the absorption curve of $NbOCl_3$ in diethyl ether showed no similarity.

It was then postulated that this species showing an absorption peak at 260 mμ might be a cation such as $NbOHCl_3^+$. This appears reasonable in that the extremely high hydrogen ion activity present in 10.5 molar perchloric acid might allow the reaction to be $Nb(OH)_2Cl_4^- + H^+ \rightarrow NbOHCl_3^+ + Cl^- + H_2O$ on decrease of chloride ion activity. In order to show that such a reaction was taking place a cation-exchange column was used to show the presence of a positive ion. Since both the anion $Nb(OH)_2Cl_4^-$ and the other species are present in the same solution it is not to be expected that all of the niobium would be removed from the solution even if the second species were a cation.

A solution of niobium 10.5 molar in perchloric acid and 0.025 molar in chloride was passed through a cation-exchange column which had first been washed with this solvent. Such a solution had a strong absorption maximum at 260 mμ, which was removed almost completely by the cation exchange resin Dowex-50. These results support the postulated cationic nature of the species absorbing at 260 mμ.

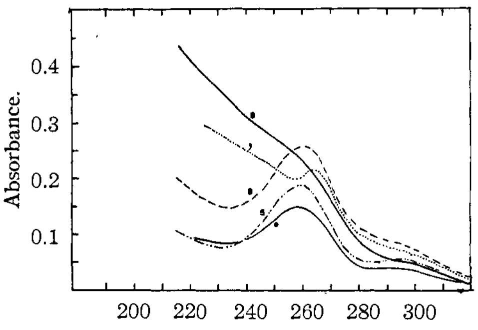

Fig. 4.—Net absorbance curves after subtracting species I, 281 mμ from curves in Fig. 1. Curve numbers are the same as Fig. 1.

As yet no explanation has been given for the absorption curves obtained for solutions of niobium in hydrochloric acid of about 4–6 molar. These solutions show no absorption maxima in the range which can be studied, but they definitely do not appear to be colloidal. Anion-exchange studies[7] show the anion-exchange distribution coefficient to decrease from about 1200 to about 20 in going from 12 to 6 molar hydrochloric acid. From this it appears that the species present in 6 molar hydrochloric acid has a zero or positive charge since a minus one charged species is present in 12 molar hydrochloric acid. It is to be expected then that the species formed in decreasing hydrochloric acid concentration below 12 molar might be $NbOCl_3$ or a hydrate of it. This is sustained by the marked similarity of the spectrum of $NbOCl_3$ in diethyl ether to those of niobium in 4.2 and 6.1 molar hydrochloric acid.

The over-all mechanism can now be shown. When chloride is decreased by decreasing hydrochloric acid below 12 molar the reaction $Nb(OH)_2Cl_4^- \rightarrow Nb(OH)_2Cl_3 + Cl^-$ takes place but at high hydrogen ion activity, $Nb(OH)_2Cl_3 + H^+ \rightarrow NbOHCl_3^+ + H_2O$. Lowering of hydrogen ion below about 2 molar at high chloride ion concentration causes colloid formation probably of the type $Nb(OH)_3Cl_2$. It appears that only three soluble chloride containing species of niobium exist to any appreciable extent in the systems studied. These are $Nb(OH)_2Cl_4^-$ in both high chloride and high hydrogen ion concentration, $NbOHCl_3^+$ at extremely high hydrogen ion concentration and low chloride ion concentration, and $Nb(OH)_2Cl_3$ at hydrogen ion and chloride ion concentrations which are both in the range of about 3 molar up to where the $Nb(OH)_2Cl_4^-$ predominates.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Solubility of Silver Sulfate in Sulfuric Acid Media at High Temperatures. Effects on the Silver, Silver Sulfate Electrode[1]

BY M. H. LIETZKE AND R. W. STOUGHTON

RECEIVED FEBRUARY 15, 1956

The solubility of Ag_2SO_4 has been determined in water and in 0.1, 0.5 and 1.0 *m* H_2SO_4 to above 250° in order to evaluate the useful range of the Ag, Ag_2SO_4 electrode in acid solutions. The effects of the increase in solubility with increasing temperature and H_2SO_4 concentration are discussed. Calculated solubilities in H_2SO_4 media based on the decrease in the HSO_4^- acid constant with temperature are compared with the observed values.

In a previous paper[2] the behavior of saturated Ag, Ag_2SO_4 and Hg, Hg_2SO_4 electrodes at high temperatures in H_2SO_4 solutions was described. It was shown that in acid concentrations high enough to repress hydrolysis of the Hg_2SO_4 electrode potentials predicted on the basis of thermodynamic calculations were obtained. However, no attempt was made to define the useful range of either the silver or mercury electrode as limited by the solubility of silver or mercurous sulfate in H_2SO_4 solutions of various concentrations. If, at a given tem-

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) M. H. Lietzke and R. W. Stoughton, THIS JOURNAL, **75**, 5226 (1953).

perature, the salt concentration in solution in either electrode compartment approaches the acid concentration, very appreciable junction potentials may be generated. Thus, the application of the electrodes to thermodynamic measurements may be seriously limited, at least for cells requiring that Ag_2SO_4 or Hg_2SO_4 be kept out of one cell compartment. Since, as previously shown, the Ag_2SO_4 electrode seemed the more promising for high temperature use, a study has been made of the solubility of Ag_2SO_4 to above 250° in water and in 0.1, 0.5 and 1.0 *m* H_2SO_4 in an effort to determine to what extent the increasing solubility of Ag_2SO_4 may limit the useful application of the electrode. In addition, an attempt has been made to calculate the high temperature solubility of Ag_2SO_4 in H_2SO_4 solutions, and the agreement between calculated and experimental values will be discussed.

Experimental

The Ag_2SO_4 used in the solubility measurements was prepared according to the method described by Archibald.[3] Weighed quantities of Ag_2SO_4 crystals and water or H_2SO_4 solutions were sealed in 6 mm. i.d. fused silica tubes. The solution volume was about 1 ml. in all cases. The tubes were mounted on a brass block provided with slits to permit observation of the solution and crystals. During heating, the block containing the tubes was slowly rotated in an oven fitted with windows at the front and back. When the tubes were illuminated by a light shining through the rear window it was very easy to observe the appearance or disappearance of crystals in the tube. The temperatures at which crystals dissolved were reproducible to within ±1°. The temperatures were measured by means of a thermocouple extending into the block and were recorded on a Brown recorder. The solubility measurements could be made only on a heating cycle since the solutions super-saturated upon cooling. After heating, the tubes were opened and the contents analyzed to determine the exact concentration of Ag_2SO_4.

Results and Discussion

Figure 1 shows the experimentally obtained solubility curves for Ag_2SO_4 in water and in 0.1, 0.5 and 1.0 *m* H_2SO_4 solutions. The results in water up to 100° were obtained from the work of Barre.[4] Barre observed in his solubility determinations "considerable decomposition" of Ag_2SO_4 in water after 10 hours at 100°. In the current work the high temperature solubilities in water were obtained during a heating period of two hours and in that time no evidence of a change in the solid was observed. When these points were checked by a second heating and the tube allowed to cool, it was observed that the crystals were slightly discolored by a brownish precipitate which did not redissolve. The formation of silver oxide shows that silver sulfate is metastable in water at the upper temperatures; however, the fact that the solubilities checked on reheating indicates that no appreciable decomposition occurred before the second determination. No brownish precipitate formed in any of the tubes containing H_2SO_4 along with the Ag_2SO_4, as previously reported.[2] Results in the H_2SO_4 solutions at 25° were obtained from Åkerlof and Thomas.[5]

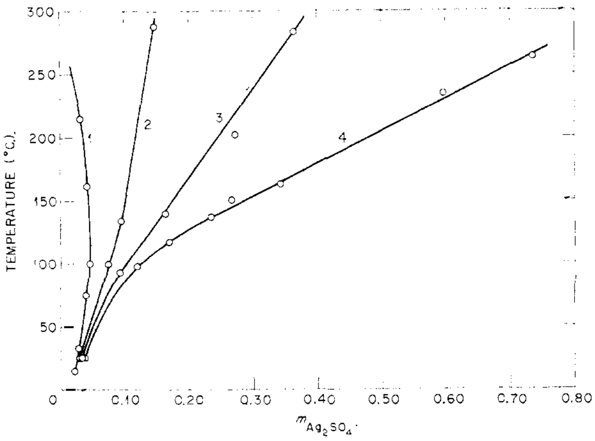

Fig. 1.—Curves showing the solubility of Ag_2SO_4 in H_2O and in H_2SO_4 solutions: 1, solubility of Ag_2SO_4 in H_2O; 2, solubility of Ag_2SO_4 in 0.1 *m* H_2SO_4; 3, solubility of Ag_2SO_4 in 0.5 *m* H_2SO_4; 4, solubility of Ag_2SO_4 in 1.0 *m* H_2SO_4.

In order to get some idea as to whether the solubility of Ag_2SO_4 was varying in an expected manner with H_2SO_4 concentration and temperature, rough calculations were made on the anticipated values. It was assumed that the only species that needed to be considered were Ag^+, H^+, $SO_4^=$ and HSO_4^-. Actually, a dissociation constant for $AgSO_4^-$ of about 0.07 at 25° has been reported by Righellato and Davies[6] from conductivity data. However, the interpretation of conductivity data in this manner may not be conclusive; further, it does not seem unreasonable to assume that under our conditions of low sulfate ion concentration Ag^+–$SO_4^=$ complexing may be neglected without serious error.

The calculated solubilities of Ag_2SO_4 in H_2SO_4 solutions at various temperatures were based on the solubilities in pure water and a curve for the HSO_4^- acid constant *vs.* temperature obtained from T. F. Young[7]

$$T \log K = -775.3835 + 6.947210T - 0.021247_2T^2 \quad (1)$$

The values of the activity acid constant were obtained from Young's equation and corresponding concentration quotients were calculated at the required ionic strengths on the assumption that the activity coefficient of any ion γ_i is given by the modified Debye–Hückel expression

$$\log y_i = \frac{-AZ_i^2\mu^{1/2}}{1 + 1.5\mu^{1/2}} \quad (2)$$

In this equation μ is the ionic strength, Z_i is the charge of the ion, and A is the Debye–Hückel coefficient, which varies with the dielectric constant of the solvent and the temperature.

Equation 2 gives a fair rough average value of an activity coefficient of a strong electrolyte out to about an ionic strength of unity, as can be verified by a plot of $(1/Z_+Z_-) \log \gamma \pm$ *vs.* $\mu^{1/2}$ for various electrolytes. In using this equation, the constant A was corrected for temperature changes and corresponding changes in the dielectric constant of water. The constant factor 1.5 in the denominator was assumed to be temperature independent. The solubility product of Ag_2SO_4 in pure water was calculated on a molality basis (assuming complete dis-

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[3] E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932.

[4] M. Barre, *Ann. chim. phys.*, [8] **24**, 211 (1911).

[5] G. Åkerlof and H. C. Thomas, THIS JOURNAL, **56**, 593 (1934).

[6] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[7] T. F. Young, private communication.

TABLE I

CALCULATED AND OBSERVED SOLUBILITIES OF Ag_2SO_4 AT VARIOUS TEMPERATURES AND CONCENTRATIONS OF H_2SO_4

$m_{H_2SO_4}$ →		0.1			0.5			1.0	
t (°C.)	$S_{calcd.}$ (uncor.)	$S_{obsd.}$	$S_{calcd.}$ (D.H. cor.)	$S_{calcd.}$ (uncor.)	$S_{obsd.}$	$S_{calcd.}$ (D.H. cor.)	$S_{calcd.}$ (uncor.)	$S_{obsd.}$	$S_{calcd.}$ (D.H. cor.)
25	0.0192	0.0292	0.0302	0.0210	0.0332	0.034	0.0213	0.0347	0.0360
100	.062	.074	.082	.098	.102	.150	.107	.123	.180
150	.083	.100	.100	.172	.180	.258	.210	.292	.344
200	.095	.118	.104	.251	.258	.362	.315	.511	.535
250	(.096)	.136	(.101)	(.320)	.317	(.403)	(.431)	.678	(.683)

sociation) at the pertinent ionic strength, *i.e.*, a value equal to three times the molal solubility. A value of the activity solubility product was obtained by extrapolation to zero ionic strength with the aid of equation 2. Also, values of the molality solubility product were calculated at the desired ionic strengths (corresponding to the three H_2SO_4 solutions at a given temperature) by using this equation for the variation of ionic activity coefficients with μ. Since the values of μ used were not stoichiometric but depended on the calculated concentrations of ions, they had to be obtained (at least in principle) by successive approximations, as did the ionic concentrations themselves. Two sets of solubilities were calculated for the 0.1, 0.5 and 1.0 m H_2SO_4 solutions at 25, 100, 150 and 200°. In one set the activity acid constant and solubility product were used; in the other, the molality quotient and solubility product corresponding to the appropriate values of μ were employed. In Table I, the former are listed as uncorrected calculated solubilities and the latter as calculated solubilities with a Debye–Hückel (D. H.) correction for changing ionic strength. Similar calculations were also made at 250° using an extrapolated solubility in pure water (0.020 m); these values are shown in parentheses.

Neglecting the figures at 250° in Table I, the following conclusions may be drawn.

(1) At 25°, as expected the observed solubilities are much closer to the calculated values based on the modified Debye–Hückel correction than those based on the assumption of unit activity coefficients throughout. Calculations based on the results of Cameron and Breazeale[8] for the solubilities of $CaSO_4$ in H_2SO_4 media at 25° also are in line with this conclusion.

(2) At 0.1 m H_2SO_4 better predicted values for the solubilities are obtained at all temperatures on the basis of the modified Debye–Hückel correction. This conclusion is consistent with the often verified fact (at lower temperatures) that expressions similar to equation (2) seem to hold for all strong electrolytes at low ionic strength.

(3) In general, the observed values lie between the two calculated ones, the point at 0.1 m H_2SO_4 and 200° being the only exception. One interpretation of this conclusion is that activity coefficients may not vary as markedly with ionic strength at the higher temperatures as indicated by equation (2)—at least not at the higher values of μ.

It is interesting to note that at 0.5 m H_2SO_4 the uncorrected predicted values are quite close to the observed solubilities at the higher temperatures, although this agreement may be fortuitous.

As seen in Fig. 1 the solubility of Ag_2SO_4 does increase markedly with H_2SO_4 concentration and the more so the higher the temperature. This effect results in a considerable restriction on the usefulness of the Ag, Ag_2SO_4 reference electrode in acid media at elevated temperatures. If it is used in a cell requiring that the Ag_2SO_4 be kept in its own compartment, then serious liquid junction potentials may be expected. If it is used in cells without liquid junction, as, for example, the cell Ag, Ag_2SO_4, $H_2SO_{4(m)}$, H_2, then relative activities can be obtained in the mixed electrolyte solution. In this case, any actual extrapolation to zero ionic strength would be uncertain at elevated temperatures. The electrode may, nevertheless, be expected to perform satisfactorily in acid media at lower temperatures or in very dilute acid media at higher temperatures.

Acknowledgments.—We wish to thank J. S. Gill and W. L. Marshall of the ORNL Chemistry Division for the use of their apparatus in which the solubility measurements were made. We also wish to express our appreciation to Dr. T. F. Young of the University of Chicago for interesting discussions concerning our high temperature EMF program.

OAK RIDGE TENN.

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(8) F. K. Cameron and J. F. Breazeale, *J. Phys. Chem.*, **7**, 574 (1903).