[Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania]

INVESTIGATIONS OF SULFATE SOLUTIONS. EXPERIMENTAL METHODS AND RESULTS ON CELLS WITHOUT LIQUID JUNCTION

By Gösta Åkerlöf

Received December 14, 1925 Published May 5, 1926

The only electromotive-force data now available on sulfate solutions have been obtained from the cells: $H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg$ which have been measured by Brönsted,[1] Lewis and Lacey[2] and Randall and Cushman;[3] $H_2 \mid H_2SO_4(m_1), M_2SO_4(m_2) \mid Hg_2SO_4 \mid Hg$ where M represents potassium and sodium; and $H_2 \mid H_2SO_4(m_1), MgSO_4(m_2) \mid Hg_2SO_4 \mid Hg$ measured by Harned and Sturgis.[4] In view of this lack of experimental data on the alkaline sulfates, and on hydroxides in sulfate solutions, the electromotive forces of the following cells have been measured: $Hg \mid Hg_2SO_4 \mid M_2SO_4(m) \mid M_xHg \mid M_2SO_4(m_1) \mid Hg_2SO_4 \mid Hg$; $H_2 \mid H_2SO_4(m_1), M_2SO_4(m) \mid Hg_2SO_4 \mid Hg$; $H_2 \mid MOH(m_1), M_2SO_4(m) \mid M_xHg \mid MOH(m_1) \mid H_2$, in which M represents lithium, sodium and potassium.

This investigation was suggested by Dr. Herbert S. Harned and has been thoroughly discussed with him. The author wishes to express his thanks for the help given him by Dr. Harned.

I. Experimental Methods

Materials

Amalgams were prepared by the method described by MacInnes and Parker,[5] Knobel[6] and Harned.[7]

Mercurous Sulfate was prepared according to the method of Hulett.[8] For the preparation of larger quantities, it was found to be more convenient and rapid to use flowing mercury than to stir the mercury surface. All finer particles were washed away and the remainder consisted of comparatively large, easily distinguishable crystals. They settled very quickly from the suspension.

Potassium, Sodium and Lithium Sulfates were dried at 500° for 10–15 hours. After this treatment, they were found to be neutral and to contain less than 0.01% of water.

Standard Acid, Hydroxide and Salt Solutions.—Standard 0.1 and 1 N potassium hydroxide solutions were made by diluting the very concentrated hydroxide, from which the carbonate had been removed by the addition of barium hydroxide. The concen-

---

[1] Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

[2] Lewis and Lacey. This Journal, **36**, 804 (1914).

[3] Randall and Cushman, *ibid.*, **40**, 393 (1918).

[4] Harned and Sturgis, *ibid.*, **47**, 945 (1925).

[5] MacInnes and Parker, This Journal, **37**, 1445 (1915).

[6] Knobel, *ibid.*, **45**, 70 (1923).

[7] Harned (a) *ibid.*, **47**, 676 (1925); (b) *Z. physik. Chem.*. **117**, 1 (1925).

[8] Hulett, *Phys. Rev.*. **32**, 257 (1911).

trated solution contained only traces of barium, which after dilution were very difficult to detect. Concd. sodium hydroxide solution dissolves a considerable quantity of barium hydroxide, and therefore a calculated amount of the latter was added and the excess cautiously precipitated with sodium sulfate until very small traces remained. A saturated lithium hydroxide solution was prepared by filtering a hot solution through asbestos. After cooling, a part crystallized, and the clear solution was drawn off and diluted to the proper concentration. This solution appeared to be free from carbonate. Acid and alkaline solutions were made up shortly before they were used, kept protected from the carbon dioxide of the air, and analyzed according to the usual methods. Standard 1 N salt solutions were necessary in order to avoid the inconvenient weighing of small amounts of salts when preparing the dilute solutions. They were analyzed gravimetrically.

Apparatus and Technique

CELLS: $H_2 \mid MOH(c_1), M_2SO_4(c) \mid M_xHg \mid MOH(c_1) \mid H_2$.—The cell used for these measurements was an improved form of that employed by Harned[7a] and is shown in Fig. 1. The chief advantage of this cell lies in the fact that it can be thoroughly washed and filled by a solution without being removed from the thermostat. This was brought about by having the tubes from the bottoms of the hydrogen electrode compartments go to the tops of the amalgam electrode compartments. By employing suction through the stopcocks at the bottom of the cell, it could be completely emptied into the waste receiving flask at the bottom of the thermostat and then refilled and washed the required number of times with the solution to be measured. This eliminated the laborious process of cleaning and drying the cell each time, and greatly reduced the time of operation. In other respects, the manipulation was the same as that described by Harned.

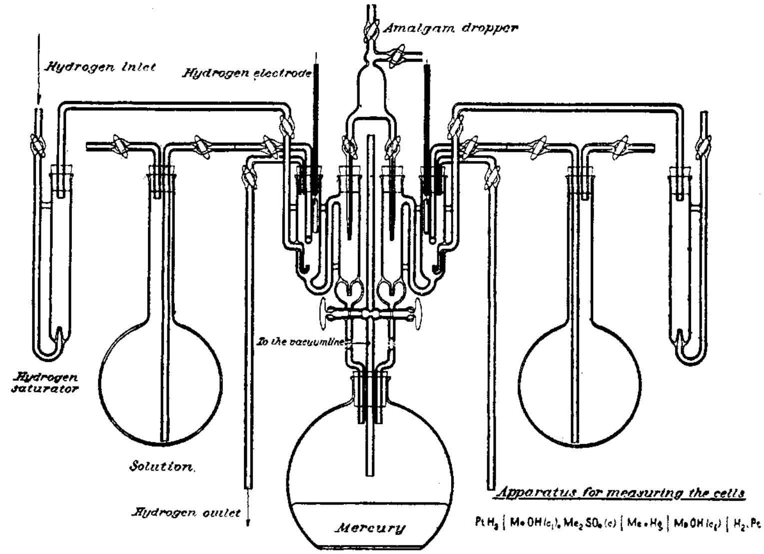

Fig. 1.

Vacuum technique was employed throughout and all solutions were boiled in a vacuum for the purpose of removing dissolved air.

Cells: Hg | Hg_2SO_4 | $M_2SO_4(c)$ | M_xHg | $M_2SO_4(c_1)$ | Hg_2SO_4 | Hg.—The apparatus employed for these measurements is shown in Fig. 2. It is impossible to use a mercurous sulfate electrode in a neutral solution because yellow basic substances are formed. On the other hand, it is impossible to use amalgam electrodes in acid solutions. Therefore, four different solutions had to be made up for every determination, two of which were neutral and two with a very little acid added. Previous investigations have shown that the mercurous sulfate electrode is not reliable in pure acid solutions below 0.01 N.[9] It was found that with a neutral sulfate present in concentrations higher than 0.05 N, the acid concentration could be decreased to 0.002 N. To get reproducible results, the solutions must be carefully boiled and guarded against the air, and the washing of the mercurous sulfate with the solution ought to be carried out with as little air present as possible. There was still another difficulty to be considered. If a pair of solutions, neutral and acid, differed in concentration, there might be present small liquid-junction potentials and, therefore, four corrections of the potential would have to be made, two for the liquid junction, and two for

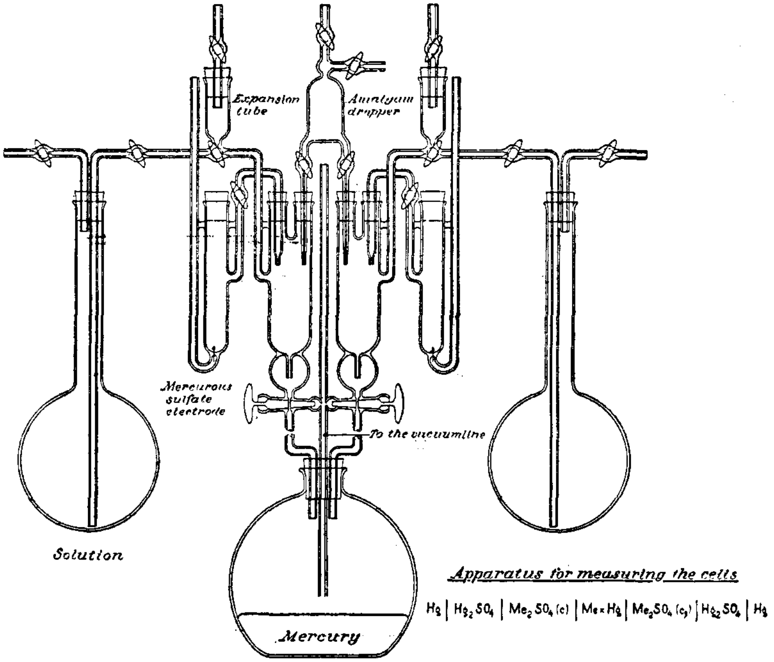

Fig. 2.

---

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 356.

the differences in concentrations at the electrodes. To avoid this, great care was exercised in order to make the total concentrations of the neutral and slightly acidified solutions the same. The color of the mercurous sulfate was always gray or white and never yellow.

The method of operation of this cell was very similar to that of the hydrogen-amalgam cells, only a little simpler. During the filling of the middle parts of the cell (Fig. 2) the stopcocks in the tubes from the mercurous sulfate electrodes were closed. They were opened shortly before the measurement.

CELLS: $H_2 \mid H_2SO_4(c_1), M_2SO_4(c) \mid Hg_2SO_4 \mid Hg$.—In this case, the mercurous sulfate electrode (Fig. 2) was combined with a hydrogen electrode (Fig. 1) at the opening of the tube in which one arm of the amalgam reservoir fits. The solution to be measured was boiled under a vacuum and the mercurous electrode was first prepared from this. After the latter was put in place, the hydrogen compartment of the cell was washed and filled two or three times and then finally filled in a vacuum by the same method as described above. The platinum wire in the mercurous sulfate electrode was covered with a column of mercury 2 to 4 cm. high in order to prevent it from coming into contact with the solution. In order to construct another mercurous sulfate electrode, the solution and the mercurous sulfate were removed by suction, and the same electrode was used several times without the tiresome procedure of cleaning and drying. In every other respect, the method adopted by Randall and Cushman[3] or Harned and Sturgis[4] was followed. During the measurement, the stopcock between the two electrodes had to be opened. There was very little probability that the hydrogen electrode would be affected by the dissolved mercurous sulfate but for the purpose of eliminating this possibility the platinum foil electrode was frequently ignited and replatinized.

Measurements and Corrections

The electromotive forces of the hydrogen—mercurous-sulfate cells rose very rapidly during the first 15–20 minutes and after 30 minutes they remained very constant. Readings were taken every half hour for three hours and the mean of these was considered the final result. The amalgam cells were operated two or three hours before they were measured. Their electromotive force was usually very constant from the beginning to the end of the time during which the amalgam flowed, showing that any decomposition of the amalgam was too little to influence the electromotive force.

Two series of measurements with solutions each containing salt were made with the hydrogen—mercurous-sulfate cells containing 0.01 and 0.1 N acid and various salt concentrations, respectively. The difference in electromotive force between these two series at corresponding salt concentrations was found to be 0.06 volt. Therefore, the corrections to round concentrations are given by the equations, $\Delta E_{0.1} = 0.06 \log C_1/0.1$; $\Delta E_{0.01} = 0.06 \log C_1/0.01$. The observed deviations from round concentrations were seldom larger than 2%. The corrections were determined graphically. The correction for the partial pressure of the hydrogen to 760 mm. for the unsymmetrical hydrogen cells was obtained graphically.

The solutions of the mercurous sulfate-amalgam cells were at round concentrations during the measurement and therefore there was no concentration correction.

The electromotive forces of the hydrogen-amalgam cells are given by the equation $E = (RT/NF)\ ln\ (a_{M(s)}\ a_{OH(s)}\ a_{H_2O(c_1)}/a_{M(c_1)}\ a_{OH(c_1)}\ a_{H_2O(s)})$ where the subscript "s" refers to the hydroxide-salt solution and c_1 to the pure hydroxide solution. Two series of results were obtained for solutions with each of the salts containing approximately 0.01 and 0.1 N hydroxides and various salt concentrations. The corrections to round concentrations may therefore be made with sufficient accuracy by the equations

$$\Delta E_{0.1} = 0.059 \log \frac{c_1\ (c + c_1)}{0.1\ (c + 0.1)} - 0.118 \log \frac{c_1}{0.1}$$

$$\Delta E_{0.01} = 0.059 \log \frac{c_1\ (c + c_1)}{0.01\ (c + 0.01)} - 0.118 \log \frac{c_1}{0.01}$$

where c is the salt concentration.

II. Experimental Results and Calculations

Accuracy and General Conditions

The measurements were carried out to salt concentrations of a little over 1 N for potassium sulfate, 5 N for sodium sulfate and 4 N for lithium sulfate. The supersaturated sodium sulfate solutions had to be introduced warm in order to prevent crystallization. In the cases of the amalgam cells containing these solutions, certain further precautions had to be observed. To prevent crystallization, every glass surface above the water level of the thermostat and the rubber stoppers on the capillaries of the amalgam dropper were carefully wetted before the amalgam dropper was introduced.

Concentrations are given in moles per 1000 cc. of solution. Most of the results recorded in the tables are mean values of two values of two measurements carried out with two different sets of apparatus and solutions. It was most difficult to obtain good reproducibility with very dilute solutions, highly concentrated solutions showed better consistency, and measurements on cells in the middle range were reproducible to within 0.1 mv.

The Activity Coefficients of Potassium, Sodium and Lithium Sulfates in Aqueous Solution

The electromotive forces of the mercurous-sulfate—amalgam cells are related to the activities of the ions by the equation

$$E = \frac{RT}{NF} ln \frac{a^2_{M(s)}\, a_{SO_4(s)}}{a^2_{M(c_1)}\, a_{SO_4(c_1)}} \qquad (1)$$

where c_1 is the standard reference concentration. If a_{c_1} is the known mean activity or the cube root of the activity product at this concentration, the mean activity a_s at any other concentration "s" is given by the equation

$$E = \frac{3\ RT}{2\ F} ln \frac{a_s}{a_{c_1}} = 0.08872 \log \frac{a_s}{a_{c_1}} \qquad (2)$$

The activity coefficient γ may then be calculated from a_s according to its definition. In order to compute γ at different concentrations by these equations, it is necessary to evaluate it at one reference concentration. This has been done by using the general approximate equation derived by Hückel[10] which for uni-bivalent electrolytes is

$$\log \gamma = -\frac{0.708\sqrt{6c}}{1 + A\sqrt{6c}} + B(6c) - \log(1 + 0.054\ m) \qquad (3)$$

where c is the salt concentration in moles per liter of solution, m in moles per 1000 g. of water, and A and B are constants. The method of evaluation of the constants was similar to that described on p. 123 of Hückel's paper except that they were changed slightly to stress the results at the higher concentrations. At 0.025 M, the calculated values of γ were found to be 0.602, 0.608 and 0.613 for potassium, sodium and lithium sulfate solutions, respectively. These were used as reference values and all of the observed activity coefficients were calculated from the electromotive forces by their use. The values given by Lewis and Randall[11] for potassium sulfate are 0.592 (interpolated) and 0.505 at 0.025 M and 0.05 M, respectively. These were obtained from the freezing-point measurements of Hall and Harkins[12] in dilute solutions and agree very well with the values obtained from the electromotive-force data in concentrated solutions when extrapolated by the aid of Equation 3. The electromotive-force data of the cells designated, the observed and calculated activity coefficients, and the constants employed in Equation 3 are all given in Table I.

TABLE I

ACTIVITY COEFFICIENTS OF POTASSIUM, SODIUM AND LITHIUM SULFATES

Cells: Hg | Hg_2SO_4 | $M_2SO_4(c)$ | M_xHg | $M_2SO_4(0.1)$ | Hg_2SO_4 | Hg

POTASSIUM SULFATE $A = 0.662$ $B = -0.014$

c	m	E	γ (obs.)	γ (calcd.)
0.025	0.025	−0.01985	0.602	0.602
.05	.05	.0	.504	.513
.125	.125	.02407	.376	.395
.25	.248	.04201	.299	.313
.5	.494	.06009	.240	.239
.625	.621	.06539	.220	.218

---

[10] Hückel, *Physik. Z.*, **26**, 93 (1925).

[11] Ref. 9, pp. 344, 362.

[12] Hall and Harkins, THIS JOURNAL, **38**, 2658 (1916).

TABLE I (*Concluded*)

SODIUM SULFATE $A = 0.719$ $B = -0.0053$

	m	*E*	γ (obs.)	γ (calcd.)
0.025	0.025	−0.02018[a]	0.608	0.608
.05	.05	.0	.514	.524
.125	.125	.02546	.398	.412
.25	.249	.04522	.332	.335
.5	.495	.06344	.266	.267
1.	.975	.08092	.209	.208
1.5	1.438	.09092	.179	.177
2.	1.882	.09607	.155	.155

LITHIUM SULFATE $A = 0.767$ $B = 0.0087$

	m	*E*	γ (obs.)	γ (calcd.)
0.025	0.025	−0.02051	0.613	0.613
.05	.05	.0	.522	.535
.125	.125	.02744	.425	.432
.25	.249	.04809	.364	.363
.5	.495	.06838	.308	.308
1.	.979	.08904	.263	.269
1.5	1.447	.10408	.259	.253
2.	1.903	.11432	.254	.248

[a] This value was interpolated. The measured result was 0.01976.

The Activity Coefficient of Sulfuric Acid in Aqueous and in Potassium, Sodium and Lithium Sulfate Solutions

The electromotive force of the cell, Hg | Hg_2SO_4 | $H_2SO_4(c_1)$, $M_2SO_4(c)$ | H_2 | $H_2SO_4(c_1)$ | Hg_2SO_4 | Hg, is obtained by subtraction of the electromotive force of the acid-salt cell from that of the pure acid cell and is given by the equation

$$E = \frac{RT}{2\,F}\,ln\,\frac{a^2{}_{H(s)}\;a_{SO_4(s)}}{a^2{}_{H(c_1)}\;a_{SO_4(c_1)}} = 0.08872 \log \frac{a_s}{a_{c_1}} \qquad (4)$$

where a_s and a_{c_1} are the cube roots of the activity products of the acid in the salt solutions and aqueous acid solutions, respectively. Thus, if the activity coefficient of the acid is known at a concentration c_1, it may be calculated in the salt solutions. Two series of results were obtained with each salt, the acid concentrations being maintained constant at 0.005 *M* and 0.05 *M*, respectively. The results are assembled in Table III. The values in the 0.05 *M* series are thought to be accurate, but experimental difficulties arise when solutions of salts of concentrations under 0.05 *M* are added to the 0.005 *M* acid. When the electromotive-force measurements (Table III) are plotted graphically against the salt concentrations, minima appear in the curves near their origins. These minima are very pronounced in the 0.005 *M* acid series but insignificant in the 0.05 *M* series. Because they appear at the same salt concentrations and are therefore independent of the nature of the salt, it is thought that they are caused by secondary effects resulting from the solubility of mercurous sulfate in dilute solutions as suggested by other investigators. If this be true, the electromotive forces of the pure acid cells would be in error in solutions more dilute than 0.05 *M*, and the activity coefficients obtained from them would be erroneous.

In order to obtain the activity coefficients of the acid in the mixtures, it is necessary to obtain values for the activity coefficient of the acid in aqueous solution at 0.005 *M* and 0.05 *M* concentrations. Lewis and Randall[13] have obtained a series of values derived from freezing-point, electromotive-force and vapor-pressure data. If Equation 3 is valid, then it is possible to obtain activity coefficients in dilute solutions from measurements in concentrated solutions. As in the cases of the alkali sulfates, the constants of the Debye-Hückel theory have been evaluated by employing the electromotive-force data of Randall and Cushman for concd. sulfuric acid solutions. The observed and calculated values are given in Table II.

TABLE II

THE ACTIVITY COEFFICIENT OF SULFURIC ACID

$A = 0.4$ $B = 0.031$

m	E	γ (obs.)	γ (calcd.)
0.01	0.8269[a]	...	0.769
.05	.7557	0.488	.488
.1	.7372	.397	.396
.505	.6960	.228	.228
1.031	.6751	.192	.194
3.637	.6187	.235	.252

[a] Calculated. The value observed (See Table III) was 0.8169.

The agreement between the observed and calculated values between 0.05 *M* and 1 *M* acid is excellent and, since it is probable that accurate experimental results are to be found in this region of concentration, it would seem that this function could be used to extrapolate to at least 0.005 *M*. According to Equation 3, it is found that γ equals 0.769 at 0.005 *M*, corresponding to an electromotive force of 0.8269 volt whereas the observed electromotive force is 0.8169, a fact which indicates a large experimental error. From the freezing-point measurements of Hausrath[14] in dilute solutions, Lewis and Linhart[15] obtained 0.696 at 0.005 *M*. Their calculation was repeated and 0.72 was found to be as high a value as could possibly be inferred from Hausrath's results. The minimum value obtainable from Debye and Hückel's theory is 0.753 and, consequently, if Hausrath's results are correct, Debye and Hückel's theory is inapplicable to dilute solutions of sulfuric acid. On the other hand, since the present method of extrapolation when applied to the sulfates gave results which were closely in accord with the more recent freezing-point measurements of Hall and Harkins, it is thought to be justifiable to employ the same method for sul-

---

[13] Ref. 9, pp. 353–357.

[14] Hausrath, *Ann. Physik*, [4] **9**, 522 (1902).

[15] Lewis and Linhart, THIS JOURNAL, **41**, 1952 (1919).

furic acid, correct the electromotive force at 0.005 *M* acid and discard the bracketed results of the 0.005 *M* acid-salt series up to a concentration of 0.05 *M*. The results are given in Table III.

TABLE III

THE ACTIVITY COEFFICIENTS OF SULFURIC ACID IN POTASSIUM, SODIUM AND LITHIUM SULFATE SOLUTIONS

Cells: $H_2 \mid H_2SO_4(c_1), M_2SO_4(c) \mid Hg_2SO_4$

	0.05 *M* H_2SO_4			0.005 *M* H_2SO_4	
c	*E*	γ (obs.)	γ (calcd.)	*E*	γ (obs.)
	POTASSIUM SULFATE $B_s = -0.0407$				
0.0	0.7558	0.488	0.488	0.8169[a]	0.769
.00625	.7556	.471	.471	(.8148)	(.777)
.0125	.7557	.454	.453	(.8137)	(.714)
.025	.7561	.423	.423	(.8144)	(.585)
.05	.7574	.371	.367	.8164	.455
.1	.7600	.303	.313	.8202	.331
.2	.7652	.216	.237	.8255	.231
.375	.7709	.162	.171	.8312	.163
.5	.7739	.137	.137	.8341	.137
.625	.7766	.119	.118	.8369	.119
	SODIUM SULFATE $B_s = -0.0091$				
0.125	0.7555	0.456	0.456	(0.8132)	(0.723)
.025	.7558	.426	.428	(.8138)	(.594)
.05	.7563	.382	.385	.8161	.458
.1	.7590	.310	.327	.8190	.321
.25	.7635	.220	.237	.8252	.217
.5	.7689	.156	.171	.8289	.157
1.	.7737	.111	.116	.8339	.110
1.5	.7766	.090	.090	.8372	.088
2.	.7781	.079	.074	.8382	.078
	LITHIUM SULFATE $B_s = 0.0051$				
0.00625	0.7554	0.473	0.473	(0.8132)	(0.810)
.0125	.7553	.459	.456	(.8129)	(.729)
.025	.7555	.430	.430	(.8135)	(.600)
.05	.7563	.382	.389	.8153	.468
.1	.7581	.319	.333	.8179	.353
.25	.7617	.230	.249	.8213	.240
.5	.7651	.172	.189	.8248	.174
1.	.7667	.133	.141	.8265	.133
1.5	.7662	.119	.119	.8253	.120
2.	.7643	.113	.107	.8232	.115

[a] The corrected electromotive force was 0.8269 volt.

An approximate calculation of the activity coefficients of the acid in the sulfate solutions may be made by the mixture equations

$$\log \gamma = -\frac{0.708\ \sqrt{6(c_a + c_s)}}{1 + A\ \sqrt{6(c_a + c_s)}} + B(6c_a) + B_s(6c_s) - \frac{1}{3}\left[2 \log (1 + 0.054\ m_H) + \log (1 + 0.054\ m_{SO_4})\right] \quad (5)$$

where A and B are the constants of the pure acid, or 0.4 and 0.031, respectively, and B_s is an arbitrary constant; c_a and c_s are the molal concentrations of the acid and salt in 1000 cc. of solution, and m_a and m_s the molal concentrations of the hydrogen and sulfate ions in 1000 g. of water. The results of the calculation for the 0.05 M series are given in the fourth column of Table III. There is a good agreement between the calculated and observed results which indicates that the approximate equations of the Debye and Hückel theory are valid for these mixtures. The agreement was not quite so good for the 0.005 M series but this is to be expected since these results are probably not so accurate as the 0.05 M series.

The Debye and Hückel Constants for Potassium, Sodium and Lithium Sulfates and Sulfuric Acid

According to the Debye-Hückel theory, A in Equation 3 equals $\mathbf{a} \times 0.232 \times 10^8$ where "**a**" is the mean distance of approach of the ions. Hückel's extension of the theory to concentrated solutions involves the assumption of the linear variation of the dielectric constant of the medium, D, upon the addition of the electrolyte according to the equation

$$D = D_0 - \Sigma\, \delta_i\, c_i$$

where D_0 is the dielectric constant of the pure solvent and δ_i is a constant characteristic of an ion. The summation is for all the ions in the solution; δ_i is highest for the ions which possess the lowest electrostatic moment, which are least deformed by the electrical field and which produce the greatest polarization of water. If the electrostatic moment of the ion is greater than that of water, δ_i is negative and the ion will cause an increase in the dielectric constant of the medium. By means of Equation 85b in Hückel's paper, $B6c$ is given by

$$B6c = \frac{0.0194 \times 10^{-8} \times 4 \times 3c\,\bar{\delta}}{a\,(1 + A\,\sqrt{6c})} - \frac{0.00225\,\sqrt{6c}\,3c\,\bar{\delta}}{(1 + A\,\sqrt{6c})^2} + \frac{0.000246 \times 10^{-8}\,6(\bar{\delta}.3c)^2}{a}\left[\frac{3}{4}\,\frac{1}{1 + A\,\sqrt{6c}} + \frac{1}{4}\,\frac{1}{(1 + A\,\sqrt{6c})^2}\right] \qquad (6)$$

where $\bar{\delta}$ equals $(2\delta_{\mathrm{M}} + \delta_{\mathrm{SO_4}})/3$, and if the approximately valid assumption be made that in case of a single electrolyte the limiting distances "a_i" are the same for both ions. In Table IV the constants for the three sulfates and sulfuric acid are given. The values of δ_{M} were obtained from the calculations of the uni-univalent chlorides by Harned[16] upon the assumption that δ_{K} equals δ_{Cl}. From these and the $\bar{\delta}$ values, the values of $\delta_{\mathrm{SO_4}}$ in the different sulfate solutions were obtained.

The "a" values for the three metallic sulfates are not unreasonable since they are nearly the same as those obtained for the uni-univalent chlorides and somewhat smaller than those of the bi-univalent chlorides. The value

---

[16] Harned, This Journal, **48**, 326 (1926).

TABLE IV

DEBYE-HÜCKEL CONSTANTS FOR POTASSIUM, SODIUM AND LITHIUM SULFATES AND SULFURIC ACID

	K_2SO_4	Na_2SO_4	Li_2SO_4	H_2SO_4
A	0.662	0.719	0.767	0.400
a	2.85×10^{-8}	3.1×10^{-8}	3.31×10^{-8}	1.72×10^{-8}
B	−0.014	−0.0053	0.0087	0.031
$\delta_{M_2SO_4} = \dfrac{2\delta_M + \delta_{SO_4}}{3}$	−3.6	−1.4	2.1	2.4
δ_{Me}	3.2	7.8	19.8	20.3
δ_{SO_4}	−17.2	−19.7	−33.3	−33.4

for sulfuric acid is considerably lower. It is interesting to note that δ_{SO_4} differs in the different sulfate solutions and is in all cases negative, which indicates that the sulfate ion possesses a greater electrostatic moment than water and for this reason causes an increase in the dielectric constant of the medium, a possibility mentioned by Hückel (p. 147). Further, according to the calculated values of δ_{SO_4}, the electrostatic moment of the sulfate ion is greater in the presence of the hydrogen and lithium ions than in the presence of the sodium and potassium ions. This may indicate that the electrostatic moment of an ion may also be influenced by the presence of another ion, particularly in a case where the influenced ion has an initially high electrostatic moment.

The Activity Coefficients of Potassium and Sodium Hydroxide in the Corresponding Sulfate Solutions

The electromotive forces of the hydrogen—amalgam cells are related to the activities of the ions by the equation,

$$E = \frac{RT}{F}\, ln\, \frac{a_{M(s)}\, a_{OH(s)}\, a_{H_2O(c_1)}}{a_{M(c_1)}\, a_{OH(c_1)}\, a_{H_2O(s)}} \tag{7}$$

Subtraction of the quantity,

$$E_{H_2O} = \frac{RT}{F}\, ln\, \frac{a_{H_2O(c_1)}}{a_{H_2O(s)}} \tag{8}$$

gives the expression for the electromotive force of transfer of the hydroxides from the salt solutions to the aqueous solutions from which the activity product of the hydroxides in the salt solutions may be obtained from its value in pure water. The relation between the activities of the solute a_2 and the solvent a_1 may be expressed by the equation

$$\int \mathrm{d} \log a_2 = -\int \frac{N_1}{N_2}\, \mathrm{d} \log a_1 \tag{9}$$

where N_1/N_2 is the mole ratio of the solvent to the solute. The experimental results are given in Table V. Two series were obtained which give the activity coefficients of 0.01 and 0.1 N potassium hydroxide in potassium sulfate solutions and two series for 0.01 and 0.1 N sodium hydroxide in sodium sulfate solutions.

Table V

The Activity Coefficients of Potassium and Sodium Hydroxides in the Corresponding Sulfate Solutions

Cells: $H_2 \mid MOH(c_1), M_2SO_4(c) \mid M_xHg \mid MOH(c_1) \mid H_2$

Potassium Sulfate $B_s = 0.0070$

	$c_1 = 0.01\ N$ KOH				$c_1 = 0.1\ N$ KOH		
c	E	E_{H_2O}	γ (obs.)	γ (calcd.)	E	γ (obs.)	γ (calcd.)
0.0	0.0	.....	0.904	0.904	0.0	0.783	0.783
.0039	.01324	.....	.877	.867	.00167	.778	.776
.0078	.02160	.....	.861	.840	.00253	.764	.768
.0156	.03154	.....	.823	.808	.00514	.753	.754
.0312	.0429	.....	.779	.764	.00926	.735	.732
.0625	.0559	.....	.730	.714	.0152	.701	.699
.125	.0696	0.00002	.687	.661	.0245	.673	.659
.25	.0815	.00006	.617	.610	.0348	.627	.616
.5	.09423	.00022	.561	.566	.0463	.578	.576
.625	.0987	.00031	.549	.555	.05055	.565	.565

Sodium Sulfate $B_s = 0.0076$

	$c_1 = 0.01\ N$ NaOH				$c_1 = 0.1\ N$ NaOH		
.0	.0	.....	.901	.901	.0	.767	.767
.0312	.0147	.....	.752	.757	.00854	.713	.716
.0625	.05385	.....	.699	.701	.0145	.680	.680
.125	.06708	.00002	.651	.645	.0235	.650	.635
.25	.0789	.00007	.585	.586	.0335	.602	.578
.5	.0918	.00024	.534	.533	.0444	.547	.543
1	.1053	.00066	.488	.502	.0573	.505	.509
1.5	.1155	.00119	.475	.490	.0663	.491	.498
2	.1232	.00176	.489	.487	.0745	.495	.495
2.5	.1306	.00235	.490	..	.08145	.501	..

The activity coefficients of potassium and sodium hydroxides in aqueous solutions have been measured by Knobel[6] and Harned.[7a] These results may also be calculated by means of Equation 3. For potassium hydroxide A and B are found to be 0.777 and 0.063 and for sodium hydroxide, 0.660 and 0.05, respectively. Substitution of these values in Equation 3 gives 0.904 and 0.901 for the activity coefficients of potassium and sodium hydroxides at 0.01 M and 0.783 and 0.767 at 0.1 M, respectively. The calculations by Equation 7 were made by employing these values.

In the fifth and last columns of Table V are given the activity coefficient of these hydroxides calculated by the approximation equation

$$\log \gamma = -\frac{0.354\sqrt{2(c_{MOH}+3c_s)}}{1+A\sqrt{2(c_{MOH}+3c_s)}} + B_{MOH}\,2c_{MOH} + B_s\,6c_s - \frac{1}{2}\left[\log(1+0.036\,m_{OH}) + \log(1+0.036\,m_{M})\right] \qquad (10)$$

when the B_s values given in the table and the A and B values of the hydroxides are employed. The agreement between these calculated and the observed results is good for both the 0.01 and 0.1 N series. This is interesting because it shows that the same general equations, which were found by Harned to be valid within ±2% for the activity coefficient of hydrogen chloride in hydrochloric acid—chloride mixtures may also be employed in calculating these hydroxide mixtures.

The Ion Activity-Coefficient Product of Water in Potassium and Sodium Sulfate Solutions

A method for the determination of the ion activity-coefficient product and the dissociation of water in chloride solutions has been developed by Harned,[17] and this method may be employed for the calculation of the ion activity-coefficient product of water in the sulfate solutions although this calculation is somewhat more complicated. The electromotive forces of the cells, $H_2 \mid MOH(c_1), M_2SO_4(c) \mid M_xHg \mid MOH(c_1) \mid H_2$, are given by the equation

$$E_1 = \frac{RT}{F} ln \frac{a_{OH(s)}\ a_{M(s)}\ a_{H_2O(c_1)}}{a_{OH(c_1)}\ a_{M(c_1)}\ a_{H_2O(s)}} = \frac{RT}{F} ln \frac{\gamma_{M(s)}\ (c_1 + 2c_2)\ \gamma_{OH(s)}\ c_1\ a_{H_2O(c_1)}}{\gamma_{M(c_1)}\ c_1\ \gamma_{OH(c_1)}\ c_1\ a_{H_2O(s)}} \quad (11)$$

The electromotive forces of the cells, $Hg \mid Hg_2SO_4 \mid H_2SO_4(\frac{1}{2}c_1), M_2SO_4(c_2) \mid H_2 \mid H_2SO_4(\frac{1}{2}c_1) \mid H_2$, are given by

$$E_2 = \frac{RT}{2\ F} ln \frac{a^2{}_{H(s)}\ a_{SO_4(s)}}{a^2{}_{H(c_1)}\ a_{SO_4(c_1)}} = \frac{RT}{F} ln \frac{\gamma_{H(s)}\ c_1 \sqrt{\gamma_{SO_4(s)}\ (\frac{1}{2}c_1 + c_2)}}{\gamma_{H(c_1)}\ c_1 \sqrt{\gamma_{SO_4(c_1)}\ \frac{1}{2}c_1}} \quad (12)$$

The electromotive forces of the cells, $Hg \mid Hg_2SO_4 \mid M_2SO_4(\frac{1}{2}c_1 + c_2) \mid M_xHg \mid M_2SO_4(\frac{1}{2}c_1) \mid Hg_2SO_4 \mid Hg$, are given by

$$E_3 = \frac{RT}{2\ F} ln \frac{a^2{}_{M(s)}\ a_{SO_4(s)}}{a^2{}_{H(c_1)}\ a_{SO_4(c_1)}} = \frac{RT}{F} ln \frac{\gamma_{M(s)}\ (c_1 + 2c_2) \sqrt{\gamma_{SO_4(s)}\ (\frac{1}{2}c_1 + c_2)}}{\gamma_{M(c_1)}\ c_1 \sqrt{\gamma_{SO_4(c_1)}\ \frac{1}{2}c_1}} \quad (13)$$

The addition of E_1 to E_2 and the subtraction of E_3 gives

$$E_4 = E_1 + E_2 - E_3 = \frac{RT}{F} ln \frac{\gamma_{H(s)}\ \gamma_{OH(s)}\ a_{H_2O(c_1)}}{\gamma_{H(c_1)}\ \gamma_{OH(c_1)}\ a_{H_2O(s)}} = \frac{RT}{F} ln \frac{K_{\gamma(s)}}{K_{\gamma(c_1)}} \quad (14)$$

where $K\gamma_{(s)}$ equals $(\gamma_{H(s)}\gamma_{OH(s)})/a_{H_2O(s)}$, since the stoichiometrical concentrations of the hydrogen and hydroxyl ions are the same in the salt as in the reference solution. It should be noted that the first of these cells contains the hydroxide (MOH) at a concentration c_1, the second contains the sulfuric acid at a concentration of $\frac{1}{2}c_1$, or a stoichiometrical hydrogen-ion concentration of c_1, and the third contains the sulfate (M_2SO_4) at a concentration of $\frac{1}{2}c_1$, or sodium ion at a concentration c_1. As before, the concentrations are given in moles per liter of solution. Equation 14 would be strictly true if, in the first place, the sulfate ion had the same activity in a solution of sulfuric acid with metallic sulfate as in the pure alkali sulfate at the same total concentration and if, in the second place, the activity of the metal ion was the same in the hydroxide-sulfate mixtures as in a pure sulfate solution of the same total sodium-ion concentration. The first of these conditions is sufficiently approximated by the acid-salt mixtures. The second condition requires a correction which is given by

---

[17] Harned, THIS JOURNAL, 47, 930 (1925); Ref. 7 b.

$$\Delta E = 0.059 \left[\log \frac{f_{\mathrm{M}}^{\mathrm{II}}(c_1 + 2c_2)}{f_{\mathrm{M}}^{\mathrm{I}} c_1} - \log \frac{f_{\mathrm{M}}^{\mathrm{IV}}(c_1 + 2c_2)}{f_{\mathrm{M}}^{\mathrm{III}} c_1} \right] \tag{15}$$

where $f_{\mathrm{M}}^{\mathrm{II}}$ and $f_{\mathrm{M}}^{\mathrm{I}}$ are the activity coefficients of the metal ion in the metal sulfate at concentrations $(\frac{1}{2}c_1 + c_2)$ and $\frac{1}{2}c_1$, respectively, $f_{\mathrm{M}}^{\mathrm{IV}}$ is the activity coefficient of the metal ion in the metal hydroxide of concentration c_1 plus the metal sulfate at c_2 and $f_{\mathrm{M}}^{\mathrm{III}}$ is its activity coefficient in the metal hydroxide at a concentration c_1. By the use of the Debye-Hückel theory, the above equation becomes

$$\Delta E = 0.059 \, [-0.354 \sqrt{6(\tfrac{1}{2}c_1)} + 0.354 \sqrt{2c_1} + 0.354 \sqrt{6(\tfrac{1}{2}c_1 + c_2)} - 0.354 \sqrt{2(c_1 + 3c_2)}] \tag{16}$$

This correction is not very large and, therefore, the *A* and *B* terms of the Debye-Hückel equations may be neglected.

The results are given in Table VI. The first column gives the concentration of added salt, the next three columns the electromotive forces, E_1, E_2 and E_3, the fifth column gives the correction, ΔE and the sixth column $(E_4 + \Delta E)$, computed by Equations 14 and 16. Two series of results were computed for both the potassium and sodium sulfate solutions. For one series, c_1 was 0.01 and for the other, 0.1. In order to calculate $K_{\gamma(s)}$ and consequently $\sqrt{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}$ or γ, it is first necessary to compute its value in the 0.005 *M* sulfate solutions. To this end, the function of the Debye-Hückel theory for moderately dilute solutions was employed, namely,

$$\log \gamma = -\frac{0.354 \sqrt{6c}}{1 + A \sqrt{6c}} \tag{17}$$

Assigning the value of 0.7 to *A*, it is found that at 0.005 *M*, γ equals 0.882 and, therefore, $K_{\gamma(s)}$ equals 0.777. All values of $K_{\gamma(s)}$ and γ of the 0.01 *M* series are referred to this one. From a graphical inspection of $(E_4 + \Delta E)$, —0.0120 volt was taken to be the difference in electromotive force between the 0.01 *M* and 0.1 *M* series. From this result, according to Equation 14, $K_{\gamma(s)}$ equals 0.487 and γ equals 0.698 in the 0.05 *M* solutions of salt. All values of $K_{\gamma(s)}$ and γ in the 0.1 *M* series were calculated from these. Since the results for potassium and for sodium sulfates were so nearly the same in the very concentrated solutions, they have been taken to be identical up to 0.1 *M*. In the computation of γ, the correction for the activity of the water was made.

The values of $K_{\gamma(s)}$ and γ in Table VI are shown plotted in Fig. 3 against the square root of the molality along with similar results for the same quantity in sodium and potassium chlorides obtained by Harned. As shown by these curves, the results obtained from the 0.1 *M* series superimpose very well on those of the 0.01 *M* series in the cases of the two sulfates. The mean error derived from a smooth curve drawn through the points is ±0.5 mv. This is very good considering that the measurements

TABLE VI

THE ACTIVITY COEFFICIENT PRODUCT AND ACTIVITY COEFFICIENT OF WATER IN POTASSIUM AND SODIUM SULFATE SOLUTIONS

c_2	E_1	E_2	E_3	ΔE	$(E_4 + \Delta E)$	$K_{\gamma(s)}$	γ
POTASSIUM SULFATE $c_1 = 0.01$							
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.777	0.882
.05	.0535	.0103	.0745	− .0005	− .0112	.503	.709
.125	.0696	.0048	.0971	− .0006	− .0233	.307	.615
.25	.0815	.0007	.1144	− .0006	− .0328	.217	.467
.375	.0887	− .0043	.1248	− .0007	− .0411	.157	.397
.5	.0942	− .0072	.1322	− .0007	− .0459	.130	.363
.625	.0987	− .0100	.1377	− .0007	− .0497	.112	.387
$c_1 = 0.1$							
.0	.0000	.0000	.0000	.0000	.0000	.487	.698
.05	.0134	− .0017	.0183	− .0007	− .0073	.366	.606
.125	.0245	− .0052	.0330	− .0010	− .0147	.275	.525
.25	.0348	− .0113	.0470	− .0013	− .0248	.186	.431
.375	.0412	− .0151	.0558	− .0014	− .0311	.145	.382
.5	.0463	− .0181	.0616	− .0015	− .0349	.125	.355
.625	.0506	− .0209	.0668	− .0015	− .0386	.108	.331
SODIUM SULFATE $c_1 = 0.01$							
.0	.0000	.0000	.0000	.0000	.0000	.777	.882
.05	.0507	.0111	.0748	− .0005	− .0135	.459	.678
.125	.0671	.0065	.0989	− .0006	− .0259	.283	.533
.25	.0789	.0017	.1181	− .0006	− .0381	.177	.422
.5	.0918	− .0020	.1359	− .0007	− .0468	.126	.356
1	.1053	− .0070	.1533	− .0007	− .0557	.089	.302
1.5	.1155	− .0103	.1632	− .0007	− .0587	.079	.288
2	.1233	− .0113	.1683	− .0007	− .0570	.084	.301
$c_1 = 0.1$							
0.0	.0000	.0000	.0000	.0000	.0000	.487	.698
.05	.0124	− .0006	.0196	− .0007	− .0085	.350	.590
.125	.0235	− .0042	.0354	− .0010	− .0171	.250	.500
.25	.0335	− .0077	.0502	− .0013	− .0257	.179	.424
.5	.0444	− .0131	.0664	− .0015	− .0366	.117	.344
1	.0573	− .0180	.0823	− .0017	− .0447	.086	.296
1.5	.0663	− .0208	.0917	− .0018	− .0480	.079	.281
2	.0745	− .0224	.0966	− .0019	− .0464	.080	.293

of three cells were necessary for the determination of one point on the curve. As in the case of the chlorides, the ion activity-coefficient product of water is slightly less in the solution of the sodium than in the corresponding potassium salt.

From the values of $K_{\gamma(s)}$, and the thermodynamic equation

$$K_w = \frac{a_{\mathrm{H}} a_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} = \frac{\gamma_{\mathrm{H}} \gamma_{\mathrm{OH}}\ c_{\mathrm{H}} c_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} = K_{\gamma(s)}\ c_{\mathrm{H}} c_{\mathrm{OH}} \qquad (17)$$

the values for the ion concentration product, c_Hc_{OH}, in these sulfate solutions may be calculated. K_w is the ionic product of pure water and equals 1.005×10^{-14} at 25°, and c_H and c_{OH} are the concentrations of the ions denoted by subscripts. According to the results in Table VI, $\sqrt{c_Hc_{OH}}$ will increase very rapidly upon the first addition of the potassium or sodium sulfate. Sodium sulfate causes a slightly greater increase than potassium sulfate. In the sodium sulfate solutions, it reaches a maximum value of 3.6×10^{-7} at 1.5 *M*, and above this concentration it decreases somewhat with increasing salt concentration. No such minimum is observed in the case of the potassium sulfate solutions, since the saturated solution of this salt is reached at about 0.7 *M*.

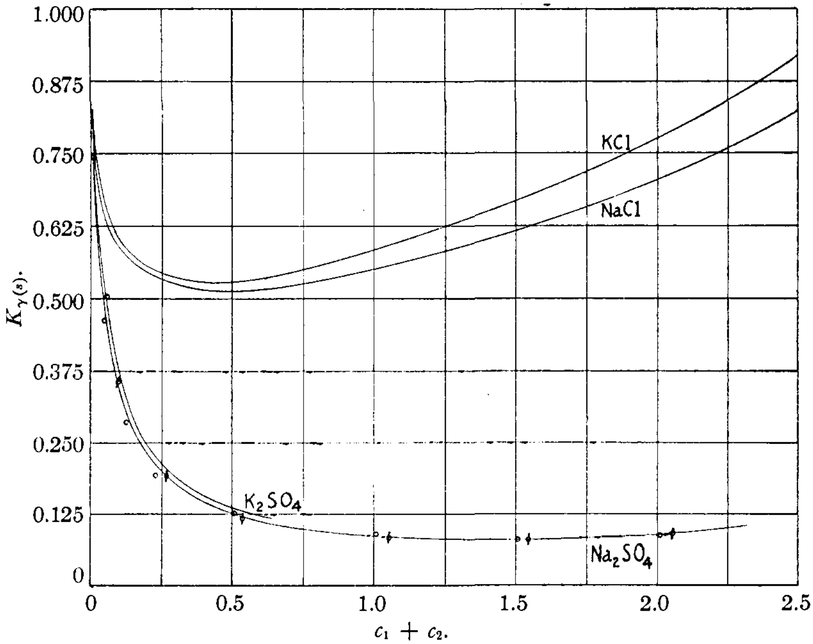

Fig. 3.—Plots of $K_{\gamma(s)}$ against $(c_1 + c_2)$. ⊙ = 0.01 *M* series; ⌽ = 0.1 *M* series.

This investigation was made possible through a Swedish Liljevalch Fellowship and part of a du Pont Fellowship. The author wishes to express his sincere thanks to Dr. Walter T. Taggart for his help in making this investigation possible.

Summary

1. Measurements of the following cells have been made:

I. $Hg \mid Hg_2SO_4 \mid M_2SO_4(c) \mid M_xHg \mid M_2SO_4(c_1) \mid Hg_2SO_4 \mid Hg$
II. $H_2 \mid H_2SO_4(c_1), M_2SO_4(c) \mid Hg_2SO_4 \mid Hg$
III. $H_2 \mid M_2SO_4(c), MOH(c_1) \mid M_xHg \mid MOH(c_1) \mid H_2$

Here c_1 is the reference and c the salt concentration. The experimental methods have been improved and discussed.

2. From the measurements of cells of Type I, the activity coefficients of potassium, sodium and lithium sulfates have been calculated. These results have been considered from the point of view of the Debye and Hückel theory, as well as the results of Randall and Cushman on pure sulfuric acid.
3. From measurements of cells of Type II, the activity coefficients of sulfuric acid in potassium, sodium and lithium sulfate solutions have been calculated.
4. From measurements of cells of Type III, the activity coefficients of potassium and sodium hydroxides in their corresponding sulfate solutions have been calculated.
5. The activity coefficients of sulfuric acid in the uni-bivalent sulfate solutions and of the hydroxides in the corresponding sulfate solutions have been calculated by approximation equations, similar to those resulting from the theory of Debye and Hückel.
6. The ion activity-coefficient of water in the salt solutions has been computed from the results of these three cells. This quantity was found to be greater in potassium than in sodium sulfate solution at a given concentration, a fact in agreement with the behavior of potassium and sodium chloride solutions.
7. From these results, it appears that the square root of the ionic concentration product of water, $\sqrt{c_Hc_{OH}}$, is rapidly increased by the first addition of the sulfates, and that sodium sulfate causes a somewhat greater increase in this quantity than potassium sulfate. In the sodium sulfate solutions, $\sqrt{c_Hc_{OH}}$ reaches a maximum at 1.5 M and then decreases somewhat with increasing salt concentration.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A MODIFIED TYPE OF GAS VOLUME-METER FOR THE DETERMINATION OF THE DENSITIES OF SOLIDS

BY GEORGE M. KARNS

RECEIVED DECEMBER 29, 1925 PUBLISHED MAY 5, 1926

Determination of the densities of solids by a method of gas displacement serves to eliminate the error due to exclusion of liquid from porous material and also avoids contamination of the sample. Density determinations have been made by computing the volume from the weight of air displaced by the sample.[1] As early as 1879 instruments were described by means of which the volumes of solids were determined by measuring the volume change with changing pressure of the residual air in a chamber in which the solid was confined.[2] Highly refined instruments of this type have been

---

[1] Baxter and Hilton, THIS JOURNAL, **45**, 700 (1923).

[2] Rüdorff, *Ber.*, **12**, 249 (1879).