[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

A Study of the Solubility of Strong Electrolytes in Concentrated Solutions

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1. **Introduction.**—This paper gives first a review of some simple relationships that exist between the thermodynamic activities of strong electrolytes in pure or mixed aqueous solutions. These relationships have been applied to some measurements of the solubility of silver sulfate in solutions of high ionic strengths and also utilized for the development of a simple empirical method of computing the composition of saturated, mixed solutions of highly soluble strong electrolytes. The equations deduced have been tested for some of the simplest cases and found to reproduce the experimental solubility curves with at least the same accuracy as that of the data employed.

For the purpose of the calculation of the activity coefficients of strong electrolytes as a function of the concentration, frequent use has been made in recent literature of the equation of Hückel,[1] which is characterized by the addition of a term linear in the concentration to the original equation of Debye and Hückel assumed to take into consideration the influence of the mean distance of approach of the ions. If for two different strong electrolytes of the same valence type the apparent ionic diameters are the same, it follows that

$$\log \gamma_1/\gamma_2 = kc \qquad (1)$$

where γ_1 and γ_2 are the activity coefficients, k is a constant, and c the molar concentration. Upon a reëxamination of the existing accurate measurements of activity coefficients of strong electrolytes we have found that they follow with unexpected accuracy and over a very wide concentration range an empirical rule that may be expressed in a manner very similar to equation (1). If we select one of a group of electrolytes of the same valence type as a reference substance, the logarithm of the ratio of the activity coefficient of any other electrolyte in this group to that of the reference electrolyte varies linearly with the molality m

$$\log \gamma/\gamma_R = k_1 m \qquad (2)$$

An excellent illustration of equation (2) in the case of uni-univalent electrolytes is given in Fig. 1. As a reference substance hydrochloric acid has been employed, since it is unusually well suited for this purpose due to numerous accurate investigations of its activity coefficient.[2]

Harned and Ehlers estimate from the results of a very comprehensive study over a concentration range from 0.001 to 4 molal and a temperature range of 0 to 60° that between 0 and 30° the probable error in the value of the activity coefficient of hydrochloric acid as calculated from the equations they give is less than ±5 in the fourth decimal place. The differences between observed activity coefficients of other uni-univalent electrolytes and the values calculated from equation (2) should in general be expected to be larger than the errors in the values of the activity coefficient of the reference substance, since the individual errors are added. In the case of such electrolytes as sodium and potassium chloride for which a large number of accurate measurements are available, the average difference between observed and calculated values in the concentration range 0.001 to 4 molal is less than 0.002, which corresponds to errors smaller than 0.2 millivolt in the case of electromotive force measurements. A survey of the activity coefficient data of 25 uni-univalent strong electrolytes, partially summarized by Fig. 1, has shown that for no one of them do the deviations from equation (2) exceed reasonable limits to be expected from ordinary experimental errors.

The behavior of a given strong uni-univalent electrolyte in mixed solution with another electrolyte of the same valence type is completely analogous to its behavior in pure solutions. That this is the case is shown in Fig. 2.[3] The logarithms of the ratios of the activity coefficient of 0.01 molal hydrochloric acid in potassium chloride solutions and those of the same acid in mixed solution with the other alkali chlorides at identical acid and corresponding total concentrations have been plotted against the latter. The measurements at present available for strong electrolytes of higher valence types are only in a few cases

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[1] Hückel, *Physik. Z.*, **26**, 93 (1925); Harned and Åkerlöf, *ibid.*, **27**, 411 (1926); Harned, THIS JOURNAL, **48**, 326 (1926); and others.

[2] Randall and Young, *loc. cit.*, give a critical study of all the older measurements; Harned and Ehlers, *loc. cit.*

[3] Data for Fig. 2 from Harned and Åkerlöf, *loc. cit.*, and Harned and Schupp, *loc. cit.*

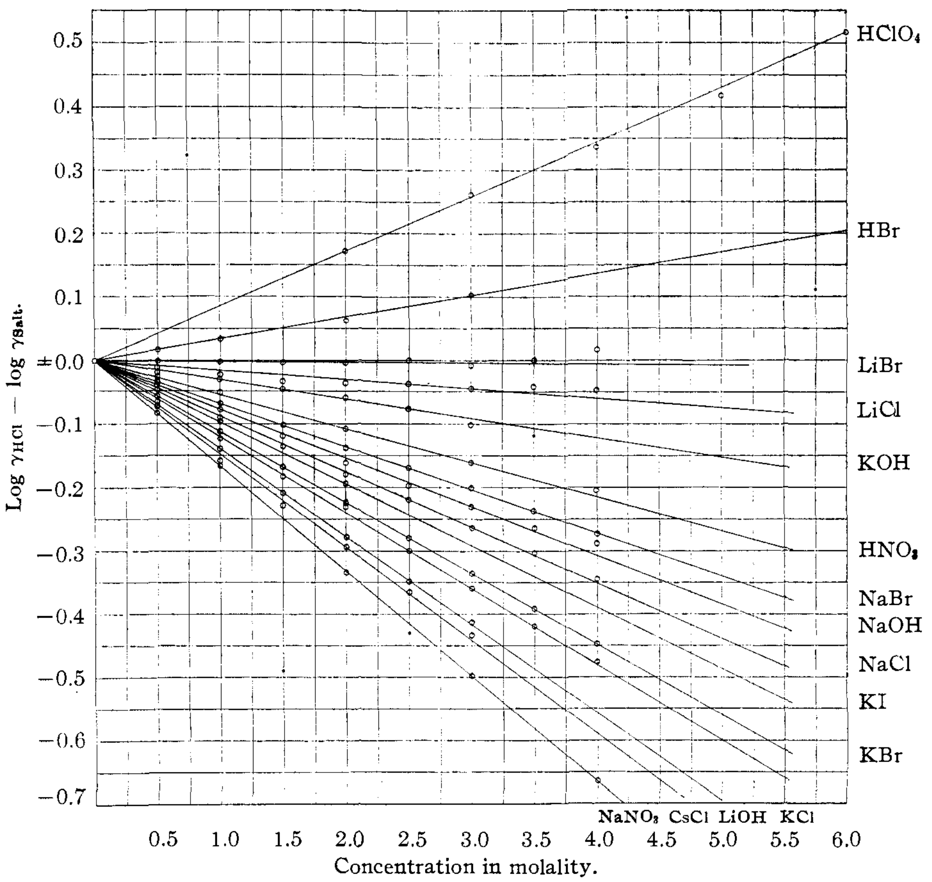

Fig. 1.—Curves for the logarithm of the ratio between the activity coefficient of hydrochloric acid and the following compounds: perchloric acid (k_1 0.086), hydrobromic acid (0.050), lithium bromide (−0.002), lithium chloride (−0.015), potassium hydroxide (−0.030), nitric acid (−0.054), sodium bromide (−0.068), sodium hydroxide (−0.077), sodium chloride (−0.088), potassium iodide (−0.097), potassium bromide (−0.112), potassium chloride (−0.118), lithium hydroxide (−0.139), cesium chloride (−0.147), sodium nitrate (−0.166). Cesium hydroxide gives for k_1 −0.020, sodium iodide −0.043.

Data for Fig. 1.—Activity coefficient of hydrochloric acid: Randall and Young, THIS JOURNAL, **50**, 989 (1928); Harned and Ehlers, *ibid.*, **55**, 2179 (1933). Activity coefficient of potassium, sodium and lithium chlorides and bromides: Harned, *ibid.*, **51**, 416 (1929); potassium chloride also Scatchard, *ibid.*, **47**, 648 (1925); Spencer, *ibid.*, **54**, 4490 (1932); Lovelace, Frazer and Sease, *ibid.*, **43**, 102 (1921); R. P. Smith, *ibid.*, **55**, 3279 (1933); sodium chloride also Harned and Nims, *ibid.*, **54**, 423 (1932); Lewis and Randall, "Thermodynamics," p. 351; Young and Vogel, THIS JOURNAL, **54**, 3030 (1932); Scatchard, *loc. cit.*; lithium chloride also MacInnes and Beattie, *ibid.*, **42**, 1123 (1920). Activity coefficient of cesium chloride: Harned and Schupp, *ibid.*, **52**, 3886 (1930). Activity coefficient of hydrobromic acid: Bates and Kirschmann, *ibid.*, **41**, 1991 (1919); Lewis and Randall, "Thermodynamics," p. 519; measurements of James published by Harned; THIS JOURNAL, **51**, 416 (1929). Activity coefficient of lithium hydroxide: Harned and Swindells, *ibid.*, **48**, 126 (1926); activity coefficient of sodium hydroxide, Harned, *ibid.*, **47**, 676 (1925); Harned and Hecker, *ibid.*, **56**, 650 (1934). Activity coefficient of potassium hydroxide: Knobel, *ibid.*, **45**, 70 (1923); Scatchard, *ibid.*, **47**, 648 (1925). Activity coefficient of cesium hydroxide: Harned and Schupp, *loc. cit.*; activity coefficient of perchloric acid, Pearce and Nelson, *ibid.*, **55**, 3075 (1933). Nitric acid: Abel, Redlich and Lengyel, *Z. physik. Chem.*, **132**, 189 (1928). Ammonium chloride and sodium nitrate: Redlich and Rosenfeld, Aktivitätskoeffizienten in Landolt-Börnstein, "Physik. Chemische Tabellen," 5th ed., 2d Erganzbd., Part 2.

sufficiently reliable or extensive for this test. Thus the alkaline earth chlorides and the alkali sulfates seem to behave quite similarly to the uni-univalent electrolytes, giving a linear variation of the logarithm of the ratio of the activity coefficients of two salts. However, in most cases the lines obtained do not pass exactly through the origin unless all the values of the activity coefficients of one of the two substances are multiplied with a factor slightly different from unity. In view of the uncertainty of the extrapolation methods this procedure might well be justified. The factor for calcium chloride is 1.030 and for sodium sulfate 1.050 with barium chloride as reference substance. The curves are shown in Fig. 3. In the case of salts of heavy metals like zinc and cadmium the data available do not appear to give a linear variation of the logarithmic differences of their activity coefficients. This may be due to the very large dispersion of the curves even at very low concentrations. A slightly incorrect choice of activity coefficient at the reference concentration adopted gives entirely erroneous values of the logarithmic differences. Hence it becomes necessary in the treatment of solutions of salts of heavy metals to employ a somewhat different method which obviates these difficulties.

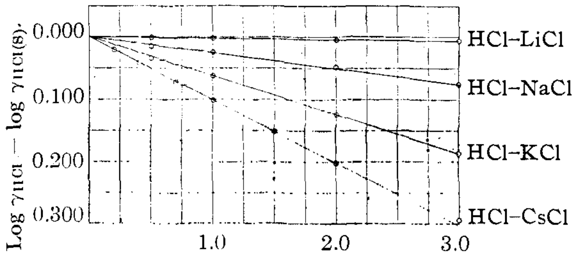

Fig. 2.—Curves for log γ_{HCl} − log $\gamma_{HCl(S)}$, where γ_{HCl} denotes the proper value in a pure aqueous solution of the same concentration as the total concentration of the 0.01 molal acid–salt solution for which the value of log $\gamma_{HCl(S)}$ was obtained.

From the geometry of Figs. 1, 2 and 3 it follows immediately that in a series of solutions with two electrolytes present at constant total ionic strength the slope of the curve obtained for the logarithm of the activity coefficient of either one of them as plotted against their respective concentrations should be independent of the total concentration and, since this is the case, the simplest form these curves could have would be linear. This seems to agree with the true conditions up to the highest concentrations at which reliable measurements have been obtained. The relation holds not only for mixtures of strong electrolytes of the same but also for mixtures of different valence types.[4] Measurements with solutions of zinc and cadmium chloride have shown that in this respect their behavior is identical with that of solutions of typical strong electrolytes such as the alkali or alkaline earth chlorides. A few curves obtained from data in the literature and some unpublished measurements are shown in Fig. 4.

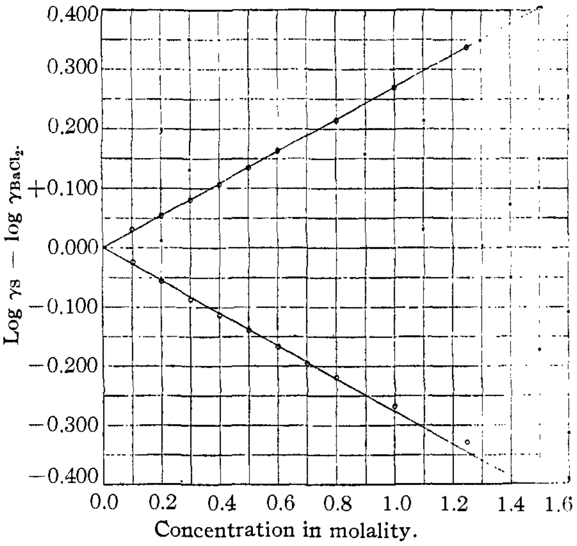

Fig. 3.—Curves for log γ_S–log γ_{BaCl_2} of calcium chloride (upper curve) and sodium sulfate (lower curve) in pure aqueous solutions as plotted against concentration in molality.

We have found that strong electrolytes with respect to each other show very simple relationships between their activity coefficients as functions of the concentrations. We will now inquire into the relationships which exist in mixed solutions, one component of which is known to be but partially dissociated. Since in mixed solutions of two strong electrolytes the logarithm of the activity coefficient of either one varies linearly with the ionic strength, it would seem safe to conclude that a similar variation should hold for a third strong electrolyte present in small quantities. It would seem to be equally safe to draw the conclusion that if one of the first two electrolytes is only partially dissociated, with the result that the actual ionic strength of the solution differs from its stoichiometrical value, a deviation from the linear variation would be obtained for the logarithm of the activity coefficient. The deviation should be the greater the smaller the

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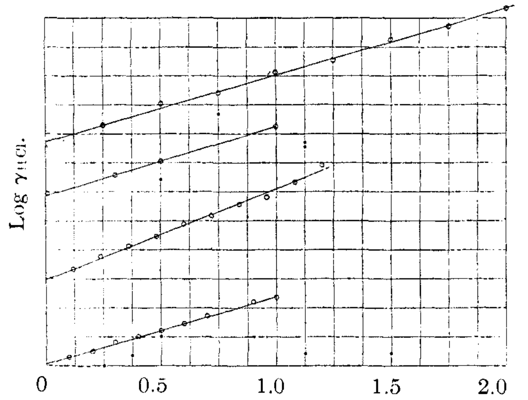
[4] Hückel, *loc. cit.*;[3] Harned and Åkerlöf, *loc. cit.*;[3] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned and Harris, THIS JOURNAL, **50**, 2633 (1928); Harned and Mason, *ibid.*, **53**, 3377 (1931); Hawkins, *ibid.*, **54**, 4480 (1932); and others.

dissociation constant of the partially dissociated electrolyte.



Ionic strength of hydrochloric acid.

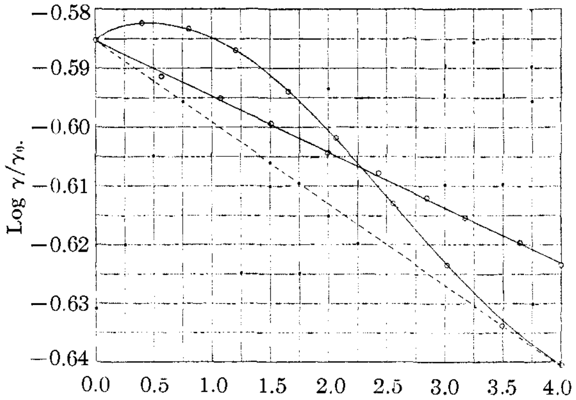
Fig. 4.—Curves for the logarithm of the activity coefficient of hydrochloric acid in mixed solutions of salts of various valence types at constant total ionic strength.

Data for Fig. 4 from Harned and Mason, *loc. cit.*, for hydrochloric acid–aluminum chloride mixtures. To Mr. M. J. Weldon and Mr. R. O. Sutherland, respectively, both of this Laboratory, we are indebted for the measurements on the mixtures hydrochloric acid–zinc chloride and hydrochloric acid–calcium chloride. Data for hydrochloric acid–sodium chloride from Harned and Åkerlöf, *loc. cit.*

2. The Solubility of Silver Sulfate in Sulfuric Acid and Sulfate Solutions.—In order to test the above conclusions the solubility of silver sulfate has been determined in mixed solutions of sulfuric acid and magnesium sulfate and also in mixed solutions of the latter electrolyte with lithium sulfate and with cadmium sulfate. In all cases solutions of the same total (constant) stoichiometrical ionic strength were used. Sulfuric acid is definitely known to be only partially dissociated. The second dissociation constant has been determined by Noyes and Sherrill using a conductance method.(5)

Silver sulfate was prepared by mixing boiling solutions of sulfuric acid and silver nitrate in equivalent amounts. After cooling the precipitated silver sulfate was washed a number of times with conductivity water. The washed crystals were collected in a Buchner funnel without filter paper and then dried in a covered porcelain dish for a period of several days at 200°. Stock solutions of the salts employed were made up from the best material available and analyzed gravimetrically according to standard methods, using three samples in each case. The average differences between the values obtained were usually within 0.06%. From the stock solutions others of the desired concentration were prepared in quantities of about 800 cc. by weighing in the calculated amount of water. Portions of 150–200 cc. of these solutions were transferred to small bottles containing about 5 g. of silver sulfate. These bottles were tightly stoppered with rubber stoppers and rotated at about 10 r. p. m. over a period of twenty hours in a water thermostat. This period was found ample for the attainment of equilibrium. The temperature of the thermostat was regulated to 25° with a precision of 0.01° and controlled with the same accuracy.

Duplicate samples of about 75 cc. were withdrawn for analysis. The pipets used in sampling were provided with a removable cotton filter to retain any solid particles. The samples were weighed in small glass-stoppered Erlenmeyer flasks, which contained about 25 cc. of water to prevent precipitation of silver sulfate when the sample cooled to room temperature. Silver was determined gravimetrically as the chloride. Three independent determinations gave the following values for the solubility of silver sulfate in pure water at 25°: 0.02677, 0.02675, 0.02676 mole per 1000 grams of water.



Stoichiometrical ionic strength of H_2SO_4 or $CdSO_4$.

Fig. 5.—Curves for the logarithm of the activity coefficient of silver sulfate in mixed solutions of (1) magnesium and cadmium sulfate (full, straight line) and (2) magnesium sulfate and sulfuric acid (curved line). The dotted line is drawn to stress the curvature of the second line. In both cases the total stoichiometrical ionic strength was kept constant.

In Fig. 5 are shown the curves representing the measurements given in Table I for mixed solutions of magnesium sulfate and sulfuric acid and magnesium and cadmium sulfates, respectively. In the first case a strongly curved line is obtained, in the second a straight line with very small variations for any one of the points. On this last curve there is only one point that is off a little more than one unit in the third place of the logarithm. Following the reasoning given above, since sulfuric acid is only partially dissociated, substitution of part of the ionic strength due to magnesium sulfate by this acid must lower the actual ionic strength of their mixed solutions.

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(5) Noyes and Sherrill, This Journal, **48**, 1861 (1926).

TABLE I

THE SOLUBILITY OF SILVER SULFATE IN MIXED SOLUTIONS OF (1) SULFURIC ACID AND MAGNESIUM SULFATE, (2) MAGNESIUM AND CADMIUM SULFATES, (3) MAGNESIUM AND LITHIUM SULFATES, (4) ALUMINUM AND ZINC SULFATES, AT CONSTANT TOTAL STOICHIOMETRICAL IONIC STRENGTH

(1) Sulfuric acid and magnesium sulfate					(2) Magnesium and cadmium sulfates				
m $MgSO_4$	m H_2SO_4	s Ag_2SO_4	μ total	$-\log \gamma/\gamma_0$	m $MgSO_4$	m $CdSO_4$	s Ag_2SO_4	μ total	$-\log \gamma/\gamma_0$
0.0000	1.333	0.03460	4.104	0.6406	0.0000	1.0000	0.03703	4.111	0.6235
.1262	1.165	.03395	4.101	.6338	.0906	0.9095	.03656	4.110	.6197
.2449	1.007	.03327	4.099	.6235	.2053	.7946	.03604	4.108	.6155
.3620	0.8505	.03259	4.097	.6130	.2884	.7116	.03563	4.107	.6121
.4835	.6889	.03188	4.096	.6018	.3922	.5906	.03499	4.036	.6078[a]
.5862	.5518	.03150	4.095	.5940	.5003	.4990	.03472	4.101	.6044
.6978	.4030	.03125	4.094	.5870	.6231	.3766	.03412	4.102	.5994
.8001	.2667	.03132	4.094	.5833	.7316	.2633	.03360	4.081	.5951[b]
.9006	.1327	.03172	4.096	.5824	.8586	.1413	.03322	4.100	.5915
1.000	.0000	.03253	4.098	.5853	1.000	.0000	.03253	4.098	.5853

[a] Corrected to $\mu = 4.104$. [b] Corrected to $\mu = 4.100$.

(3) Magnesium and lithium sulfates[a]					(4) Aluminum and zinc sulfates[b]				
m $MgSO_4$	m Li_2SO_4	s Ag_2SO_4	μ total	$-\log \gamma/\gamma_0$	m $ZnSO_4$	m $Al_2(SO_4)_3$	s Ag_2SO_4	μ total	$-\log \gamma/\gamma_0$
0.0000	1.333	0.03354	4.101	0.6348	0.0000	0.2667	0.03035	4.091	0.5337
.1250	1.166	.03340	4.100	.6291	.1000	.2400	.03086	4.093	.5421
.2500	1.000	.03302	4.099	.6211	.2000	.2133	.03135	4.094	.5501
.3750	0.8333	.03288	4.099	.6151	.3000	.1867	.03187	4.096	.5582
.5000	.6667	.03257	4.098	.6074	.4000	.1600	.03239	4.098	.5662
.6250	.5000	.03247	4.097	.6013	.5000	.1333	.03302	4.099	.5750
.7500	.3333	.03233	4.097	.5948	.6000	.1067	.03352	4.101	.5825
.8750	.1667	.03246	4.097	.5904	.8000	.0533	.03477	4.104	.5992
1.000	.0000	.03250	4.098	.5851	.9000	.0267	.03524	4.106	.6060
					1.000	.0000	.03594	4.108	.6147

[a] Measurements of Mr. J. G. Baxter of this Laboratory. [b] Measurements of Mr. N. D. Embree of this Laboratory. In these cases the analyses were done by electrometric titration.

The activity coefficient of silver sulfate increases with decreasing ionic strength and it was to be expected that the curve for the acid-salt mixtures would first show a rise, pass through a maximum and then fall off to the value found for the pure acid solution. The curve for mixed solutions of magnesium and cadmium sulfates shows a behavior analogous to that of, say, hydrochloric

TABLE II

THE SOLUBILITY OF SILVER SULFATE IN PURE AQUEOUS SOLUTIONS OF (1) MAGNESIUM SULFATE, (2) COPPER SULFATE, (3) ZINC SULFATE, (4) SULFURIC ACID

(1) Magnesium sulfate			(2) Copper sulfate			(3) Zinc sulfate		
m $MgSO_4$	s Ag_2SO_4	$-\log \gamma/\gamma_0$	m $CuSO_4$	s Ag_2SO_4	$-\log \gamma/\gamma_0$	m $ZnSO_4$	s Ag_2SO_4	$-\log \gamma/\gamma_0$
0.1273	0.02488	0.2335	0.1061	0.02587	0.2242	0.1225	0.02567	0.2357
.3017	.02636	.3615	.2160	.02711	.3262	.2528	.02715	.3441
.4611	.02789	.4356	.3262	.02856	.3960	.3855	.02885	.4134
.6266	.02948	.4942	.4465	.03018	.4547	.5256	.03058	.4779
.7986	.03093	.5420	.5634	.03170	.5011	.6784	.03234	.5296
.9711	.03222	.5815	.6789	.03314	.5399	.8285	.03399	.5720
1.143	.03335	.6144	.8224	.03482	.5811	.9601	.03529	.6036
1.343	.03442	.6463	.9426	.03613	.6109	1.152	.03707	.6436
1.545	.03525	.6731	1.097	.03770	.6447	1.322	.03842	.6734
1.718	.03569	.6919	1.235	.03899	.6712	1.507	.03971	.7016
1.973	.03618	.7155						
			(4) Sulfuric acid[c]					
0.0050	0.02695	0.0279	0.7500	0.03416	0.5597	1.750	0.03428	0.6797
.1000	.02919	.2531	1.000	.03468	.6042	2.000	.03376	.7042
.2510	.03115	.3850	1.250	.03481	.6366	2.500	.03269	.7167
.5000	.03315	.4951	1.500	.03522	.6658	2.973	.03092	.7252

[c] Measurements of Mr. W. M. Steinecke of this Laboratory.

acid–sodium chloride mixtures, in other words analogous to that of typical strong electrolytes. In this case the actual ionic strength may coincide with the stoichiometrical value. The determinations of the activity coefficient of silver sulfate in solutions of magnesium and lithium sulfates and also in solutions of zinc and aluminum sulfates give the same general result, a linear variation of the logarithm of the activity coefficient.

As previously mentioned, in mixed solutions of two strong electrolytes at constant total ionic strength the slopes of the curves for the logarithm of the activity coefficient of either one of the two as plotted against their respective concentrations are independent of the total concentration. That this must be true for mixed solutions of various sulfates has been found by a study of the data given in Table II for solutions of magnesium, copper and zinc sulfates. Interpolations on large scale plots to round values of the ionic strength do show a slight trend in the slope for mixed solutions of a given salt pair even at fairly high values of ionic strength. This trend is due to the changing ratio between the concentrations of silver sulfate and salt present. By applying a small correction factor the values obtained for the slope at different concentrations are constant. On the other hand, the data in Table II for sulfuric acid indicate that in mixed solutions of this acid and a metal sulfate, assuming linear variation of the logarithm of the activity coefficient, the slope is constantly changing with the total concentration, which fact is also evident from the curves in Fig. 6.

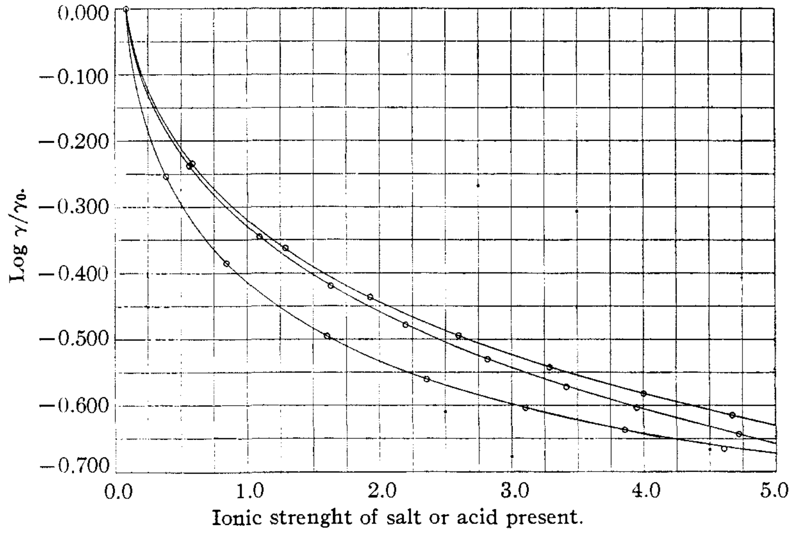

Fig. 6.—Curves for the logarithm of the activity coefficient of silver sulfate in pure solutions of (1) magnesium sulfate (top curve), (2) zinc sulfate (middle curve) and (3) sulfuric acid.

3. The Calculation of the Composition of Saturated, Mixed Solutions of Highly Soluble Strong Electrolytes.—The conclusions inferred from the experimental results given above are on closer analysis untenable if extended to other cases without certain precautions. They do, however, suggest a very simple method of analysis of equilibrium conditions and a method for the calculation of the composition of saturated mixed solutions of highly soluble strong electrolytes. Since the activity of a substance in solution must be constant in the presence of the solid phase, the activity in a series of solutions with the same solid phase may be determined at any point desired. For easily soluble strong electrolytes actual measurements at the saturation point are not available in a single case. It is necessary first to find a method which allows an accurate calculation of the activity of the electrolyte in saturated solution. The method needed is indicated by our introductory discussion. Thus if the curve for the activity coefficient of a given strong electrolyte is known at higher concentrations than the saturation point of some other electrolyte of the same valence type, the logarithm of the activity coefficient of the latter at this point may be obtained simply by adding the product of a certain constant and the saturation concentration to the logarithm of the activity coefficient of the first electrolyte at the same concentration.

The next step in our calculations is the evaluation of the activity coefficient of the substance forming the solid phase in a solution containing one other strong electrolyte at an arbitrary concentration. The principle of the linear variation of the logarithm of the activity coefficient of an electrolyte in solutions of constant total ionic strength gives immediately the method desired for this purpose. Using a measured value for the solubility of the first electrolyte in the presence of the one added to an arbitrary concentration, the activity coefficient which the first electrolyte would have in a real or hypothetical pure solution of the same total ionic strength as the solution in which the solubility determination was made is calculated by the same method as was described above for the computation of the activity coefficient at the saturation point. The activity coefficient of the saturating electrolyte in the mixed solution is calculated using the previously obtained value for the activity at the saturation point in the pure solvent according to the usual method. We now have all the data necessary for the calculation of the slope of the curve for the logarithm of the activity coefficient of the electrolyte forming the solid phase in all solutions of constant total ionic strength. The value of this slope in a number of cases may be calculated independently of any solubility determination from electromotive force measurements on solutions of the same composition.

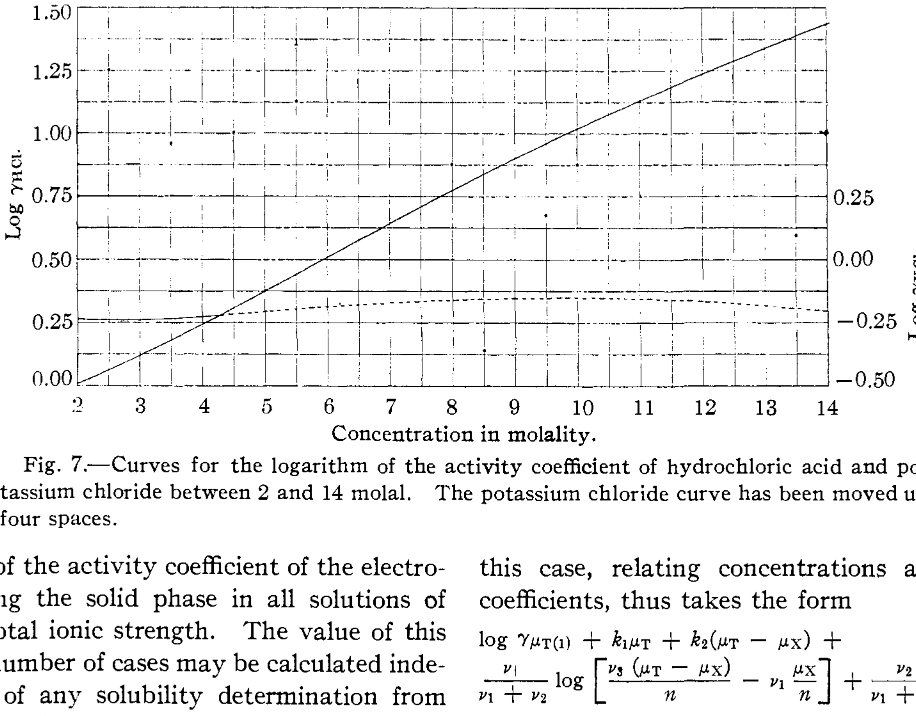

Fig. 7.—Curves for the logarithm of the activity coefficient of hydrochloric acid and potassium chloride between 2 and 14 molal. The potassium chloride curve has been moved up four spaces.

With the values for the slope of the curve for the logarithm of the activity coefficient at constant total ionic strength and the activity of the solid phase known, the changes of solubility in a series of solutions of varying total concentration may be calculated from the general equations to be given below either by successive approximation or by graphical interpolation. The logarithm of the activity coefficient $\gamma_{s(2)}$ of the saturating electrolyte at the saturation point m_s of the pure solution is given by

$$\log \gamma_{s(2)} = \log \gamma_{s(1)} + k_1 m_s \tag{3}$$

where $\gamma_{s(1)}$ denotes the activity coefficient of the reference electrolyte at the concentration m_s. The equations used for the calculation of the activity coefficient of the saturating electrolyte in solution with hetero- or homoionic electrolytes are given in a number of places and need not be repeated here.[6] Let us assume that the electrolyte dissociates into ν_1 positive and ν_2 negative ions. The total ionic strength of the solution is μ_T and that part of it due to the electrolyte forming the solid phase is μ_X. The second electrolyte present is assumed to be homoionic with respect to the positive ion. It dissociates into ν_3 positive and ν_4 negative ions, respectively, and has an ionic strength factor n. The general equation for this case, relating concentrations and activity coefficients, thus takes the form

$$\log \gamma_{\mu_T(1)} + k_1\mu_T + k_2(\mu_T - \mu_X) + \frac{\nu_1}{\nu_1 + \nu_2} \log \left[\frac{\nu_3\ (\mu_T - \mu_X)}{n} - \nu_1 \frac{\mu_X}{n}\right] + \frac{\nu_2}{\nu_1 + \nu_2} \log \frac{\mu_X}{n} = \log \gamma_{s(1)} + k_1 m_s + \log m_s\ [\nu_1^{\nu_1}\nu_2^{\nu_2}]^{\frac{1}{\nu_1 + \nu_2}} \tag{4}$$

where the constant k_2 is the slope of the curve for solutions of constant total ionic strength. In the case of solutions with heteroionic solutes equation (4) is considerably simplified

$$\log \gamma_{\mu_T(1)} + k_1\mu_T + k_2(\mu_T - \mu_X) + \log \frac{\mu_X}{n} = \log \gamma_{s(1)} + k_1 m_s + \log m_s \tag{5}$$

It should be stressed that equations (4) and (5) are valid only so long as the composition of the solid phase remains unchanged. When replacement occurs and a new solid phase appears all constants must be changed in order to be in accord with the varied conditions.

We may now test the validity of the equations

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[6] Falkenhagen, "Elektrolyte," Verlag S. Hirzel, Leipzig, 1932, p. 69; Harned, "Electrochemistry of Solutions" in Taylor's "Treatise on Physical Chemistry," 2d ed., Vol. I, p. 793.

by calculating the composition of the solution phase in a ternary system. We will apply the method to the system hydrochloric acid–potassium chloride–water with the second electrolyte present as the solid phase. This system represents the simplest case possible. Solubility measurements for potassium chloride in aqueous solutions of hydrochloric acid have been carried out by Malquori.[7] In Fig. 7 have been plotted the curves for the logarithms of the activity coefficients of hydrochloric acid and potassium chloride, respectively. The dotted extension of the curve for potassium chloride beyond the saturation point indicates the course this curve presumably would have in the hypothetical case of this electrolyte being more soluble than is actually the case. Figure 8 shows the curve for the change of the value of log $\gamma_{HCl}/\gamma_{KCl}$ with increasing concentration. From this last figure the following equation may be derived

$$\log \gamma_{KCl} = \log \gamma_{HCl} - 0.1177\,\mu_T + 0.0075 \qquad (6)$$

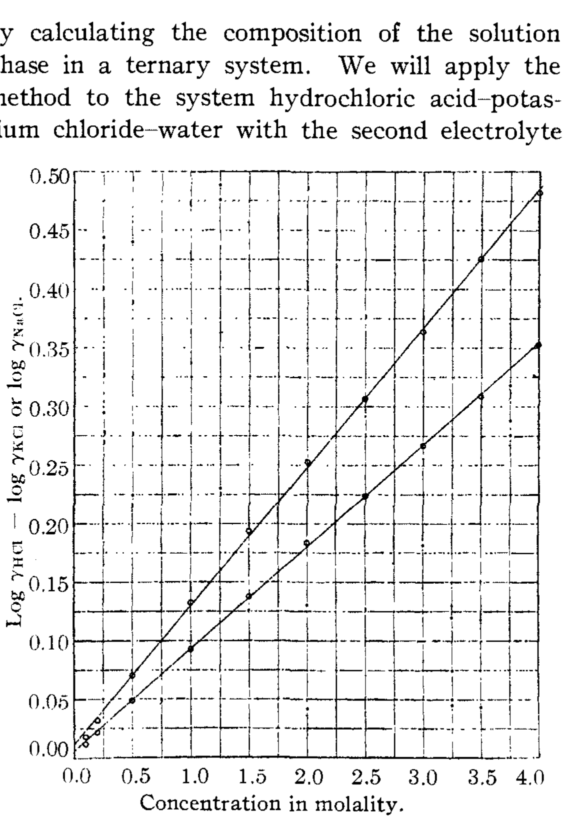

Fig. 8.—Curve for the differences between the logarithms of the activity coefficients of hydrochloric acid and (1) potassium chloride (upper curve) and (2) sodium chloride. The diameter of the circles indicating the experimental points corresponds to an error of ±0.001 in the activity coefficient. For sodium chloride have been used the mean values of the data of Harned and Harned and Nims [Harned, This Journal, **51**, 416 (1929); Harned and Nims, *ibid.*, **54**, 423 (1932)].

The third term on the right side of equation (6) is added as a correction term since the curve in Figure 8 does not pass exactly through the origin. According to measurements of Foote the concentration of a pure aqueous potassium chloride solution saturated at 25° is 4.826 molal.[8] Using the data employed for plotting the curve for the activity coefficient of hydrochloric acid in Fig. 7 and equation (6) the activity of potassium chloride at the saturation point is found to be 2.990. The data of Malquori give as the slope of the curve for the logarithm of the activity coefficient of potassium chloride in solutions of constant total molality a value of 0.0492. Thus we arrive at the following equation for the calculation of the solubility of potassium chloride at an arbitrary total ionic strength μ_T

$$\log \gamma_{HCl(\mu_T)} - 0.1177\,\mu_T + 0.0492\,(\mu_T - \mu_X) + \frac{1}{2}\log \mu_T + \frac{1}{2}\log \mu_X = 0.4681 \qquad (7)$$

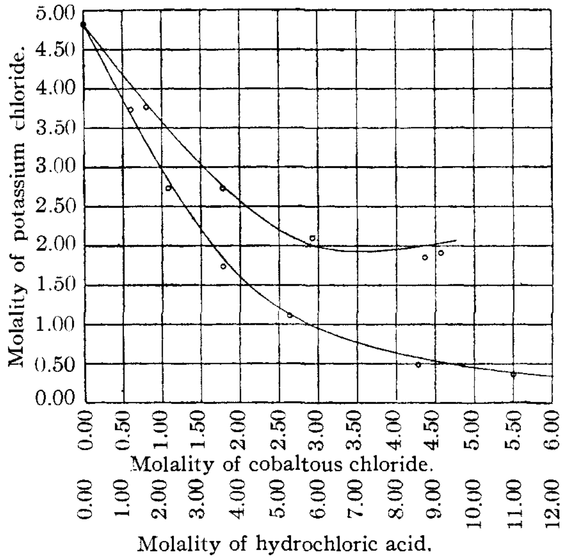

Fig. 9.

where μ_X is the desired potassium chloride concentration. Introducing in equation (7) different values for μ_T and solving for μ_X the curve shown in Fig. 9 is obtained for the solubility of potassium chloride in solutions of hydrochloric acid of varying concentration. Considering the very large extrapolations that have been made, the agreement between the calculated curve and the experimental points is quite remarkable. A summary of all calculations is given in Table III. An idea of the agreement between observed and calculated solubilities may be obtained from the comparison

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(7) Malquori, *Rend. R. Acc. Nazionale Lincei*, **5**, 577 (1927). Compare also "Tables Annuelles," Vol. VIII, part 2, p. 1620.

(8) Foote, *Am. J. Sci.*, [5] **13**, 158 (1927).

m HCl	1.21	2.16	3.56	5.27	8.56	10.97
m KCl observed	3.73	2.73	1.74	1.11	0.49	0.36
m KCl calculated	3.69	2.82	1.84	1.13	0.57	0.38

It should be noted that neither in this case nor in the case of the solubility measurements with silver sulfate in sulfuric acid–magnesium sulfate solutions has the hydrogen ion been treated as H_3O^+. In both cases such a treatment would have changed all concentrations and activity coefficients in the same direction. Since in the former case the calculated solubilities of potassium chloride apparently agree very well with the observed values, the strongly curved line for the logarithm of the activity coefficient of silver sulfate in mixed solutions of sulfuric acid and sulfate salts at constant total stoichiometrical ionic strength is not caused by neglect of the possibility of the presence of hydronium ions. Figure 4 gives further evidence in support of this point of view.

TABLE III

THE COMPOSITION OF THE SOLUTION PHASES IN THE SYSTEMS (1) HYDROCHLORIC ACID–POTASSIUM CHLORIDE–WATER AND (2) COBALTOUS CHLORIDE–POTASSIUM CHLORIDE–WATER WITH POTASSIUM CHLORIDE AS THE SOLID PHASE IN BOTH CASES

			(1) Hydrochloric acid potassium chloride		(2) Cobaltous chloride potassium chloride	
μ_T	log γ_{HCl}	log $\gamma_{KCl}+1$	*m* KCl	*m* HCl	*m* KCl	*m* $CoCl_2$
5.00	0.3757	0.7946	2.795	2.205	4.680	0.107
5.50	.4416	.8017	1.720	3.780	4.286	.405
6.00	.5078	.8090	1.285	4.715	3.937	.688
6.50	.5748	.8172	1.095	5.405	3.594	.969
7.00	.6403	.8238	0.952	6.048	3.310	1.230
8.00	.7705	.8363	.735	7.265	2.813	1.729
9.00	.9000	.8483	.581	8.419	2.406	2.198
10.00	1.0189	.8494	.483	9.518	2.167	2.614
11.00	1.1338	.8465	.405	10.595	1.994	3.002
12.00	1.2367	.8315	.354	11.646	1.947	3.351
13.00	1.3375	.8147			1.926	3.692
14.00	1.4368	.7965			1.927	4.024
15.00	1.5344	.7763			1.995	4.335
16.00	1.6276	.7519			2.028	4.657

The second test case treated is the system cobaltous chloride–potassium chloride–water with the latter electrolyte present as the solid phase. This system has been studied in detail by Foote at a temperature of 25°. He found that approaching equilibrium from pure cobaltous chloride solutions the phase first formed consists of this salt crystallizing with 6 moles of water. However, this phase soon disappears and is replaced by pure potassium chloride.[8] Just after this change has taken place at an ionic strength of about 14 a very slight minimum appears in the potassium chloride concentration in the solution phase. A correct and sensitive method for the calculation of the composition of this phase must be able to reproduce this minimum. Actually the results of the calculations presented in Table III do show a minimum of the correct order of magnitude and at the experimentally correct concentration.

For the calculation of the composition of the solution phase of this system apparently only one new constant is necessary, the slope of the curve for the logarithm of the activity coefficient of potassium chloride in mixed solution with cobaltous chloride at constant total ionic strength. Using the measurements of Foote the value of this slope was found to be 0.00313. From the general equation (4) the following formula is obtained

$$\log \gamma_{KCl(\mu_T)} + 0.00313\,(\mu_T - \mu_X) + \frac{1}{2}\log\,(2\mu_T + \mu_X)/3 + \frac{1}{2}\log \mu_X = 0.4681 \quad (8)$$

where μ_X as before designates the desired potassium chloride concentration. Solving for μ_X by successive approximation and graphical interpolation we obtain the result summarized in Table III and shown graphically in Fig. 9. Allowing for ordinary experimental errors the curve for the results given in Table III shows that the measured solubility values without doubt would give a curve practically coinciding with the calculated one.

Summary

The relationships between the thermodynamic activities of strong electrolytes have been discussed and applied to some measurements of the solubility of silver sulfate in pure and mixed aqueous solutions of sulfuric acid and sulfate salts. On the basis of the results obtained a general method has been discussed for the calculation of the composition of the solution phase in three component systems with two strong electrolytes.

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