[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 328]

Solubility Relations of Barium Sulfate in Aqueous Solutions of Strong Electrolytes

BY EDWARD W. NEUMAN[1]

In two preceding articles[2,3] a method for the determination of the solubility of slightly soluble inorganic salts in aqueous solutions of strong electrolytes was described and applied to a uni-univalent salt, silver chloride. In the second paper the data were discussed from the viewpoint of the recent developments in the interionic attraction theory of solutions of Debye and Hückel[4] as presented by Gronwall, La Mer and Sandved[5] and by La Mer, Gronwall and Greiff.[6]

In the present paper the same experimental method and treatment of the data have been applied to a di-divalent type salt, barium sulfate, in an attempt further to test the extension of the theory.

Experimental

The technique, applicability and limitations of the experimental method have already been described and discussed in detail. Materials used in the preparation of solutions were all carefully purified and tested. Water was twice distilled. The second time it was done through a block tin condenser. The maximum conductivity of several samples was 1.2×10^{-6} mho. Water and solutions were prepared in small quantities so as to minimize the effects of solubility of glass. The effect of carbonic acid in the water in equilibrium with carbon dioxide in the air will be described later. Experiments were made showing that the same results obtained whether equilibrium was attained from the solid or from the liquid phase.

Data and Discussion

The solubility of barium sulfate was measured at 25° in the presence of the chlorides and the nitrates of potassium, magnesium and lanthanum up to an ionic strength of about 0.04.

The value of the solubility, S_0, in otherwise pure water was determined statistically from the data on each solvent salt by applying the method of moments and the relation

$$S = S_0 + A\mu^{1/2} \tag{1}$$

to the five lowest points where a straight line relationship may be considered sufficient. Here S is the observed solubility at a given molality of the solvent salt which is expressed in terms of the ionic strength μ, and A is a con-

---

(1) National Research Fellow in Chemistry.

(2) Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853 (1930).

(3) Neuman, THIS JOURNAL, **54**, 2195 (1932).

(4) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

(5) Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

(6) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

stant. An extrapolation for S_0 is necessary because the experimental method does not permit a direct measurement. The value of $\log f_0$, where f_0 is the activity coefficient corresponding to S_0, was evaluated similarly, with the use of the formula

$$\log (S/S_0) = \log f_0 + b\mu^{1/2} \tag{2}$$

where b is a constant, and μ is the ionic strength. Here μ contains, in addition, the concentration of the solute salt.

The ionic strength of all of the solutions contains a correction which accounts for ionized carbonic acid in the water in equilibrium with the carbon dioxide of the air. This correction amounts to $0.615 \times 10^{-5}\ \mu$, and it is an average value calculated from the work of Kendall for equilibrium water.[7] This correction becomes negligible above 0.01 μ, but it amounts to about 6% of the ionic strength at 0.0001 μ. When the correction is not made S_0 becomes 0.3%, and f_0 about 0.2% greater. These differences, however, are less than the experimental error which is due to measuring of solutions and to error in the tyndallometric readings involved in fixing the end-points. Moreover, it should be noted also that the theoretical results, and all comparisons with theory, depend only on the precision of relative values produced by salt additions so that a slight error in absolute value does not obviate comparison with the theory.

The results of the statistical treatment of the lowest points are given in Table I. The mean deviation in S_0 is 0.01×10^{-5}, or about 1%; that in f_0, about 0.002 or 0.2%. The values f in the third column represent the slope from the data on each solvent salt, and if the limiting law were obeyed in each case they should equal 2.026, the value α in the Debye–Hückel formula for a (2, −2) valence type solute salt. The deviations from the limiting law as expressed by the ratio b/α increase with greater complexity of the solvent salt in the order $(3, -1) > (2, -1) > (1, -1)$; that is, for a given ionic strength and anion, the solution effect of the various cations is in the order $La^{+++} > Mg^{++} > K^{+}$. These ratios indicate also that for a given cation, nitrates increase the solubility more than do chlorides. This

TABLE I

EMPIRICAL PARAMETERS FROM STATISTICAL TREATMENT OF DATA

Salt	$S_0 \times 10^5$	$-\log f_0$	b	b/α	f_0
KCl	0.970	0.00891	2.592	1.28	0.980
KNO_3	.971	.00960	2.624	1.30	.978
$MgCl_2$	.955	.01053	3.064	1.51	.976
$Mg(NO_3)_2$	.961	.01061	3.095	1.53	.976
$LaCl_3$	.947	.01085	3.592	1.77	.975
$La(NO_3)_3$	.938	.01096	3.706	1.83	.975
Mean Cl^-	.957	.01011	...	..	.977
Mean NO_3^-	.957	.01040	...	..	.976
Average	.957	.01026	...	..	.977
Not corr. for H_2CO_3	.960	.00938	...	..	.979

---

[7] Kendall, THIS JOURNAL, **38**, 1480 (1916).

effect, however, is very slight; and were it not for the consistency with which it appears in all of the cases noted it might be attributed to experimental error. Values of S_0, f_0 and $-\log f_0$, calculated without the correction for carbonic acid, appear at the bottom of the table.

The experimental data appear in Table II. The average values, $S_0 = 0.957 \times 10^{-5}$ m./l. and $\log f_0 = -0.01026$, were used throughout for the calculation of $\log f$ by means of the relation

$$-\log f = \log (S/S_0f_0) \qquad (3)$$

TABLE II

SOLUBILITY RELATIONS OF BARIUM SULFATE

$S \times 10^5$	$M_{\text{Solvent Salt}}$	$\mu^{1/2}$	$-\log f_{(\text{obs.})}$	$-\Delta$	$-a_{[1]}$	$a_{[2]}$
		Solutions of Potassium Chloride				
1.002	0.00002004	0.00814	0.0303	0.0138	162	
1.067	.0002631	.01762	.0575	.0218	65.5	
1.123	.0006477	.02643	.0798	.0262	37.8	2.30
1.193	.001361	.03763	.1070	.0308	23.3	2.60
1.274	.002526	.05082	.1345	.0316	14.1	2.90
1.354	.003875	.06273	.1620	.0348	10.4	2.98
1.445	.005631	.07546	.1892	.0363	7.73	3.13
1.532	.007611	.08763	.2150	.0374	6.04	3.05
1.615	.009974	.10022	.2375	.0345	4.41	3.34
1.715	.01263	.1167	.2636	.0372	1.95	3.50
1.797	.01543	.1249	.2839	.0308	2.48	3.35
1.885	.01885	.1375	.3047	.0261	1.90	3.38
1.975	.02141	.1466	.3249	.0279	1.78	3.39
2.090	.02631	.1624	.3495	.0204	1.09	3.36
2.195	.03053	.1750	.3708	.0162	0.759	3.35
2.320	.03501	.1874	.3949	.0151	0.621	3.28
		Solutions of Potassium Nitrate				
1.007	0.00002014	0.00816	0.0324	0.0159	183	
1.085	.0003566	.02015	.0648	.0240	55.9	
1.143	.0008528	.03008	.0874	.0242	28.0	2.59
1.213	.001554	.04011	.1132	.0299	20.0	2.67
1.277	.002456	.05013	.1356	.0340	15.2	2.86
1.412	.004848	.07008	.1792	.0371	8.99	3.05
1.565	.008031	.09000	.2239	.0415	6.27	3.08
1.695	.01203	.11002	.2585	.0356	3.81	3.10
1.855	.01684	.1300	.2977	.0342	2.68	3.26
2.010	.02252	.1503	.3326	.0279	1.70	3.27
2.185	.02884	.1699	.3688	.0245	1.19	3.25
2.355	.03602	.1899	.4014	.0166	0.662	3.26
		Solutions of Magnesium Chloride				
						$a_{[3]}$
1.002	0.00001002	0.00874	0.0302	0.0125	144	
1.085	.0001198	.02027	.0648	.0238	55.3	
1.167	.0002856	.03016	.0964	.0353	36.9	
1.240	.0005173	.04009	.1228	.0416	25.7	0.43

TABLE II (*Concluded*)

$S \times 10^5$	$M_{\text{Solvent Salt}}$	$\mu^{1/2}$	$-\log f_{(\text{obs.})}$	$-\Delta$	$-a_{[1]}$	$a_{[3]}$
1.309	0.0008120	0.04984	0.1463	0.0453	18.9	0.64
1.388	.001179	.05997	.1718	.0502	14.8	.90
1.547	.002113	.08003	.2189	.0567	9.85	1.16
1.705	.003227	.09876	.2611	.0610	7.20	1.38
1.845	.004773	.1200	.2957	.0522	4.49	1.64
2.015	.006410	.1390	.3337	.0520	3.41	1.76
2.185	.008512	.1601	.3688	.0444	2.29	1.87
2.340	.01064	.1790	.4001	.0373	1.58	1.96
Solutions of Magnesium Nitrate						
1.007	0.00001007	0.00875	0.0324	0.0147	158	
1.098	.0001199	.02027	.0700	.0289	62.0	
1.172	.0002856	.03016	.0983	.0371	38.1	
1.253	.0005174	.04011	.1273	.0460	27.4	0.40
1.322	.0008151	.05004	.1506	.0492	19.9	.54
1.474	.001609	.06994	.1979	.0561	12.3	.99
1.633	.002686	.09016	.2424	.0597	8.31	1.33
1.784	.004008	.1100	.2808	.0579	5.70	1.56
1.935	.005699	.1299	.3161	.0528	3.91	1.73
2.110	.007461	.1499	.3537	.0499	2.86	1.80
2.285	.009593	.1700	.3883	.0438	2.01	1.90
2.458	.01199	.1897	.4200	.0351	1.34	1.97
Solutions of Lanthanum Chloride						
1.007	0.00000668	0.00930	0.0324	0.0136	137	
1.113	.00005571	.01962	.0759	.0361	73.7	2.11
1.194	.0001550	.03137	.1064	.0428	39.0	2.78
1.285	.0002543	.03851	.1383	.0602	34.3	2.83
1.375	.0004026	.04977	.1677	.0668	24.4	3.32
1.468	.0005849	.05979	.1961	.0749	19.4	3.63
1.695	.001070	.08059	.2585	.0952	13.9	3.92
1.832	.001667	.10041	.2923	.0888	9.20	4.39
2.014	.002400	.1204	.3334	.0896	6.79	4.53
2.208	.003353	.1421	.3734	.0855	4.90	4.58
2.394	.004296	.1609	.4085	.0825	3.82	4.62
Solutions of Lanthanum Nitrate						
1.003	0.00000667	0.00930	0.0307	0.0120	128	
1.112	.00005923	.02017	.0755	.0346	69.1	1.40
1.182	.0001447	.03037	.1020	.0404	39.6	2.62
1.290	.0002599	.04022	.1398	.0583	31.5	2.92
1.390	.0004102	.05022	.1733	.0716	25.0	3.29
1.485	.0005924	.06016	.2011	.0792	19.9	3.55
1.573	.0008107	.07023	.2261	.0838	16.1	3.83
1.664	.001071	.08061	.2525	.0892	13.3	4.04
1.845	.001652	.09996	.2954	.0928	9.56	4.28
2.037	.002374	.1197	.3384	.0958	7.20	4.37
2.223	.003315	.1414	.3763	.0871	4.98	4.48
2.405	.004276	.1605	.4105	.0853	3.94	4.55

The values Δ represent deviations from the Debye-Hückel limiting law obtained from

$$\begin{aligned}\Delta &= 2.0262\ \mu^{1/2} - \log f \\ &= \log f_{[1]} - \log f_{(\text{obs.})} \end{aligned} \quad (4)$$

The maximum deviations from the limiting law, in the range studied, occur at about 0.0077 μ for the potassium salts, 0.0090 μ for the magnesium salts and 0.011 μ for the lanthanum salts.

The apparent ionic diameters, $a_{[1]}$, are the parameters necessary to make $\log f_{[1]}$ of the Debye-Hückel first approximation formula coincide with $\log f_{(\text{obs.})}$. They are evaluated from the relation

$$a_{[1]} = -\Delta/0.3287\ \mu^{1/2} \log f_{(\text{obs.})} \quad (5)$$

which is derived from the first approximation formula. The apparent ionic diameters, $a_{[3]}$, are similarly derived from the third approximation formula of La Mer, Gronwall and Greiff[6] for unsymmetrical valence type electrolytes; and the $a_{[5]}$ values are derived from the formula of Gronwall, La Mer and Sandved[5] for symmetrical valence type electrolytes. All of the a values are given in Ångström units in the tables.

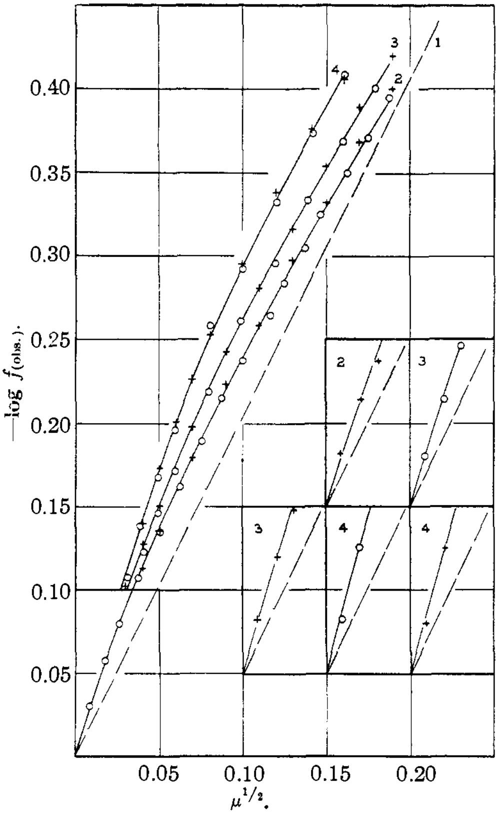

Fig. 1.—The logarithm of the observed activity coefficient as a function of the square root of the ionic strength: circles, chlorides; crosses, nitrates. 1, Debye-Hückel limiting law; 2, potassium salts; 3, magnesium salts; 4, lanthanum salts. The small figures are the portions of the curves between the 0 and 0.05 abscissas and the 0 and 0.1 ordinates.

From a consideration of the deviations Δ, and the a values, it is apparent that neither the limiting law nor the first approximation formula is in accord with the data. The $a_{[1]}$ values are both inconstant and negative, thereby contradicting the theory. There is a more exact agreement with the extended formulas of La Mer and of Gronwall, as is indicated by the $a_{[3]}$ and the $a_{[5]}$ values, which are more nearly constant and positive; and they are of reasonable magnitude. The agreement in the case of the fifth approximation for symmetrical valence types is especially striking, chiefly at the greater ionic strengths.

The $a_{[3]}$ and $a_{[5]}$ values which were omitted from the tables were only approximated. They were positive, but they became very small for the very low ionic strength. It is here that the theoretical curves for log f begin to converge into the limiting law, which is not the case with the data. Consequently, also, small errors in log $f_{(\text{obs.})}$, in this region, are greatly magnified in the resulting a values, whether they are derived from the first approximation formula or from the extended forms, and the a values, therefore, lose much of their value as a means of comparison of experiment and theory. Furthermore, their calculation is greatly complicated by increasing difficulty in accurate interpolation on curves of functions required in their computation. Because of these considerations they were omitted entirely from the tables.

In Fig. 1 the values of $-\log f_{(\text{obs.})}$ are plotted against the square root of the ionic strength. The lower portions of the curves, between 0 and 0.05 $\mu^{1/2}$, are plotted separately to avoid confusion of points which belong to the various solvent salts. The broken line represents the slope of the limiting law. The heavy lines are drawn only through the chloride points which are represented by circles. The nitrate points are designated by crosses.

Summary

The solubility of barium sulfate was determined in water at 25° in the presence of the chlorides, and the nitrates of potassium, magnesium and lanthanum over a concentration range, 0 to 0.04 ionic strength.

The solubility, and the activity coefficient of the salt in pure water, were evaluated statistically and found to be 0.957×10^{-5} m./l., and 0.977, respectively.

The activity coefficients, and the apparent ionic diameters, were calculated, and were used as a means of comparison of the data with recent developments in the interionic attraction theory of solutions.

PASADENA, CALIFORNIA

RECEIVED JULY 6, 1932
PUBLISHED MARCH 7, 1933