of hydrofluoric acid solutions with the oxide is analogous to an acid-base reaction. When an excess of oxide is present, hydrofluoric acid is completely consumed according to the stoichiometry of Equation 2 and the solid phase becomes a mixture of the oxide and the dioxyfluoride.

The conclusion reached in this study, suggesting the $NbOF_5^{-2}$ ion as the primary niobium-containing species in 0 to 5*M* H_2NbOF_5 solutions, is the same as that arrived at by Nikolaev and Buslaev (*9*). Although the results of the present study are in good agreement with those of Nikolaev and Buslaev regarding the composition and densities of the saturated solutions, there is marked disagreement as to the composition of the equilibrium solid phase. Nikolaev and Buslaev, who equilibrated the hydrous oxide with hydrofluoric acid solutions and used the wet residue method to determine the solid phase, concluded that $Nb_2O_5 \cdot 2H_2O$ was the equilibrium solid phase. The dioxyfluoride was always present in the solid phases obtained in this study. This disparity in results is inexplicable unless it is assumed that Nikolaev and Buslaev used very large amounts of oxide relative to the amounts of hydrofluoric acid present in their samples. If this were the case, all the hydrofluoric acid could have been consumed without markedly depleting the amount of niobic oxide present.

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Solubility of Calcium Sulfate Dihydrate in the System $NaCl–MgCl_2–H_2O$ from 28° to 70° C.

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Solubility data are presented for calcium sulfate dihydrate in the system $NaCl–MgCl_2–H_2O$ for 28°, 38°, 50°, 70°, and 90° C. and in ranges of concentration up to 5.50 molal NaCl and 0.340 molal $MgCl_2$ in admixtures. Thermodynamic solubility products are given for calcium sulfate at 28°, 38°, 50°, 70°, and 90° C. Empirical equations describing the solubility of calcium sulfate dihydrate in these systems are also given.

THERE is widespread interest in the solubility of calcium sulfate dihydrate in solutions of various concentrations of sodium chloride and magnesium chloride and at various temperatures. Geologists and geochemists are interested because of gypsum and anhydrite conversion occurring in nature (*1*, *6*, *11*). Engineers involved in production of petroleum or water desalination are interested because of deposition of calcium sulfate scales. These scales are also a problem facing cooling tower operators (*3*). Solubility data for calcium sulfate in the simple solutions have been available in the literature for a long time but there has been no knowledge of the influence of mixtures of these salts on the solubility of calcium sulfate, particularly at temperatures above ambient. Some early work on gypsum solubility in water at different temperatures was done by Cameron (*2*) who measured gypsum solubility in sodium chloride solution at 23°, 30°, 52°, 70°, and 82° C. Shternina (*10*) measured the solubility of calcium sulfate in the presence of sodium chloride, magnesium chloride, sodium nitrate, magnesium nitrate, and ammonium chloride, but not in mixtures of these salts. Shternina formulated a method of calculating calcium sulfate solubility in these salt solutions at 25° C. which was based on the Debye-Hückel limiting law. Bock (*1*) determined the solubility of both anhydrite and gypsum in sodium chloride solutions at 25°, 30°, 40°, and 50° C. Denman (*3*) measured the solubility of gypsum in water and in dilute concentrations of sodium sulfate and a magnesium sulfate solution and formulated a calculation of calcium sulfate solubility based on ionic strength and activity coefficients. Solubility of calcium sulfate has been measured in concentrations of sodium chloride up to 4 molal at temperatures ranging from 40° to 200° C. and the Debye-Hückel theory applied as a method of calculating calcium sulfate solubility in these systems (*5*). Recently, solubilities of γ and β-hemihydrate, β-soluble anhydrite, and insoluble anhydrite have been measured (*8*). Zen (*11*) has measured the solubility of both gypsum and anhydrite at 35°, 50°, and 70° C., in various sodium chloride concentrations.

The solubility of calcium sulfate has been determined at temperatures of 28°, 38°, 50°, and 70° C. for sodium chloride molatities up to 5.5 and for admixtures with magnesium chloride between 0.01 and 0.325 molal.

EXPERIMENTAL PROCEDURE

Chemicals and Apparatus. All chemicals used were of reagent quality. Solutions were made from distilled water. Solution saturations were made in thermostated water or oil baths regulated at ±0.5° C. Solutions were held in three-necked 1-liter round-bottom flasks and stirred with ¼-inch titanium stirring rods rotated with 600-r.p.m. constant speed motors. The stirring rods were run through a ¼-inch oilless bushing inserted through a rubber stopper used to seal the flask at 28°, 38°, and 50° C. At 70° C., a specially designed sealed magnetic stirrer was used (*7*). All saturations were made at atmospheric pressure.

Procedure. Solutions for solubility determinations were made from either distilled water and stock solutions of sodium chloride and magnesium chloride or from weighed salts dissolved in distilled water. Some test saturations were approached from both the undersaturated and supersaturated directions. From the undersaturated condition, solid Baker's Analyzed $CaSO_4 \cdot 2H_2O$ was used and from the supersaturated condition, concentrated solutions of calcium chloride and sodium sulfate were added in equal molar amounts to the test solution after it had equilibrated with respect to temperature. Sulfate determinations made at 2-day intervals during saturation with the solid gypsum indicated that the saturation was reached within 48 hours. Similar tests were made on a supersaturated solution.

After saturation, stirrers were stopped, and the solid was permitted to settle before sampling. In one sampling procedure, samples were drawn by means of suction directly from the saturation flasks immersed in the temperature baths, through an in-line 0.45-μ membrane filter positioned outside but immediately adjacent to the saturation flask, through a cooling coil packed in an ice-water mixture, and collected in a flask packed in ice. Solutions saturated at 70° C. were sampled by removing the saturation flask from the bath and setting it in an insulated holder which, in turn, was placed in a pressure vessel. The vessel was sealed, and 15 p.s.i. air pressure was applied forcing the solution through a sampling tube, a 0.45-μ in-line membrane filter, a cooling coil, and into a sample container. In this second procedure, the temperature was not controlled, but because of the insulated holder and the rapid removal of sample, the slight change in solution temperature did not alter the solubility measurement. After the solution sample was taken, the solid phase was removed by filtration, washed first with 95% ethanol, and then with acetone. The solid was then identified by x-ray procedures. Only solubility data for solutions where gypsum was the only solid phase identified are reported here.

Analysis of Saturated Solutions. The chemical compositions of solutions studied in this investigation were based on the determination of calcium, magnesium, sulfate, and chloride ions, and specific gravity. Calcium ion determinations were made as a check of the sulfate analyses of solutions containing equal molal amounts of calcium and sulfate. When the solutions were supersaturated by the addition of stoichiometric amounts of calcium chloride and sodium sulfate solutions, the calcium ion determination was used in determining calcium sulfate solubility. Sodium ion was not determined, but was calculated as the difference between the chloride ion concentration and twice the magnesium ion concentration. When calcium chloride was added in conjunction with sodium to produce calcium sulfate, the amount of this added was included also in the sodium calculation.

Magnesium ion was determined either gravimetrically as the pyrophosphate or by titration with EDTA. The more convenient but less accurate EDTA titration was suitable for this investigation because minute differences in magnesium ion content have a negligible effect on the solubility of the calcium sulfate in the sodium chloride.

Sulfate was determined as barium sulfate. This was the most accurate analytical method used. Since the sulfate determination as barium sulfate is a more accurate method than calcium determination by EDTA titration, the sulfate determination was used as a check of the calcium determination in many cases. Results of sulfate determinations were used in calculating gypsum solubility for all data at 28°, 38°, and 90° C., and most of those at 50° C. The sulfate determination sufficiently corroborated the EDTA titration, so that solubility in solutions saturated with solid calcium sulfate at 70° C. was calculated from the calcium determination using EDTA. The Mohr method was used in analyzing solutions for chloride ion.

Calcium ion was determined by titration with EDTA and gravimetrically by oxalate precipitation. In solutions where the magnesium concentration was low and the saturation had been with solid calcium sulfate, the more rapid and less accurate EDTA titration was used.

Solution specific gravity was measured with a hydrometer that could be read to the second decimal place and estimated to the third. Hydrometers used here were checked by use of a specific gravity (Chainomatic Westphal) balance and proved accurate. From the specific gravity and the calculated total dissolved solids in the saturated solutions, a factor was calculated that was used to convert the concentrations from grams or moles per liter to grams per thousand grams of water and molal units.

EXPERIMENTAL RESULTS

The solubility of calcium sulfate in distilled water measured in this investigation as a function of temperature is shown in Figure 1. This curve shows that the solubility decreases with an increase in temperature. Data shown here agree very closely with those measured by Denman (*3*), Hulett and Allen (*4*), Marshall, Slusher, and Jones (*5*), and Power, Fabuss, and Satterfield (*8*), but are somewhat lower at 40° and 50° C. than those given by Bock (*1*). Using the least squares method, Equation 1 was determined

$$CaSO_4 \text{ (grams/1000 grams } H_2O) = 2.052 + 0.00439t - 0.00009t^2 \quad (1)$$

from the data shown in Figure 1 as representing the solubility in water over the temperature range 28° to 90° C.

To determine the necessary saturation time from either the undersaturated condition using solid gypsum or from supersaturated solutions made by the addition of equal molal amounts of sodium sulfate and calcium chloride solutions, similar solutions were made, placed in the bath at 28°, 38° C., etc., and stirred for 9 days. At the end of this period, dissolved calcium sulfate was determined in each of the solutions and found to be essentially identical. This indicated that saturation could be reached from either the under- or oversaturated condition in a relatively short period of time.

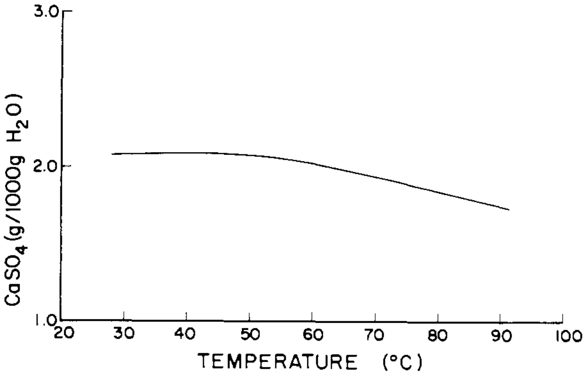

Figure 1. Variation in gypsum solubility in water with temperature

This experiment showed that saturation could be attained within a reasonable length of time by dissolving finely divided calcium sulfate dihydrate. An additional experiment was performed to determine the minimum time required to saturate the solutions with the solid salt at the stirring rate used. In this experiment, samples were withdrawn from the solution at specified times, and the time for saturation was determined. These data indicated that two days' stirring was sufficient time for reaching saturation with a precision of 6.60 ± 0.02 grams, which is comparable with the analytical precision involved in determining the concentrations of ions in the test solution. However, no saturations were continued for less than 3 days.

The solubilities measured at 28°, 38°, 50°, and 70° C. are shown in Table I. Data for each temperature are grouped according to magnesium chloride concentrations. It was intended that magnesium chloride concentrations be identical for each solution within a magnesium chloride grouping, but deviations occurring during the make-up of these solutions have resulted in slight variations. Because of the presence of sodium chloride in the solutions and its effect on gypsum solubility, it is not thought that these

Table I. Solubility of Calcium Sulfate Dihydrate

NaCl, *m*	$MgCl_2$, *m*	$CaSO_4$, G./1000 G. H_2O
28° C.		
0	0	2.08
0.200		3.68
0.273		4.00
0.400		4.58
0.600		5.20
1.00		6.14
2.21		7.58
2.86		7.67
3.38		7.62
4.32		7.44
5.50		6.85
0.0501	0.0100	2.93
0.100	0.0100	3.26
0.266	0.0103	4.21
0.320	0.0101	4.30
0.505	0.0101	5.17
1.02	0.0102	6.43
2.23	0.0108	7.63
2.81	0.0109	7.84
3.38	0.0110	7.71
4.32	0.0108	7.21
5.50	0.0110	6.39
0.262	0.0205	4.34
2.22	0.0215	7.64
2.78	0.0214	7.83
3.35	0.0218	7.72
0.259	0.0405	4.60
2.20	0.0425	7.64
2.76	0.0427	7.78
3.33	0.0423	7.74
0.0501	0.0501	3.86
0.100	0.0503	4.06
0.506	0.0506	5.58
1.02	0.0511	6.68
2.08	0.0521	7.76
3.18	0.0530	7.89
4.32	0.0540	7.34
5.50	0.0550	6.42
0.246	0.0794	5.09
2.15	0.0836	7.78
2.68	0.0833	7.76
3.25	0.0832	7.85
0.0501	0.100	4.59
0.100	0.100	4.85
0.303	0.100	5.48
0.507	0.100	6.04
1.02	0.102	7.01
2.07	0.104	7.92
3.19	0.106	7.85
4.33	0.108	7.23
5.50	0.110	6.26
0.245	0.152	5.89
2.02	0.157	7.81
2.54	0.157	7.88
3.05	0.156	7.75
0.508	0.203	6.68
0.622	0.206	6.97
1.67	0.210	7.90
2.09	0.208	7.95
2.77	0.214	7.95
3.20	0.213	8.02
3.83	0.219	7.51
0.101	0.304	6.95
0.429	0.307	7.36
0.510	0.306	7.43
1.50	0.313	8.09
28° C.		
2.10	0.315	8.16
2.60	0.321	8.00
3.20	0.320	7.73
3.73	0.325	7.39
38° C.		
0	0	2.14
0.275		4.02
0.560		5.05
1.23		6.53
2.05		7.46
2.51		7.66
3.04		7.74
4.01		7.53
4.10		7.53
0	0.210	6.07
0.118	0.206	6.25
0.805	0.215	7.24
1.57	0.214	7.95
1.87	0.206	8.15
2.01	0.218	8.19
2.76	0.224	8.11
3.57	0.211	7.76
0	0.105	4.57
0.064	0.106	4.81
0.342	0.104	5.68
1.02	0.107	6.91
1.41	0.103	7.28
1.87	0.101	7.69
2.27	0.109	7.96
2.65	0.100	7.86
3.03	0.0932	7.87
3.38	0.106	7.73
3.82	0.0901	7.59
0.169	0.0515	4.45
0.232	0.0230	4.22
0.444	0.0542	5.32
0.510	0.0296	5.19
1.13	0.0539	6.66
1.21	0.0230	6.60
1.98	0.154	8.00
2.00	0.014	7.53
2.40	0.0626	7.80
2.46	0.0271	7.82
3.16	0.0397	7.78
3.13	0.0556	7.85
3.96	0.0310	7.58
50° C.		
0	0	2.08
0.266		3.96
0.608		5.20
1.23		6.48
1.85		7.23
2.55		7.58
2.85		7.52
2.96		7.72
3.12		7.69
3.21		7.77
4.13		7.54
0	0.0700	4.11
0.264	0.0731	5.13
0.310	0.0682	5.16
0.909	0.0684	6.60
1.04	0.0673	6.81
50° C.		
1.51	0.0722	7.08
1.54	0.0690	7.31
2.06	0.0671	7.68
2.71	0.0731	7.78
3.20	0.0667	7.87
3.69	0.0706	7.77
4.00	0.0669	7.68
4.36	0.0717	7.24
0	0.100	4.63
0.202	0.0996	5.36
0.622	0.0992	6.28
0.717	0.0960	6.26
0.864	0.0979	6.79
1.25	0.0967	7.17
1.86	0.0986	7.62
2.15	0.0904	7.85
2.87	0.0973	7.87
3.16	0.0992	7.66
3.55	0.0974	7.62
3.88	0.0971	7.49
0	0.200	5.60
0.218	0.199	6.33
0.725	0.204	7.15
1.57	0.205	8.00
1.904	0.208	8.12
2.356	0.202	8.22
2.637	0.199	8.16
3.19	0.201	7.84
3.83	0.196	7.53
4.14	0.209	7.42
0.386	0.0159	4.91
0.533	0.0626	5.77
1.06	0.0310	6.58
1.11	0.0129	6.41
2.15	0.0904	7.85
2.31	0.0383	7.68
2.34	0.0222	7.58
2.84	0.0383	7.84
3.99	0.0155	7.50
0	0.0410	3.47
	0.0683	4.07
	0.100	4.63
	0.136	5.15
	0.197	5.80
60° C.		
0	0	2.01
70° C.		
0	0	1.93
0.089		2.89
0.566		4.94
0.890		5.81
0.988		5.89
1.00		6.04
1.55		6.91
2.04		7.28
2.53		7.75
2.60		7.78
2.80		7.86
3.01		7.89
3.30		7.94
3.40		7.95
3.80		7.88
4.15		7.63
0	0.0650	3.90
70° C.		
0.198	0.0657	4.67
0.484	0.0656	5.45
0.806	0.0652	6.26
1.12	0.0652	6.75
1.54	0.0649	7.17
2.00	0.0657	7.58
2.48	0.0652	7.80
2.67	0.0640	7.85
2.82	0.0658	7.85
3.01	0.0678	7.98
3.17	0.0648	7.94
3.39	0.0674	7.92
3.92	0.0653	7.72
0	0.109	4.72
0.200	0.109	5.29
0.474	0.110	5.92
0.900	0.107	6.73
1.50	0.107	7.42
2.01	0.108	7.77
2.40	0.108	8.03
2.90	0.115	8.06
3.11	0.109	8.04
3.63	0.110	8.01
4.12	0.109	7.79
0	0.190	5.81
0.182	0.190	6.25
0.482	0.190	6.78
0.800	0.190	7.15
1.11	0.188	7.57
1.49	0.187	7.81
1.89	0.190	8.09
2.37	0.191	8.09
2.76	0.191	8.15
3.01	0.189	8.15
3.18	0.190	8.14
3.40	0.185	8.19
3.55	0.187	7.93
3.71	0.186	7.89
3.80	0.189	8.09
4.18	0.189	7.82
0	0.0270	2.93
	0.0548	3.66
	0.0818	4.22
	0.108	4.68
	0.136	5.13
	0.141	5.13
	0.192	5.83
	0.340	7.34
80° C.		
0	0	1.82
90° C.		
0	0	1.79
0.247		3.47
0.257		3.58
0.484		4.44
0.512		4.53
0.967		5.75
1.019		5.89
1.560		6.64
0.218	0.207	6.43
0.765	0.198	7.32
1.569	0.205	8.01

slight variations will prevent these groupings from being plotted as isopleths of magnesium chloride or in formulating an empirical method for calculating calcium sulfate solubility at these temperatures.

Some fragmentary data at 90° C. also are included in Table I. Because of the possibility of gypsum dehydration to anhydrite in approximately 2*m* sodium chloride solutions at 90° C. (*6*), these measurements were not made in solutions greater than this concentration.

Figure 2 is a graphic presentation of 38° C. data grouped according to the magnesium chloride concentrations of zero, 0.105, and 0.210 molal. These curves were used in conjunction with the other 38° C. data shown in Table I in formulating empirical equations for the solubility of calcium sulfate in the sodium chloride–magnesium chloride–calcium sulfate–water system at 38° C. by the following procedure. One of the saturations listed in Table I but not included in the three curves shown in Figure 2 was plotted as calcium sulfate *vs.* magnesium chloride concentration. At the sodium chloride concentration of this particular saturated solution, calcium sulfate values in solutions containing zero, 0.105*m*, and 0.210*m* magnesium chloride were taken from the curves in Figure 2. These values also were plotted as calcium sulfate solubility *vs.* magnesium chloride concentration. A straight line then was drawn through these points that showed the variation in calcium sulfate dihydrate solubility *vs.* magnesium chloride concentration at constant sodium chloride concentration. This procedure was repeated for each of the solubility values at 38° C. not included in data shown in Figure 2. From the series of curves obtained by this procedure, calcium sulfate solubility values in sodium chloride solutions at magnesium chloride concentrations of 0.010, 0.025, 0.050, 0.075, 0.100, 0.125, 0.150, 0.175, and 0.200*m* were read, and solubility curves plotted. By using the least squares method, Equation 2 was determined for these curves. Coefficients for this equation at various temperatures are shown in Table II.

$$S = a + b(m\ \mathrm{NaCl}) + c(m\ \mathrm{NaCl})^2 + d(m\ \mathrm{NaCl})^3 + e(m\ \mathrm{NaCl})^4 \quad (2)$$

At NaCl concentration greater than 1.13 molal, the curves are straight lines which essentially pass through the plotted points of solubility data. At lower NaCl concentrations, the value for zero $MgCl_2$ did not fall on this straight line through the other points. Curves for low NaCl concentration were used only from 0.025*m* $MgCl_2$ through 0.20*m* $MgCl_2$. Equation 2, then, is not suitable for calculating calcium sulfate dihydrate solubility in distilled water, but gives good agreement between calculated and measured values when NaCl and $MgCl_2$ are present in solution.

This same procedure was used to obtain coefficients for use in Equation 2 for calculating gypsum solubility at 28°, 50°, and 70° C. The curves shown in Figure 2 are representative in shape of curves obtained by plotting the other data in Table I.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental results show that the presence of small amounts of $MgCl_2$ in NaCl solutions markedly influences gypsum solubility up to approximately 2.5*m* NaCl. At higher molalities of NaCl the effect of $MgCl_2$ decreases until at approximately 4*m* NaCl, no difference in gypsum solubility is noticeable between the NaCl solution and those containing both NaCl and $MgCl_2$.

Equation 2 offers an empirical expression of solubility data in solutions of sodium and magnesium chlorides at 28°, 38°, 50°, and 70° C. As an example of the agreement between measured and calculated values in a solution of 0.169*m* NaCl and 0.0515*m* $MgCl_2$ at 38° C., the measured solubility was 4.45 grams and calculated was 4.40 grams as $CaSO_4$. For a solution of 2.64*m* NaCl and 0.199*m* $MgCl_2$, the measured value at 50° C. was 8.16 grams and the calculated solubility value was 8.13 grams as $CaSO_4$.

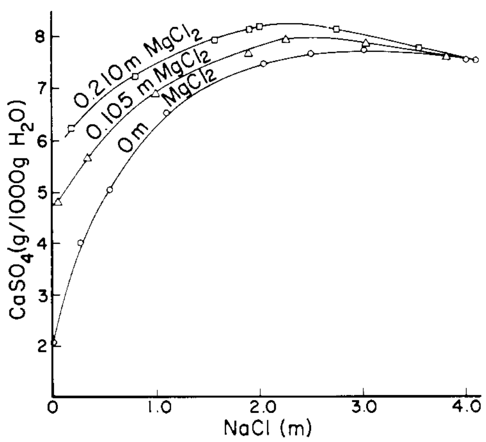

Figure 2. Gypsum solubility at constant $MgCl_2$ concentration but varying NaCl at 38° C.

Table II. Coefficients Used in Equation 2 for Calculating Gypsum Solubility[a]

$MgCl_2$	Coefficients				
m	a	b	c	d	e[b]
			28° C.		
0	2.341	6.284	−2.748	0.5250	−0.0375
0.010	2.648	5.930	−2.470	0.4430	−0.0304
0.025	3.171	4.637	−1.474	0.1447	
0.050	3.661	4.150	−1.306	0.1259	
0.075	4.158	3.722	−1.176	0.1130	
0.100	4.542	3.246	−0.9779	0.08793	
0.125	4.864	2.921	−0.8590	0.07410	
0.150	5.169	2.709	−0.8033	0.06905	
0.175	5.436	2.547	−0.7682	0.0647	
0.200	5.708	2.402	−0.7462	0.06071	
0.300	6.746	1.628	−0.5300	0.0341	
			38° C.		
0	2.209	6.733	−3.407	0.8240	−0.0773
0.010	3.258	3.905	−1.077	0.09214	
0.025	3.532	3.705	−1.026	0.08748	
0.050	3.809	3.549	−0.9862	0.08292	
0.075	4.142	3.311	−0.9146	0.07452	
0.100	4.497	3.076	−0.8577	0.06914	
0.125	5.141	2.281	−0.5093	0.02114	
0.150	5.1011	2.694	−0.7477	0.05614	
0.175	5.454	2.425	−0.6586	0.04493	
0.200	5.782	2.234	−0.6206	0.04220	
			50° C.		
0	2.173	7.041	−3.902	1.026	−0.101
0.010	2.307	4.685	−1.297	0.1135	
0.025	3.296	4.369	−1.418	0.1493	
0.050	3.875	3.713	−1.141	0.1110	
0.075	4.336	3.171	−0.9012	0.07663	
0.100	4.701	2.864	−0.7835	0.05997	
0.125	5.031	2.630	−0.7057	0.04945	
0.150	5.297	2.526	−0.7117	0.05326	
0.175	5.510	2.506	−0.7205	0.05291	
0.200	5.867	2.326	−0.7070	0.05628	
			70° C.		
0	2.204	6.280	−3.152	0.808	−0.0814
0.010	2.715	4.624	−1.380	0.1359	
0.025	3.045	4.257	−1.234	0.1170	
0.050	3.741	3.445	−0.9126	0.07679	
0.075	4.173	3.172	−0.8756	0.07985	
0.100	4.603	2.822	−0.7398	0.05977	
0.125	4.978	2.586	−0.6864	0.05557	
0.150	5.338	2.389	−0.6517	0.05389	
0.175	5.671	2.229	−0.6313	0.05397	
0.200	5.979	2.129	−0.6469	0.05970	
			90° C.		
0	1.769	9.423	−0.1190	9.2510	−2.6960

[a] Solubility expressed as grams of $CaSO_4$ per 1000 grams of H_2O.
[b] Coefficient *e* is used only where indicated in this column, and may be neglected for concentrations of NaCl < 0.6*m* except at 90° C.

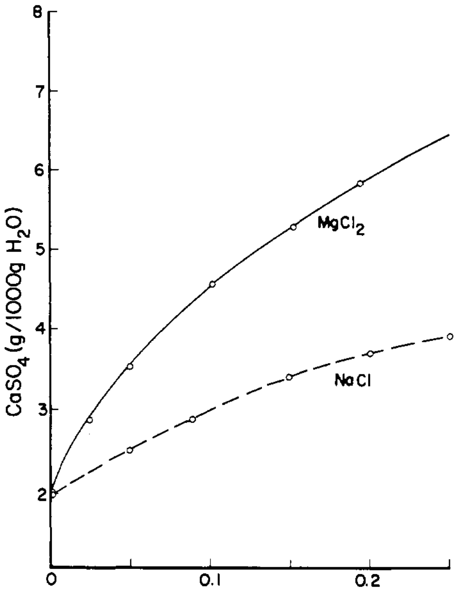

Figure 3. Comparison of gypsum solubility in $MgCl_2$ and NaCl Solutions at 70° C.

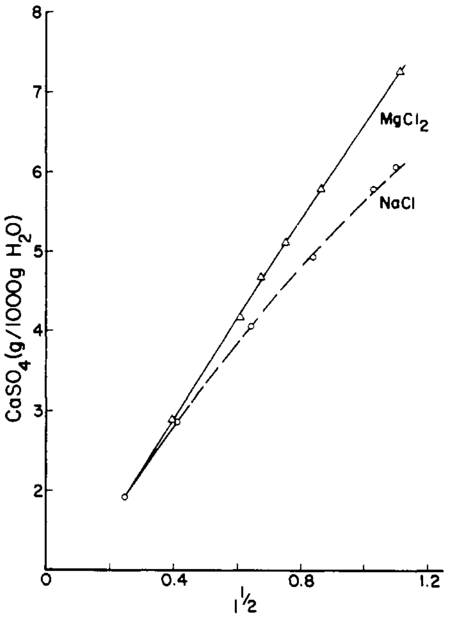

Figure 4. Gypsum solubility *vs.* ionic strength in NaCl and $MgCl_2$ solutions at 70° C.

A comparison of the effect low concentrations of $MgCl_2$ and NaCl have on calcium sulfate solubility is shown in Figures 3 and 4. In Figure 3, for the same concentration of $MgCl_2$ or NaCl, the $MgCl_2$ causes a larger increase in solubility. This effect is not additive. For example, at 70° C., solubility (as $CaSO_4$) in 0.200*m* NaCl is 3.68 grams and in 0.109*m* $MgCl_2$, it is 4.71 grams. If the effects of these two components in a solution were additive, the solubility in a 0.200*m* NaCl and 0.109*m* $MgCl_2$ solution would be 8.39 grams. The measured solubility is 5.28 grams. For a 3.00*m* NaCl and 0.190*m* $MgCl_2$ solution, the measured solubility is 8.16 grams, but if the effects of the ions were additive, it would be 13.69 grams. These examples illustrate the degree of error resulting from adding the solubility in $MgCl_2$ solution to the solubility in NaCl solution. Figure 4 is a graphic comparison of the influence of ionic strength on the solubility of $CaSO_4$ in $MgCl_2$ and NaCl solutions. For the same ionic strength (I), $MgCl_2$ causes a greater increase in solubility than NaCl.

The solubility product, K_{sp}, can be expressed by Equation 3 where γ_{Ca} and γ_{SO_4} are the activity coefficients of calcium and sulfate ions, respectively, and m_{Ca} and m_{SO_4} the concentrations of these ions. Since individual activity coefficents

$$K_{sp} = \gamma_{Ca}\, m_{Ca}\, \gamma_{SO_4}\, m_{SO_4} \tag{3}$$

$$K_{sp} = \gamma_{\pm}^2\, m_{\pm}^2 \tag{4}$$

$$\log K_{sp} = \frac{-AZ_i^2\, I^{1/2}}{1 + Ba_i\, I^{1/2}} + 2 \log m \tag{5}$$

cannot be determined, but only the average of two, and because data in Table I were for solutions of equal calcium and sulfate ion concentration, the solubility product equation can be written as Equation 4. Substituting the Debye-Hückel equation for calculating γ, Equation 4 can become Equation 5. Terms for the Debye-Hückel equation are given by Robinson and Stokes (*9*).

Solutions containing several dissolved components at relatively high concentrations similar to those described here do not conform strictly to thermodynamic theories or theories of electrolyte solutions which pertain to the solubility of a dissolved component, but deviate from these theories. Equation 5 was, therefore, applied only to a limited portion of the data tabulated in Table I. Specifically, K_{sp} was calculated only for calcium sulfate in sodium chloride solutions of $I^{1/2}$ less than 0.8. At higher values of $I^{1/2}$ or in solutions containing both magnesium chloride and sodium chloride, pronounced deviations from theory occurred, and even the addition of the empirical extended terms would not compensate satisfactorily for the deviation.

Calculated K_{sp} values for relatively dilute sodium chloride solutions were plotted *vs.* $I^{1/2}$ and extrapolated to zero ionic strength to give a value termed the thermodynamic solubility product or equilibrium product. Values obtained by extrapolating these lines are 45.2 × 10^{-6} at 28° C., 47.2 × 10^{-6} at 38° C., 43.3 × 10^{-6} at 50° C., 36.4 × 10^{-6} at 70° C., and 30.8 × 10^{-6} at 90° C.

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