Solubility of Anhydrite in Several Aqueous Salt Solutions between 250° and 325° C.

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The solubility of anhydrite has been determined in a number of salt solutions at elevated temperatures and at pressures just above the vapor pressure. The system $CaSO_4$–H_2O was studied from 200° to 325° C., and the results obtained are significantly lower than existing literature values. The $CaSO_4$–NaCl–H_2O system was investigated at 250°, 275°, 300°, and 325° C. from essentially zero to about 6 molal NaCl. Other supporting electrolytes studied at 250° or 300° C. were sodium nitrate, calcium chloride, magnesium chloride, sodium sulfate, and magnesium nitrate. The systems $CaSO_4$–$CaCl_2$–NaCl–H_2O and $CaSO_4$–Na_2SO_4–NaCl–H_2O were studied at constant ionic strength I = 0.5 and 0.9 molal, at 250° and 300° C. The system $CaSO_4$–$MgCl_2$–NaCl–H_2O was studied at I = 0.5 molal at 250° and 300° C. Calcium sulfate is more than 90% dissociated in solutions of sodium chloride and sodium nitrate, and for these cases the extended Debye-Hückel equation is obeyed reasonably well. However, the enhanced solubility of anhydrite in solutions of calcium chloride and sodium sulfate above what can be ascribed to ionic strength effects can be explained in terms of the formation of complexes such as $CaSO_4^\circ$, $Ca_2SO_4^{2+}$, and $Ca(SO_4)_2^{2-}$. Similarly, the enhanced solubility of anhydrite in magnesium chloride solutions can be ascribed to the formation of $MgSO_4^0$ and $Mg_2SO_4^{2+}$

ANHYDRITE, $CaSO_4$, is the stable phase of calcium sulfate above 100° C. in the $CaSO_4$-H_2O and $CaSO_4$-NaCl-H_2O systems, and presumably would be the stable phase above 100° C. in contact with any natural brine. Its solubility in aqueous salt solutions at elevated temperatures is of practical interest in hydrothermal geology and in connection with scale precipitation in field heaters during wet steam or hot water injection for thermal oil recovery. The same solubility data are of theoretical interest as a means of testing whether conventional ideas concerning the behavior of "strong" electrolytes in aqueous solution below 100° C. (specifically the Debye-Hückel theory and the relatively complete dissociation of all salts into simple ions) are tenable as the temperature approaches the critical point (374° C.).

The solubility of anhydrite in pure water along the vapor pressure curve above 200° C. has been studied by Partridge and White (*20*), Straub (*24*), and Booth and Bidwell (*3*). These data were compared by Linke and Seidell (*14*) and are in good agreement with each other up to 320° C. (only Booth and Bidwell have extended the measurements to 400° C.). Dickson, Blount, and Tunell (*4*) studied the solubility of anhydrite in pure water from 100° to 275° C. and from 1 to 1000 bars pressure, but their highest temperature studied along the vapor pressure curve was 157° C. and 15 bars. Dickson, Blount, and Tunell (*4*) have extrapolated their $CaSO_4$-H_2O data to predict significantly smaller values in the 200° to 400° C. range than those of these previous investigators.

Zdanovskii (*25*) and Marshall, Slusher, and Jones (*15*) have published data for the solubility of anhydrite in sodium chloride solutions at pressures just above the vapor pressure up to 200° C. More recently Marshall and Jones (*17*) have reported work on the solubility of anhydrite in sodium chloride and sulfuric acid solutions up to 350° C.

In this study a flow apparatus was used to investigate the $CaSO_4$-H_2O system between 200° and 325° C.; various ternary systems of the type $CaSO_4$-AB-H_2O, where AB includes chlorides, nitrates, and sulfates of sodium, calcium, and magnesium, up to 325° C.; and the quaternary systems $CaSO_4$-$CaCl_2$-NaCl-H_2O, $CaSO_4$-Na_2SO_4-NaCl-H_2O, and $CaSO_4$-$MgCl_2$-NaCl-H_2O at 250° and 300° C. at ionic strengths of 0.5 and 0.9 molal. The results have been interpreted according to the Debye-Hückel theory, with the postulation of complex calcium sulfate and magnesium sulfate species where necessary.

EXPERIMENTAL

High Temperature Flow Solubility Apparatus. In contrast to the batch cell equipment used by most previous workers (*15, 4*), Morey and Hesselgesser (*18*) described a flow solubility apparatus for use at elevated temperatures. When the flow method is used with a solid phase whose solubility increases with increase in temperature, such as quartz in superheated steam, one must take care that the solute stays in supersaturated solution in the cooled effluent. Such a difficulty does not arise with a solid whose solubility decreases monotonically with increase in temperature, such as anhydrite. Under these circumstances, after filtration at the equilibration temperature, the cooled effluent solution will be undersaturated and rapidity of analysis is not critical.

The authors have constructed a similar flow system largely from Type 316 stainless steel tubing, either 1/4- or 1/8-inch O.D., with associated Tylok and Swagelok fittings. Nitrogen pressure (up to 2500 p.s.i.g.) is applied to a mercury filled system to displace the feed brine into an equilibration coil and filter contained in a constant temperature water-steam chamber. The water-steam chamber is a separate system surrounded by vermiculite insulation, whose temperature was regulated to within ±1° C. at set temperatures between 200° and 350° C.

The equilibration coil was wound from about 10 feet of ¼-inch O.D. stainless steel tubing, with a volume of about 32 ml. and ends in a stainless steel filter snubber of 0.5 micron pore diameter placed inside the high temperature chamber. The outflow end of the snubber is a fitting for attaching ⅛-inch O.D. stainless steel tubing. Such tubing conducts the filtered solution out of the high temperature region through a water cooled jacket to a needle valve which controls the flow rate. After passing through the needle valve, samples for chemical analysis are collected in test tubes under atmospheric conditions.

The solubilities being determined here are essentially along the "boiling curve"—i.e., at absolute pressures slightly above the vapor pressure at the temperature in question. Literature data (*4*) indicate that the slight increase of the solubility of $CaSO_4$ arising from a pressure inside the flow cell greater than the solution vapor pressure will be of the order of the experimental scatter in the values of m_{CaSO_4} in the $CaSO_4$-$NaCl$-H_2O system at 250° C. To ensure that no vapor phase exists in the flow system at, say, 250° C., the downstream pressure is kept at about 700 p.s.i.g., while the upstream pressure is kept at about 900 p.s.i.g. Allowing a differential up to 500 p.s.i.g. between the applied nitrogen pressure and the test chamber steam pressure, this apparatus can be used up to 336° C. (2000 p.s.i.g. steam) with nitrogen pressures of 2500 p.s.i.g.

The equilibrium coil was filled with loosely packed (5 to 15 grams) anhydrite, and solutions with a known amount of NaCl and/or other supporting salts flowed through the apparatus at rates from 3 to 30 ml. per hour (corresponding to 1 to 10 hours of residence time in the coil). The $CaSO_4$ content of the feed brines was fixed so that in about half of the systems the equilibrium was approached from lower $CaSO_4$ concentrations (analyses marked b in Tables I to V), and in the other half of the systems equilibrium was approached "from above" (analyses designated a in Tables I to V). Since no systematic difference could be noted between the "from below" and "from above" solubility values, the authors concluded that true equilibrium between anhydrite and the brines was attained for these operating conditions.

Reagents and Analytical Methods. All salts used in mixing the feed brine solutions were of Baker analyzed reagent grade or equivalent, as was the anhydrite used in the equilibration coil. Distilled water was used in making up the solutions.

On each effluent sample, spectrophotometric methods were used to determine either calcium (*2*), or sulfate (*6*), or both when possible. For some cases, calcium was determined by EDTA titration. The molality of each ion was calculated based on appropriate density values from the $NaCl$-H_2O system at 25° C. (*19*). When the supporting electrolyte contains no Ca^{2+} or SO_4^{2-}, then $(m_{Ca})_T$ and $(m_{SO_4})_T$ should be equal in the equilibrated solution, where $(m_i)_T$ designates the total analytical molality of the species in question. Practically $(m_{Ca})_T$ and $(m_{SO_4})_T$ may differ owing to analytical errors or impurities. Consequently, m_{CaSO_4} may be based on

$$m_{CaSO_4} = [(m_{Ca})_T \cdot (m_{SO_4})_T]^{1/2} \tag{1}$$

$$m_{CaSO_4} = (m_{Ca})_T \tag{2}$$

or

$$m_{CaSO_4} = (m_{SO_4})_T \tag{3}$$

Equation 1 is preferred when it is possible to determine both $(m_{Ca})_T$ and $(m_{SO_4})_T$, since it averages analytical devia-

Table I. Solubility of Anhydrite in Water, 200° to 325° C.

Temp., ° C.	Number of Samples[a]	m_{CaSO_4}: $(m_{Ca})_T$	m_{CaSO_4}: $(m_{SO_4})_T$	m_{CaSO_4}: $[(m_{Ca})_T(m_{SO_4})_T]^{1/2}$	Total Cations by Resin Exchange as $(m_{Ca})_T$
200	21b	$5.16 \times 10^{-4} \pm 0.15$	$4.95 \times 10^{-4} \pm 0.21$	$5.05 \times 10^{-4} \pm 0.16$	$5.07 \times 10^{-4} \pm 0.01$
225	23b	$2.84 \times 10^{-4} \pm 0.06$	$2.73 \times 10^{-4} \pm 0.09$	$2.78 \times 10^{-4} \pm 0.05$	$2.72 \times 10^{-4} \pm 0.05$
250	24b	$1.28 \times 10^{-4} \pm 0.06$	$1.23 \times 10^{-4} \pm 0.05$	$1.25 \times 10^{-4} \pm 0.03$	$1.33 \times 10^{-4} \pm 0.06$
275	18a	$7.30 \times 10^{-5} \pm 0.09$	$5.63 \times 10^{-5} \pm 0.40$	$6.40 \times 10^{-5} \pm 0.24$	$7.16 \times 10^{-5} \pm 0.25$
	9b	$7.28 \times 10^{-5} \pm 0.17$	$5.41 \times 10^{-5} \pm 0.25$	$6.27 \times 10^{-5} \pm 0.21$	
300	29b	$3.93 \times 10^{-5} \pm 0.20$	$3.39 \times 10^{-5} \pm 0.30$	$3.64 \times 10^{-5} \pm 0.18$	$4.25 \times 10^{-5} \pm 0.20$
325	27a	$2.14 \times 10^{-5} \pm 0.36$	$1.11 \times 10^{-5} \pm 0.34$	$1.49 \times 10^{-5} \pm 0.20$	

[a] Symbols a and b denote whether equilibrium was approached from above or below.

Table II. Solubilities of $CaSO_4$ in $NaCl$-H_2O Solutions from 250° to 325° C.

250° C.		275° C.		300° C.		325° C.	
m_{NaCl}	m_{CaSO_4}[a]	m_{NaCl}	m_{CaSO_4}[a]	m_{NaCl}	m_{CaSO_4}[a]	m_{NaCl}	m_{CaSO_4}[a]
0.000260	0.000129b	0.000235	0.0000612b	0.00615	0.0000428b	0.0177	0.0000311b
0.000934	0.000145b	0.00363	0.0000767b	0.00862	0.0000494b	0.0518	0.0000645a
0.00359	0.000166b	0.00621	0.0000862b	0.00876	0.0000477b	0.0882	0.000108a
0.00468	0.000171a	0.00893	0.000107b	0.0187	0.0000614b	0.174	0.000215a
0.00611	0.000186b	0.0169	0.000118b	0.0208	0.0000636a	0.176	0.000212b
0.00844	0.000197b	0.0428	0.000191b	0.0356	0.0000883b	0.534	0.000780b
0.01826	0.000249a	0.0517	0.000254a	0.0533	0.000122a	0.905	0.00153b
0.01874	0.000252b	0.0620	0.000248b	0.0886	0.000189a	0.913	0.00157a
0.03526	0.000321b	0.0866	0.000357a	0.1726	0.000351a	1.500	0.00303a
0.0521	0.000388a	0.1750	0.000565a	0.1755	0.000334b	1.920	0.00415a
0.0542	0.000393b	0.1767	0.000574b	0.549	0.00113b	1.921	0.00408a
0.0806	0.000547a	0.1772	0.000559a	0.8874	0.00185b	1.921	0.00409b
0.0859	0.000554b	0.526	0.00147b	0.9004	0.00192a	3.044	0.00753b
0.178	0.000902a	0.902	0.00258b	1.526	0.00363a	4.163	0.0122a
0.533	0.00217a	0.908	0.00256a	1.909	0.00465a	4.186	0.0123a
0.553	0.00211b	1.500	0.00427a	1.926	0.00464b	4.196	0.0124b
0.908	0.00344b	1.919	0.00544b	3.210	0.00904b	4.245	0.0126b
0.927	0.00342a	1.920	0.00550a	4.208	0.0123b	5.684	0.0186b
1.485	0.00579a	3.044	0.00892a	4.316	0.0122a		
1.914	0.00711a	4.208	0.0130b	5.145	0.156a		
2.045	0.00736b	4.209	0.0131a	5.690	0.0187a		
3.043	0.0111a	5.759	0.0185b				
3.063	0.0107b						
4.336	0.0148a						
4.335	0.0149b						
5.017	0.0167a						
5.766	0.0192a						

[a] Symbols a and b denote whether equilibrium was approached from above or below.

Table III. Solubilities of $CaSO_4$ In $NaNO_3$–H_2O Solutions at 300° C.

$m_{\mathrm{NaNO_3}}$	$m_{\mathrm{CaSO_4}}$[a]	$m_{\mathrm{NO_2}}$–Detected
0.0200	0.0000753b	0.00092
0.0507	0.000133b	0.0017
0.0507	0.000161a	
0.0753	0.000183b	0.00096
0.1000	0.000230b	0.00028
0.1000	0.000237a	0.0015
0.3017	0.000603a	0.00029
0.5030	0.00102b	0.0012
0.7569	0.00159b	0.0016
1.0105	0.00223b	0.0013
1.0105	0.00229a	0.0018
1.5123	0.00369a	
2.0113	0.00542b	0.0039
2.0113	0.00545b	
2.0113	0.00536a	
2.9596	0.00803b	0.0025
4.0142	0.0121b	0.0029
4.0142	0.0120a	
5.0397	0.0159a	0.0047

[a] Symbols a and b denote whether equilibrium was approached from above or below.

Table IV. Solubilities of $CaSO_4$ in Various 2 to 1 Salt Solutions

$CaSO_4$–$CaCl_2$–H_2O System

$m_{\mathrm{CaCl_2}}$	$m_{\mathrm{CaSO_4}}$[a]
250° C.	
0.0333	0.000119b
0.100	0.000198b
0.100	0.000193a
0.1666	0.000237b
0.300	0.000364b
300° C.	
0.0333	0.0000417b
0.100	0.0000943b
0.100	0.0000872a
0.1666	0.000110b
0.300	0.000223b

$CaSO_4$–$MgCl_2$–H_2O System

$m_{\mathrm{MgCl_2}}$	$m_{\mathrm{CaSO_4}}$
250° C.	
0.0328	0.00187b
0.0965	0.00392b
0.0965	0.00390a
0.1631	0.00568b
0.2956	0.00909a
300° C.	
0.0328	0.00127b
0.0982	0.00294b
0.1631	0.00456b
0.1631	0.00455a
0.2956	0.00792b

$CaSO_4$–Na_2SO_4–H_2O System

$m_{\mathrm{Na_2SO_4}}$	$m_{\mathrm{CaSO_4}}$
250° C.	
0.03332	0.000166b
0.03332	0.000153a
0.09998	0.000320a
0.1666	0.000488b
0.1666	0.000486b
0.1666	0.000468a
0.300	0.000826b
300° C.	
0.03332	0.0000807a
0.09998	0.000165b
0.09998	0.000183a
0.1666	0.000319a
0.300	0.000693b
0.300	0.000689a

$CaSO_4$–$Mg(NO_3)_2$–H_2O System

$m_{\mathrm{Mg(NO_3)_2}}$	$m_{\mathrm{CaSO_4}}$
250° C.	
0.03083	0.00203b
0.09441	0.00414a
0.09441	0.00420b
0.1576	0.00615b
0.2881	0.01042a
0.2881	0.01045b

[a] Symbols a and b denote whether equilibrium was approached from above or below.

tions from both sources; this has been done for the data for $CaSO_4$–NaCl–H_2O. For the study of $CaSO_4$–$NaNO_3$–H_2O where $(m_{\mathrm{SO_4}})_T$ cannot be measured because of nitrate interference, Equation 2 was used.

When the supporting electrolyte contains Ca^{2+} but no SO_4^{2-} as in the case of $CaCl_2$ feed solutions, then Equation 3 must be used. Conversely, when the supporting electrolyte contains SO_4^{2-} but no Ca^{2-} as in the case of Na_2SO_4 feed solutions, then Equation 2 must be used.

In the $CaSO_4$–NaCl–H_2O system, each flow method point is an average result from the analysis of four to 10 consecutive samples in a given run. The precison of these data is in the range of ±2% of the value of $m_{\mathrm{CaSO_4}}$. The molality of NaCl corresponding to each $m_{\mathrm{CaSO_4}}$ value was calculated from experimental measurements of the weight fraction of total dissolved salts by evaporation, corrections being made for the $CaSO_4$ dissolved. If m_{NaCl} is very much greater than $(m_{\mathrm{Ca}})_T$ or $(m_{\mathrm{SO_4}})_T$, one hardly needs to make the correction for $CaSO_4$ in the total dissolved salts. On the other hand, if the sodium chloride content becomes of the same order of magnitude as the $CaSO_4$ content, the sum of dissolved cations should be determined by adsorbing Ca^{2-} and Na^+ on a cation-exchange resin in the hydrogen form, and titrating for total released acidity in the effluent as was done by Marshall, Slusher, and Jones (*15*). This procedure was used by the present authors for a few measurements at low salinities at each temperature.

RESULTS

$CaSO_4$–H_2O. Table I contains solubility data for the $CaSO_4$–H_2O system for temperatures from 200° to 325° C., at intervals of 25° C., averaged from the analysis of more than 20 samples at each temperature. It was possible to measure these data only with an anhydrite pack which had not been contacted with any salt solutions and which had been given an extended washing with distilled water. Each of $(m_{\mathrm{Ca}})_T$, $(m_{\mathrm{SO_4}})_T$, and $[(m_{\mathrm{Ca}})_T(m_{\mathrm{SO_4}})_T]^{1/2}$ is an independent estimate of $m_{\mathrm{CaSO_4}}$, reflecting deviations owing to analytical errors and impurities in the reagents. The $(m_{\mathrm{Ca}})_T$ data tend to be systematically higher than the $(m_{\mathrm{SO_4}})_T$ values; hence, the $[(m_{\mathrm{Ca}})_T(m_{\mathrm{SO_4}})_T]^{1/2}$ values are considered to be the best estimate of $m_{\mathrm{CaSO_4}}$ that can be obtained from the present experiments.

At each temperature the acidity-release resin exchange scheme was used to measure the total salt cations on a solution sample. These results expressed as $(m_{\mathrm{Ca}})_T$ are listed in the last column of Table I. At temperatures between 200° and 250° C. these resin exchange values are practically equivalent to the analytically determined values of $(m_{\mathrm{Ca}})_T$ and $(m_{\mathrm{SO_4}})_T$. At temperatures of 275° C. and above the resin exchange method becomes subject to more uncertainty as the magnitude of the solubility decreases; in fact, at 325° C. it was not practical to get a result by the resin exchange method. At 275° and 300° C. the resin exchange values agree well with the $(m_{\mathrm{Ca}})_T$ values, indicating that some calcium salts other than $CaSO_4$ have been dissolved from the pack. However, the amounts of these extraneous calcium salts are of the same order of magnitude as the deviations from the mean of the various average solubility values. Consequently, it still seems that $[m_{\mathrm{Ca}})_T(m_{\mathrm{SO_4}})_T]^{1/2}$ is the best estimate of $m_{\mathrm{CaSO_4}}$ in the $CaSO_4$–H_2O system.

$CaSO_4$–NaCl–H_2O. Table II gives m_{NaCl}, $m_{\mathrm{CaSO_4}}$ data for temperatures of 250°, 275°, 300°, and 325° C., covering almost the entire range of m_{NaCl}.

$CaSO_4$–$NaNO_3$–H_2O. Table III gives $m_{\mathrm{NaNO_3}}$, $m_{\mathrm{CaSO_4}}$ data for 300° C., where an attempt was made to get anhydrite solubilities over a wide range of $m_{\mathrm{NaNO_3}}$.

In all these runs, the residence time was kept below 2 hours, and nitrate stability was checked by determination of nitrite formation by a permanganate method. No measurements are listed where nitrite formation exceeded 5% of the original nitrate concentration.

Ternary Systems with 2 to 1 Salts. Table IV contains $m_{\mathrm{CaSO_4}}$ data for several systems in which the supporting electrolyte is a 2 to 1 salt. The following systems were studied over a range of stoichiometric ionic strength, *I*, between 0.1 and 0.9 molal, at the indicated temperatures: $CaSO_4$–$CaCl_2$–H_2O, 250° and 300° C.; $CaSO_4$–$MgCl_2$–H_2O, 250° and 300° C.; $CaSO_4$–Na_2SO_4–H_2O, 250° and 300° C.; and $CaSO_4$–$Mg(NO_3)_2$–H_2O, 250° C. Since $Mg(NO_3)_2$ and $MgCl_2$ supporting electrolytes give essentially the same $m_{\mathrm{CaSO_4}}$ at the same *I* and *T*, only the $MgCl_2$ results will be used in the discussion of magnesium-sulfate ion association.

Table V. Solubilities of $CaSO_4$ in Solutions of Constant Ionic Strength for Some Quaternary Systems

$CaSO_4$-$CaCl_2$NaCl-H_2O System		
m_{CaCl_2}	m_{NaCl}	m_{CaSO_4}[a]
	250° C., I = 0.50	
...	0.492	0.00199
0.0080	0.4747	0.000496a
0.0080	0.4747	0.000517b
0.0250	0.4246	0.000263b
0.0250	0.4246	0.000262b
0.0700	0.2898	0.000236b
0.0700	0.2898	0.000244a
0.1666	...	0.000237b
	250° C., I = 0.90	
...	0.8868	0.00330
0.0040	0.8763	0.00186a
0.0100	0.8653	0.00109b
0.0180	0.8434	0.000746a
0.0250	0.8231	0.000532b
0.0400	0.7788	0.000420b
0.0800	0.6594	0.000372b
0.0800	0.6594	0.000370b
0.0800	0.6594	0.000364a
0.100	0.5995	0.000360b
0.200	0.2996	0.000366b
0.200	0.2996	0.000385a
0.300	...	0.000364b
	300° C., I = 0.50	
	0.496	0.00100
0.0080	0.4747	0.000184a
0.0250	0.4246	0.0000939b
0.0250	0.4246	0.0000970a
0.0700	0.2898	0.0000889b
0.0700	0.2898	0.0000913a
0.1666	...	0.000110b
	300° C., I = 0.90	
...	0.892	0.00189
0.0040	0.8763	0.000802a
0.0180	0.8434	0.000315a
0.0400	0.7788	0.000210a
0.0400	0.7788	0.000217b
0.0800	0.6594	0.000166b
0.200	0.2996	0.000208b
0.200	0.2996	0.000195a
0.300	...	0.000223b

$CaSO_4$-Na_2SO_4-NaCl-H_2O System		
$m_{Na_2SO_4}$	m_{NaCl}	m_{CaSO_4}
	250° C., I = 0.50	
...	0.492	0.00199
0.00290	0.4878	0.00101b
0.00600	0.4803	0.000673b
0.00600	0.4803	0.000667a
0.0200	0.4395	0.000351b
0.0600	0.3198	0.000326a
0.1666	...	0.000488b
0.1666	...	0.000486b
0.1666	...	0.000468a
	250° C., I = 0.90	
...	0.887	0.00330
0.0060	0.8769	0.00154a
0.0170	0.8462	0.000801b
0.0400	0.7788	0.000546b
0.0400	0.7788	0.000542a
0.100	0.5995	0.000490b
0.100	0.5995	0.000490a
0.300	...	0.000826b
	300° C., I = 0.50	
...	0.496	0.00100
0.00290	0.4878	0.000354b
0.00600	0.4803	0.000204a
0.0200	0.4395	0.000144b
0.0600	0.3198	0.000144b
0.0600	0.3198	0.000153a
0.1666	...	0.000319a
	300° C., I = 0.90	
...	0.892	0.00189
0.0060	0.8769	0.000629a
0.0170	0.8462	0.000354b
0.0170	0.8462	0.000345a
0.0400	0.7788	0.000269a
0.100	0.5995	0.000313b
0.300	...	0.000693b
0.300	...	0.000689a

$CaSO_4$-$MgCl_2$-NaCl-H_2O System		
m_{MgCl_2}	m_{NaCl}	m_{CaSO_4}
	250° C., I = 0.50	
...	0.492	0.00199
0.00295	0.4853	0.00204b
0.00811	0.4694	0.00218b
0.00811	0.4694	0.00214a
0.0204	0.4320	0.00262b
0.0204	0.4320	0.00260a
0.0608	0.3070	0.00358b
0.0608	0.3070	0.00360a
0.1219	0.1240	0.00490b
0.1219	0.1240	0.00492a
0.1631	...	0.00568b
	300° C., I = 0.50	
...	0.496	0.00100
0.00295	0.4853	0.00107a
0.00295	0.4853	0.00107b
0.00811	0.4694	0.00131a
0.0204	0.4320	0.00166a
0.0608	0.3070	0.00251b
0.0608	0.3070	0.00265a
0.1219	0.1240	0.00378a
0.1631	...	0.00456b
0.1631	...	0.00455a

[a] Symbols a and b denote whether equilibrium was approached from above or below

Quaternary Systems. Table V contains composition data for three quaternary systems.

$CaSO_4$-NaCl-$CaCl_2$-H_2O. Mixtures of sodium and calcium chlorides covering the range from pure NaCl-H_2O to pure $CaCl_2$-H_2O at constant stoichiometric ionic strength

$$I = \tfrac{1}{2}\sum m_i Z_i^2 = m_{NaCl} + 3m_{CaCl_2} + 4m_{CaSO_4} \qquad (4)$$

were used as solvents for anhydrite for the following conditions. 250° C., I = 0.500 and 0.900; 300° C., I = 0.500 and 0.900.

$CaSO_4$-NaCl-Na_2SO_4-H_2O. Mixtures of sodium chloride and sodium sulfate covering the range from pure NaCl-H_2O to pure Na_2SO_4-H_2O at constant I were used to study this system as follows: 250° C., I = 0.500 and 0.900; 300° C., I = 0.500 and 0.900.

$CaSO_4$-NaCl-$MgCl_2$-H_2O. Mixtures of sodium and magnesium chlorides covering the range from pure NaCl-H_2O to pure $MgCl_2$-H_2O at constant I were equilibrated with anhydrite for the following conditions: 250° C., I = 0.500; 300° C., I = 0.500.

DISCUSSION

If we write the reaction

$$CaSO_4(s) \rightleftarrows Ca^{2+} + SO_4^{2-} \qquad (5)$$

with its accompanying thermodynamic solubility product

$$K_s = a_{Ca^{2+}} \cdot a_{SO_4^{2-}} = \gamma_\pm^2 m_{Ca^{2+}} \cdot m_{SO_4^{2-}} \qquad (6)$$

and its corresponding concentration solubility product

$$K_s' = m_{Ca^{2+}} \cdot m_{SO_4^{2-}} = K_s/\gamma_\pm^2 \qquad (7)$$

(where a_i denotes the activity of species i, and $\gamma_\pm$ denotes the mean activity coefficient of $CaSO_4$ in solution), we assume Ca^{2+} and SO_4^{2-} to be the only ionic species resulting from solution of $CaSO_4$. On this basis for the $CaSO_4$-NaCl-H_2O system at some particular value of m_{NaCl}

$$K_s' = (m_{CaSO_4})^2 \qquad (8)$$

These assumptions are tenable if the data at low ionic strength can be extrapolated to I = 0 in reasonable agreement with the Debye-Hückel theory. Associated ionic species should be considered only when the solubility exceeds that attributable to interionic attraction.

Leitzke and Stoughton (*8-12*) studied the solubility of Ag_2SO_4 in aqueous solutions of KNO_3, K_2SO_4, H_2SO_4, HNO_3, and $MgSO_4$ up to 200° C. All of these ternary Ag_2SO_4-supporting electrolyte-H_2O systems were treated on the basis of complete dissociation of all salts when the supporting electrolyte was not an acid, and for the H_2SO_4 and HNO_3 cases only the associated species HSO_4^- and

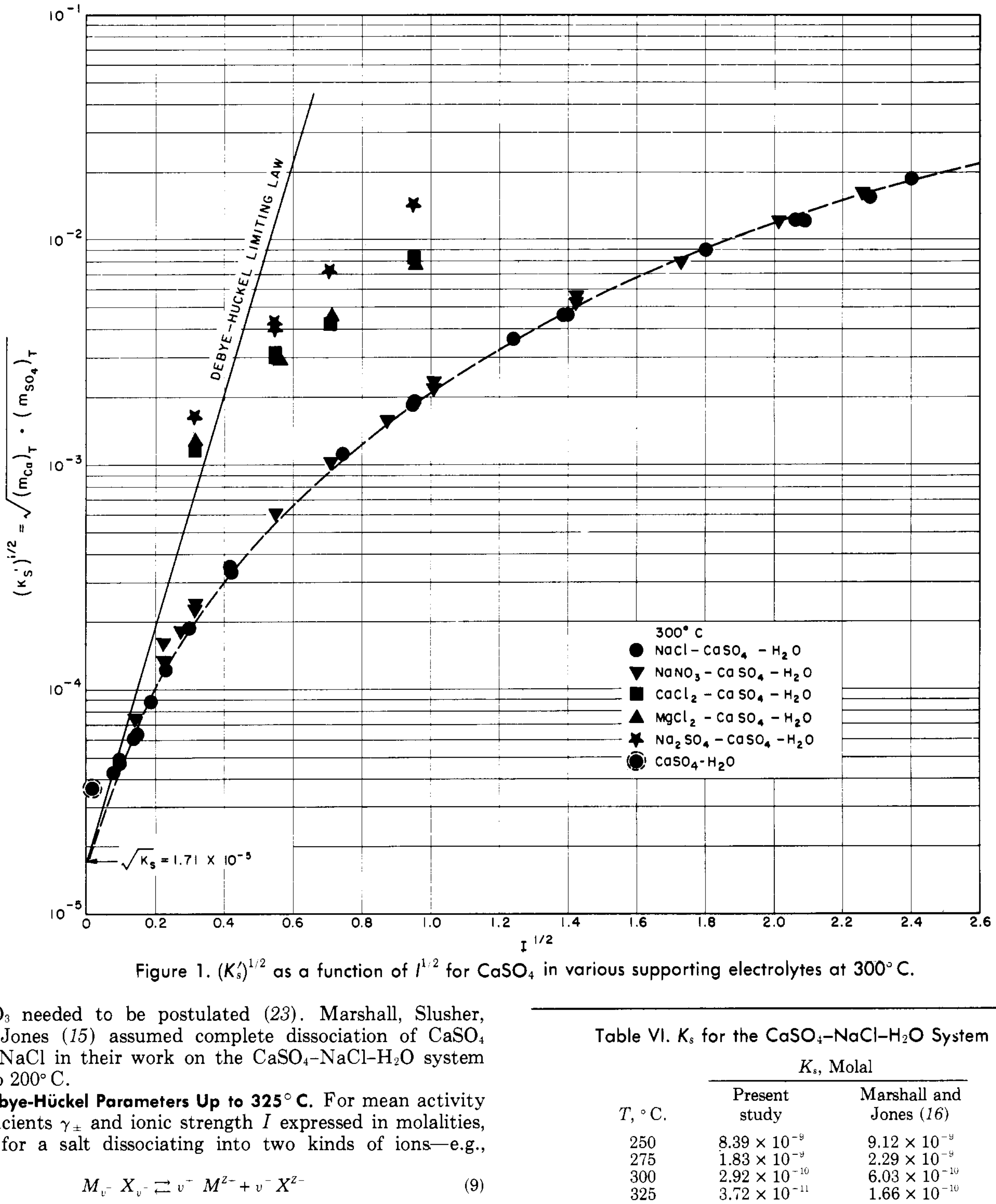

Figure 1. $(K_s')^{1/2}$ as a function of $I^{1/2}$ for $CaSO_4$ in various supporting electrolytes at 300° C.

HNO_3 needed to be postulated (*23*). Marshall, Slusher, and Jones (*15*) assumed complete dissociation of $CaSO_4$ and NaCl in their work on the $CaSO_4$-NaCl-H_2O system up to 200° C.

Debye-Hückel Parameters Up to 325° C. For mean activity coefficients $\gamma_\pm$ and ionic strength I expressed in molalities, and for a salt dissociating into two kinds of ions—e.g.,

$$M_{\nu^-} X_{\nu^-} \rightleftarrows \nu^- M^{Z-} + \nu^- X^{Z-} \tag{9}$$

the Debye-Hückel equation (*5, 13, 21*) may be written as

$$\log \gamma_= = \frac{-A\gamma|Z_+Z_-|I^{1/2}}{1 + aB\gamma I^{1/2}} = -\frac{A\gamma|Z_+Z_-|I^{1/2}}{1 + CI^{1/2}} \tag{10}$$

where

$$A\gamma = \frac{d_0^{1/2}(1.8246)(10^6)}{(DT)^{3/2}} \tag{11}$$

$$B\gamma = (50.29)\cdot\left(\frac{d_0}{DT}\right)^{1/2} \tag{12}$$

d_0 is the density of the solvent, D is the dielectric constant of the solvent, T is the temperature on the Kelvin scale, and a in angstrom units is the mean distance of "closest approach" between the centers of M^{Z-} and X^{Z-}. Values of the dielectric constant of water at elevated temperatures

Table VI. K_s for the $CaSO_4$–NaCl–H_2O System

T, ° C.	K_s, Molal Present study	 Marshall and Jones (*16*)
250	8.39×10^{-9}	9.12×10^{-9}
275	1.83×10^{-9}	2.29×10^{-9}
300	2.92×10^{-10}	6.03×10^{-10}
325	3.72×10^{-11}	1.66×10^{-10}

Table VII. Smoothed Values of m_{CaSO_4} as a Function of m_{NaCl} for the $CaSO_4$–NaCl–H_2O System between 250° and 325° C.

m_{NaCl}	$[K_s']^{1/2} = m_{CaSO_4}$ 250° C.	 275° C.	 300° C.	 325° C.
0.0	0.000110	0.0000493	0.0000190	0.0000066
0.01	0.000206	0.000105	0.0000480	0.0000209
0.03	0.000320	0.000174	0.0000861	0.0000423
0.06	0.000461	0.000262	0.000139	0.0000752
0.1	0.000626	0.000372	0.000208	0.000122
0.3	0.00133	0.00087	0.000580	0.000373
0.6	0.00232	0.00162	0.00121	0.00090
1.0	0.00377	0.00281	0.00219	0.00173
2.0	0.00720	0.00585	0.0050	0.00429
3.0	0.0104	0.00918	0.0083	0.0075
4.0	0.0135	0.0127	0.0118	0.01095
5.0	0.0168	0.0162	0.0154	0.0149

were taken from the data of Akerloff and Oshry (*1*). The density of water along the boiling curve may be calculated from standard tables (*7*). For 250°, 275°, 300°, and 325° C., respectively, the calculated $A\gamma$ values were 0.986, 1.112, 1.287, and 1.547; and the calculated $B\gamma$ values were 0.3805, 0.3889, 0.3998, and 0.4131.

Evidence for Existence of Sulfate Complexes of Calcium and Magnesium at 300° C. Combination of Equations 7 and 10 yields

$$\log (K_s')^{1/2} = \log (K_s)^{1/2} + \frac{A\gamma|Z_+Z_-|I^{1/2}}{1 + CI^{1/2}} \tag{13}$$

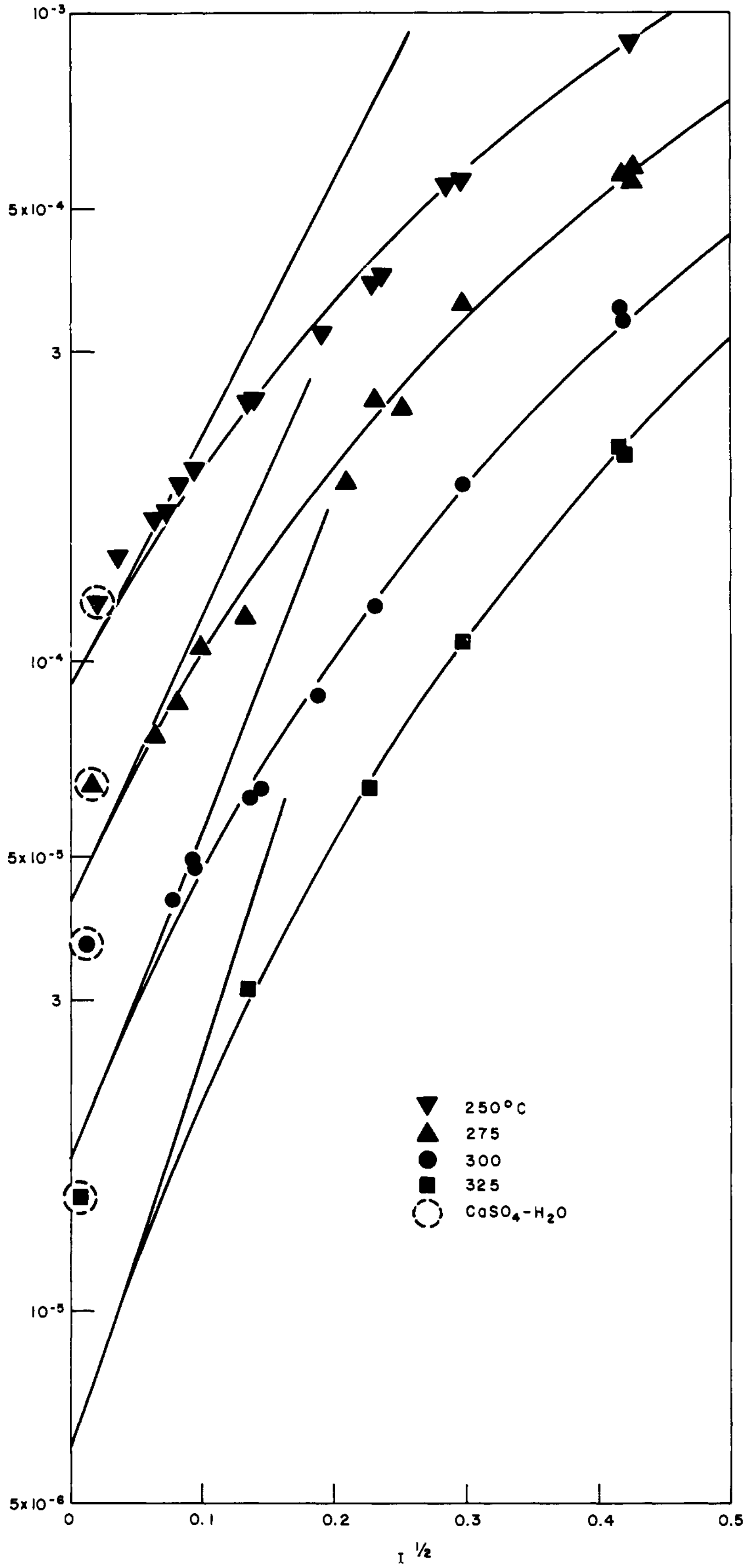

Figure 2. Determination of K_s from $CaSO_4$–NaCl–H_2O system, 250° to 325° C., according to Debye-Hückel theory

When the supporting electrolyte contains neither Ca^{2+} nor SO_4^{2-}, one may write

$$\log m_{CaSO_4} = \log (K_s)^{1/2} + \frac{4A\gamma I^{1/2}}{1 + CI^{1/2}} \quad (14)$$

When the supporting electrolyte contains either Ca^{2-} or SO_4^{2-}, there are other equations for $(K_s')^{1/2}$—e.g., for $CaSO_4$–$CaCl_2$–H_2O:

$$(K_s')^{1/2} = [(m_{Ca})_T(m_{SO_4})_T]^{1/2} = [(m_{CaSO_4} + m_{CaCl_2})(m_{CaSO_4})]^{1/2} \quad (15)$$

and, for $CaSO_4$-Na_2SO_4-H_2O:

$$(K_s')^{1/2} = [(m_{CaSO_4})(m_{CaSO_4} + m_{Na_2SO_4})]^{1/2} \quad (16)$$

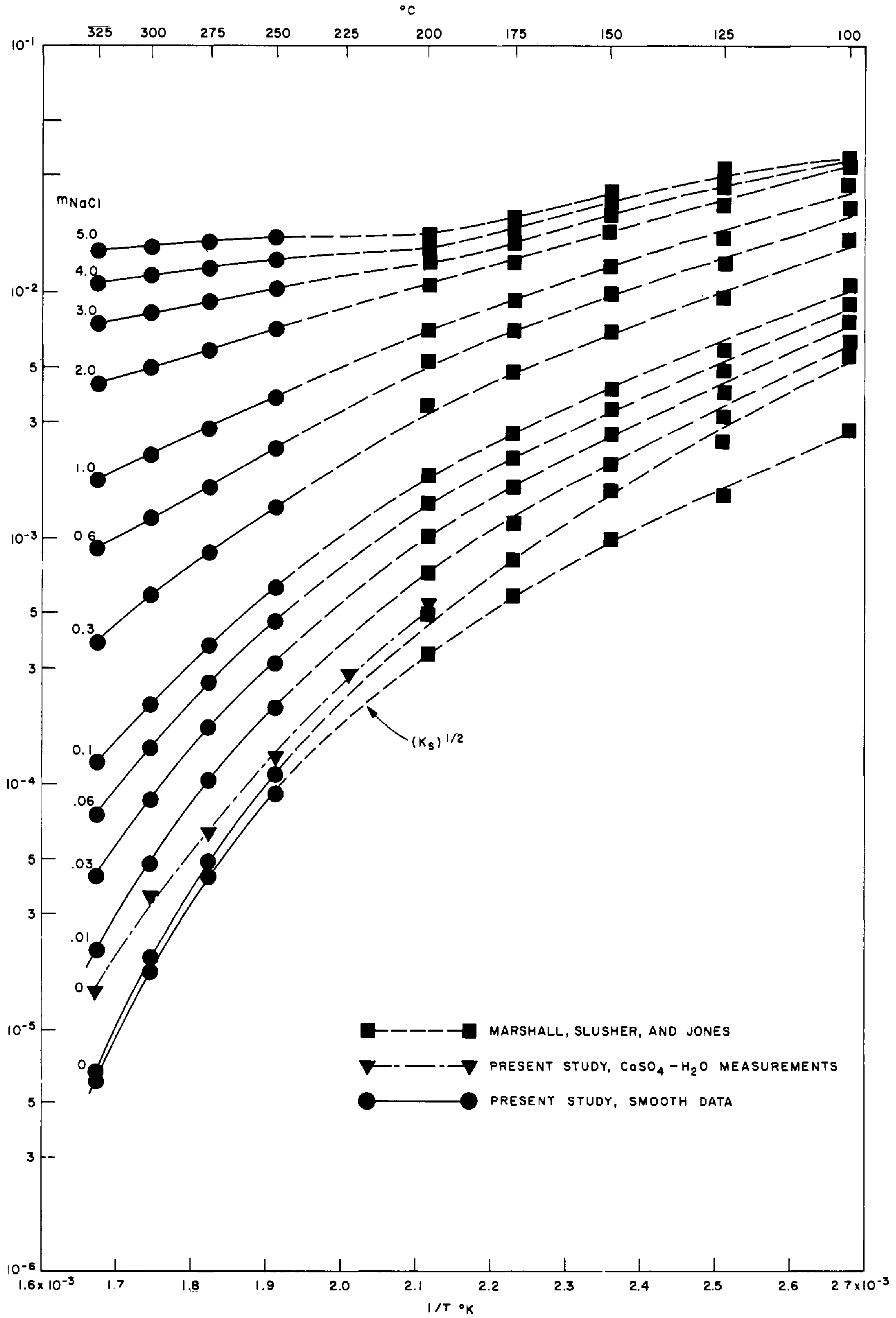

Figure 3. Solubility of anhydrite in $NaCl$–H_2O solutions from 100° to 325° C.

In Figure 1, log $(K_s')^{1/2}$ at 300° C. has been plotted as a function of $I^{1/2}$ for the supporting electrolytes NaCl, $NaNO_3$, $CaCl_2$, $MgCl_2$, and Na_2SO_4. A separation of the supporting electrolytes into two classes is apparent. For NaCl and $NaNO_3$ a single dashed curve has been drawn; the points for $CaCl_2$, $MgCl_2$, and Na_2SO_4 all lie much higher than the NaCl-$NaNO_3$ line. Obviously, sulfate complexing of calcium is much more pronounced than nitrate or chloride complexing of calcium, and sulfate complexing of magnesium is almost identical to that of calcium.

The Debye-Hückel limiting law has been drawn in for a value of $(K_s)^{1/2} = 1.71 \times 10^{-5}$. This particular value of the intercept $(K_s)^{1/2}$ at 300° C. is compatible with Equation 13 and the points for the $CaSO_4$-NaCl-H_2O and $CaSO_4$-$NaNO_3$-H_2O systems at 300° C. Consequently, these two systems may be considered with little error to be amenable to treatment by the Debye-Hückel theory and the absence of associated molecules. (The fact that the $CaSO_4$-H_2O point in Figure 1 lies too high to be consistent with the $CaSO_4$-NaCl-H_2O curve is believed to be due to residual impurities in the "$CaSO_4$-H_2O" system.) By the same token, the fact the points for the $CaSO_4$-$CaCl_2$-H_2O, $CaSO_4$-Na_2SO_4-H_2O, and $CaSO_4$-$MgCl_2$-H_2O systems all lie well above the NaCl-$NaNO_3$ line means that marked formation of $CaSO_4^\circ$ and $MgSO_4^\circ$ (if not also higher associated species) is occurring in these systems. Further, if the three points near $I^{1/2} = 0.32$ for these systems were placed in Equation 13 with $(K_s)^{1/2} = 1.71 \times 10^{-5}$, C would be negative, which means a negative value of a.

Treatment of the $CaSO_4$-NaCl-H_2O System According to Debye-Hückel Theory. For the $CaSO_4$-NaCl-H_2O system at a given temperature, Equation 14 relates $m_{CaSO_4} = (K_s')^{1/2}$ to $I = m_{NaCl} + 4m_{CaSO_4}$ and the constants K_s, A_γ, and C. A_γ has the values given above, and K_s and C may be used as adjustable constants to fit statistically the (m_{CaSO_4}, m_{NaCl}) points to Equation 14. A computer program

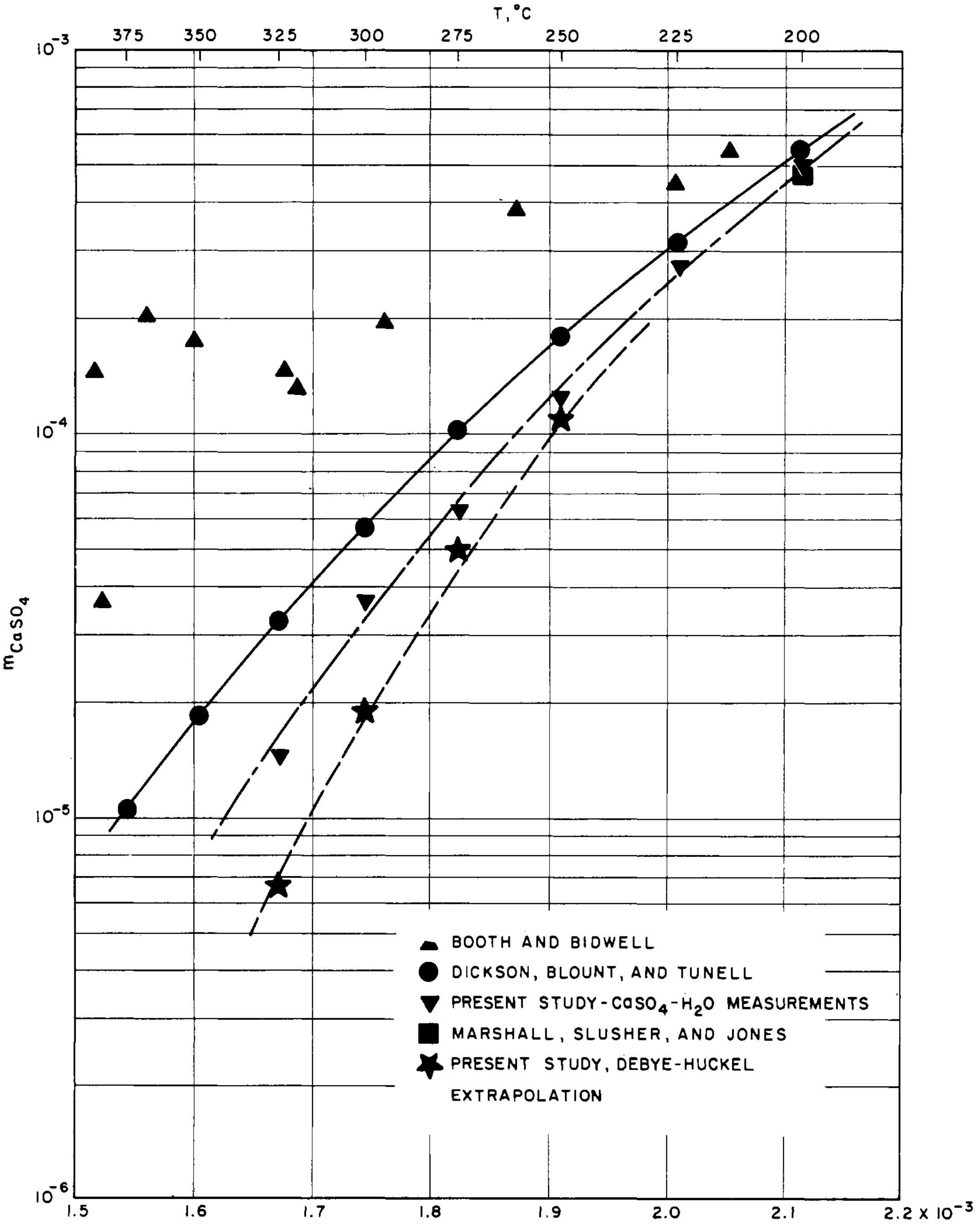

Figure 4. Solubility of $CaSO_4$ in water along boiling curve as a function of temperature, from various sources

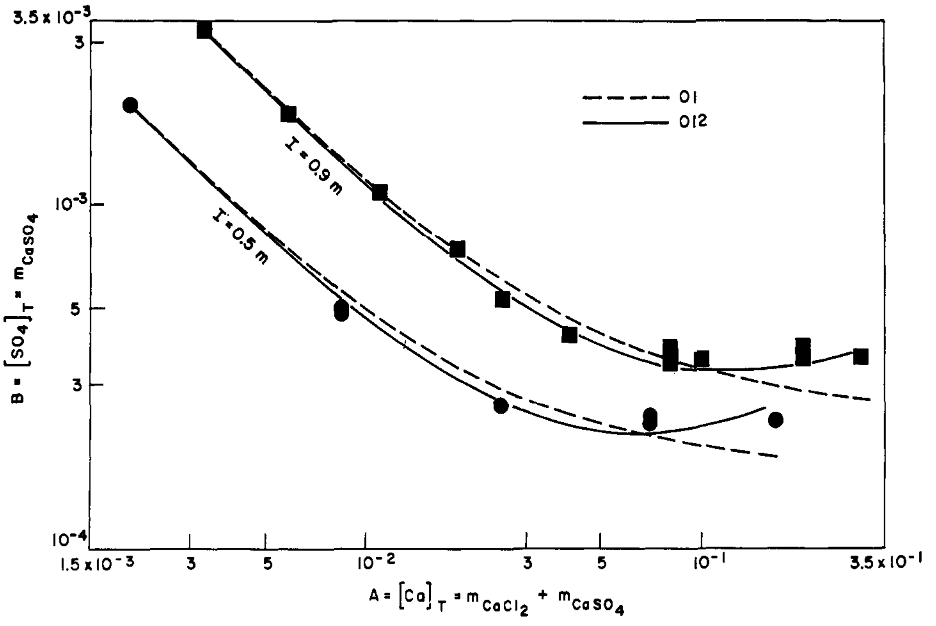

Figure 5. Solubility of anhydrite in $CaCl_2$-NaCl-H_2O solutions at I = 0.5 and 0.9 molal at 250° C.

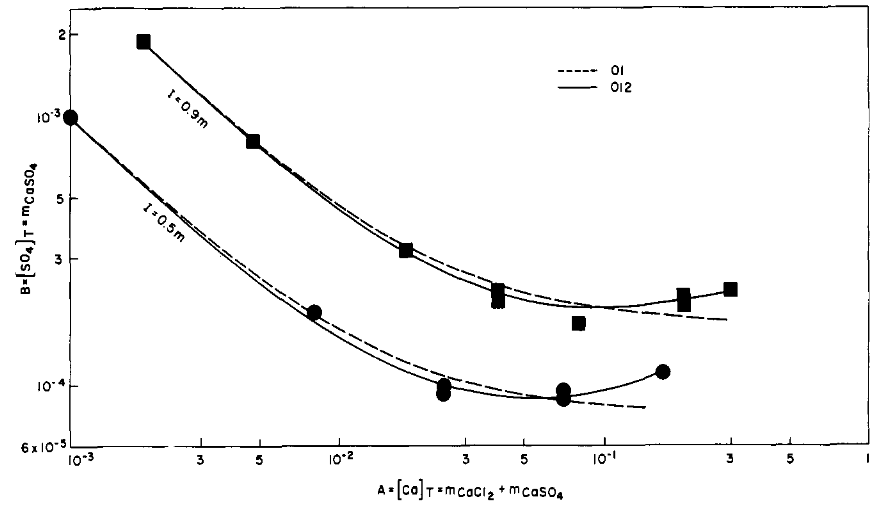

Figure 6. Solubility of anhydrite in $CaCl_2$-NaCl-H_2O solutions of I = 0.5 and 0.9 molal at 300° C.

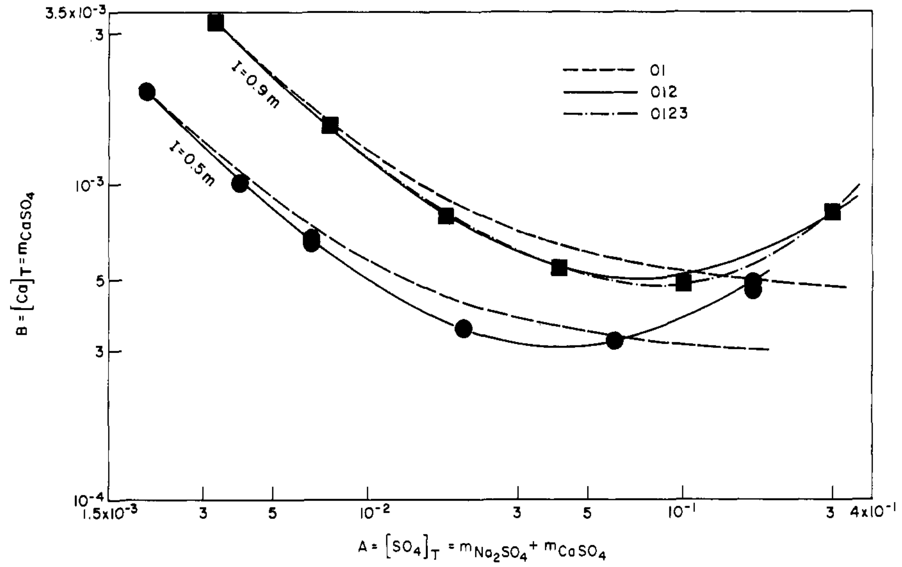

Figure 7. Solubility of anhydrite in Na_2SO_4-NaCl-H_2O solutions of I = 0.5 and 0.9 molal at 250° C.

was worked out to calculate K_s and C, or to calculate K_s with C fixed, to give the least mean squares sum of deviations of calculated m_{CaSO_4} from the experimental values.

The computer was first used at each temperature to fix C and K_s to get the best statistical fit for the data in Table II, for points where I = <0.2 molal. The resulting C values were all between 1.5 and 1.7, but showed no significant trend with temperature. These results suggest the use of a single value of C = 1.6 between 250° and 325° C., which agrees precisely with the experience of Marshall and Jones (*17*) with similar data up to 350° C. [Marshall and Slusher (*16*) in re-evaluating previous solubility data for $CaSO_4$ in NaCl-H_2O from 125° C. to 200° C. (*15*), also

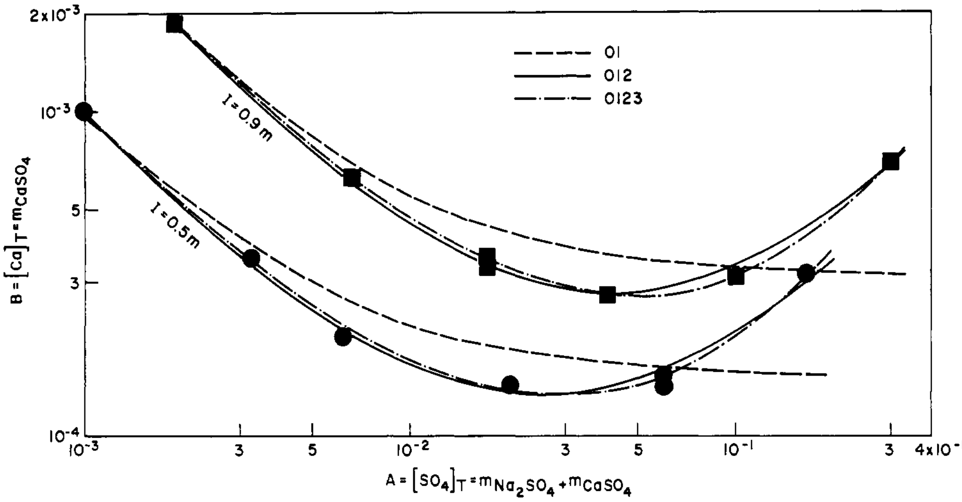

Figure 8. Solubility of anhydrite in Na_2SO_4–NaCl–H_2O solutions of I = 0.5 and 0.9 molal at 300° C.

used 1.6 for C (their A_{sp}) to replace their original value of 1.5]. Thus the present calculations were repeated at each temperature for C equal to 1.6 with the resulting K_s values listed in Table VI. Table VI also contains estimates for K_s given by Marshall and Jones (*17*), based on solubilities of $CaSO_4$ in aqueous NaCl, $NaNO_3$, and $LiNO_3$ solutions determined by Marshall and Slusher (which have not yet been published in detail). There is good agreement between the present results and those of Marshall and Jones at 250° and 275° C.; however at 300° and 325° C, the present results are lower than those of Marshall and Jones. This disagreement amounts to a factor of 4.5 at 325° C. This situation can probably not be resolved without additional measurements, for which improved experimental techniques may be needed.

The present values of K_s were used to draw the ordinate intercepts for each temperature in Figure 2, in which $(K_s)^{1/2} = m_{CaSO_4}$ is plotted *vs.* $I^{1/2}$ up to $I^{1/2} = 0.5$. The straight lines drawn are Debye-Hückel limiting slopes, while the curved lines have been calculated from Equation 14. The curves agree well enough with the experimental points that one can say that the Debye-Hückel theory of complete dissociation is followed reasonably well between 250° and 325° C. in the $CaSO_4$-NaCl-H_2O system. (Thus, in the discussion of the quaternary systems, it will be seen that $CaSO_4$ is 92 to 95% dissociated in sodium chloride solutions at these temperatures.)

Smoothed data for $(K_s')^{1/2} = m_{CaSO_4}$ as a function of m_{NaCl} listed in Table VII were calculated from Equation 14 up to $m_{NaCl} = 0.2$ and estimated by graphical means at higher values of m_{NaCl}. These data have been plotted in Figure 3 as log m_{CaSO_4} *vs.* (1/*T*, ° K.). Figure 3 also shows the smooth data of Marshall, Slusher, and Jones (*15*) between 100° and 200° C. All these data may be used with values of K_s for the calculation of mean activity coefficients, $\gamma_{\pm} = (K_s/K_s')^{1/2}$. Anhydrite is the only salt for which such a set of activity coefficients is available over such a range of ionic strength and temperature (100° to 325° C.).

$CaSO_4$–H_2O System above 200° C. The discussion (under Results) of the $CaSO_4$–H_2O data in Table I showed that the effects of trace soluble impurities in the solid anhydrite or from corrosion of the solubility apparatus were not completely eliminated. The effect of any impurity will be to raise I and hence m_{CaSO_4}. Consequently, all the published "boiling curve" solubility data for the $CaSO_4$–H_2O system are suspected to be too high, as for example, those of Dickson, Blount, and Tunell (*4*) and of Booth and Bidwell (*3*). In Figure 4 m_{CaSO_4} for "$CaSO_4$–H_2O" has been plotted *vs.* (1/*T*, ° K.). The solid curve drawn corresponds to predictions calculated from an equation given by Dickson, Blount, and Tunell (*4*) for "pressure slightly greater than the vapor pressure of the system" based on extrapolation from measurements made between 96° and 157° C.—namely

$$\log X = 2.54315 - 0.0098533T \tag{17}$$

where X is weight per cent $CaSO_4$ and T is in °K. The experimental points from Booth and Bidwell are high of this line, the deviation increasing with the temperature. The point calculated by Marshall, Slusher, and Jones (*15*) at 200° C. by means of the Debye-Hückel equation is just slightly lower than the Dickson, Blount, and Tunell line. The present authors' points at 250°, 275°, 300°, and 325° C. as calculated from Equation 14 are shown as well as the experimental $CaSO_4$–H_2O points from Table I. A judgment must be made whether to believe the data of Table I, in which $(m_{Ca})_T$ and $(m_{SO_4})_T$ were never quite equal, or the data calculated from the Debye-Hückel extrapolation of the $CaSO_4$–NaCl–H_2O system. The authors prefer the calculated values since they reflect the only available theoretical basis for correlating these data.

Association Quotients for Calcium Sulfate Complexes. The method of the constant ionic medium, as described by Rossotti and Rossotti (*22*), may be used to calculate association concentration quotients, in the hope that the various activity coefficients will have constant values at constant I. For the $CaSO_4$–$CaCl_2$–NaCl–H_2O system, the ionic species shall be considered as follows, since the solubility method is limited to mononuclear complexes:

$$Ca^{2+} + SO_4^{2-} \rightleftarrows CaSO_4^{\circ},\ n = 1 \tag{18}$$

$$2Ca^{2+} + SO_4^{2-} \rightleftarrows Ca_2SO_4^{2-},\ n = 2 \tag{19}$$

$$nCa^{2+} + SO_4^{2-} \rightleftarrows Ca_nSO_4^{(2n-2)-} \tag{20}$$

For the $CaSO_4$–Na_2SO_4-NaCl–H_2O system a corresponding set of species mononuclear with respect to calcium is postulated—i.e., $CaSO_4^{\circ}$, $Ca(SO_4)_2^{2-}$, . . . , $Ca(SO_4)_n^{(2n-2)-}$.

If $[BA_n]$ denotes the molal concentration of species BA_n, the desired association quotients are

$$\beta_1 = \frac{[AB]}{[A^{2-}][B^{2-}]} = \frac{[AB]}{a \cdot b} \tag{21}$$

$$\beta_2 = \frac{[A_2B^{2-}]}{[A^{2-}]^2[B^{2-}]} = \frac{[A_2B^{2-}]}{a^2 b} \tag{22}$$

$$\beta_n = \frac{[A_nB^{(2n-2)-}]}{a^n b} \tag{23}$$

where a and b denote the concentrations of the free ions, respectively, $[A^{2-}]$ and $[B^{2-}]$. The molal concentration solubility product will now be denoted

$$P = ab \tag{24}$$

Capital letters A and B will be used to denote total dissolved amounts of the two radicals. Hence

$$A = a + (\beta_1 P + 2\beta_2 Pa + \ldots + n\beta_n Pa^{n-1}) \qquad (25)$$

and

$$B = P/a + (\beta_1 P + \beta_2 Pa + \ldots + \beta_n Pa^{n-1}) \qquad (26)$$

For the $CaSO_4$-$CaCl_2$-$NaCl$-H_2O system

$$A = m_{CaSO_4} + m_{CaCl_2} \qquad (27)$$

and

$$B = m_{CaSO_4} \qquad (28)$$

In Figure 5, for $I = 0.5$ and for $I = 0.9$ at 250° C., individual (A, B) points for the $CaSO_4$-$CaCl_2$-$NaCl$-H_2O system are plotted on a log log scale.

In a plot like Figure 5, any number of (A, B) points can be estimated from any smooth curve drawn through the experimental points. A computer program was written for calculating the best statistical values of the constants P, $\beta_1, \ldots, \beta_n$ corresponding to eight smooth (A, B) values which were read from the plot. Having determined the proper values of the constants, it also calculated values of A and B corresponding to these constants. The case giving a reasonable fit of the (A, B) data for the smallest value of n may be considered as the true description of the system. To distinguish between cases, we shall use 01 for species B and AB; 012 for species B, AB, and A_2B; etc. The above methods, through the 0123 case, have been applied to the data for the $CaSO_4$-$CaCl_2$-$NaCl$-H_2O and the $CaSO_4$-Na_2SO_4-$NaCl$-H_2O systems as given in Table V. The corresponding (A, B) plots are shown in Figures 5 and 6 for the $CaSO_4$-$CaCl_2$-$NaCl$-H_2O system and in Figures 7 and 8 for the $CaSO_4$-Na_2SO_4-$NaCl$-H_2O system. For all the $CaSO_4$-$CaCl_2$-$NaCl$-H_2O data, and for $I = 0.5$, 250° C. in the $CaSO_4$-Na_2SO_4-$NaCl$-H_2O system, a 0123 fit was not possible with the computer program, either β_2 or β_3 taking on a meaningless negative value.

Inspection of Figures 5 through 8 will show that the 01 curves do not adequately fit the experimental points, since no upturn in B at high values of A is predicted in the 01 case. The 012 case shows such an upturn, which fits the upturn shown by the experimental points reasonably well. The differences between the 012 and 0123 curves

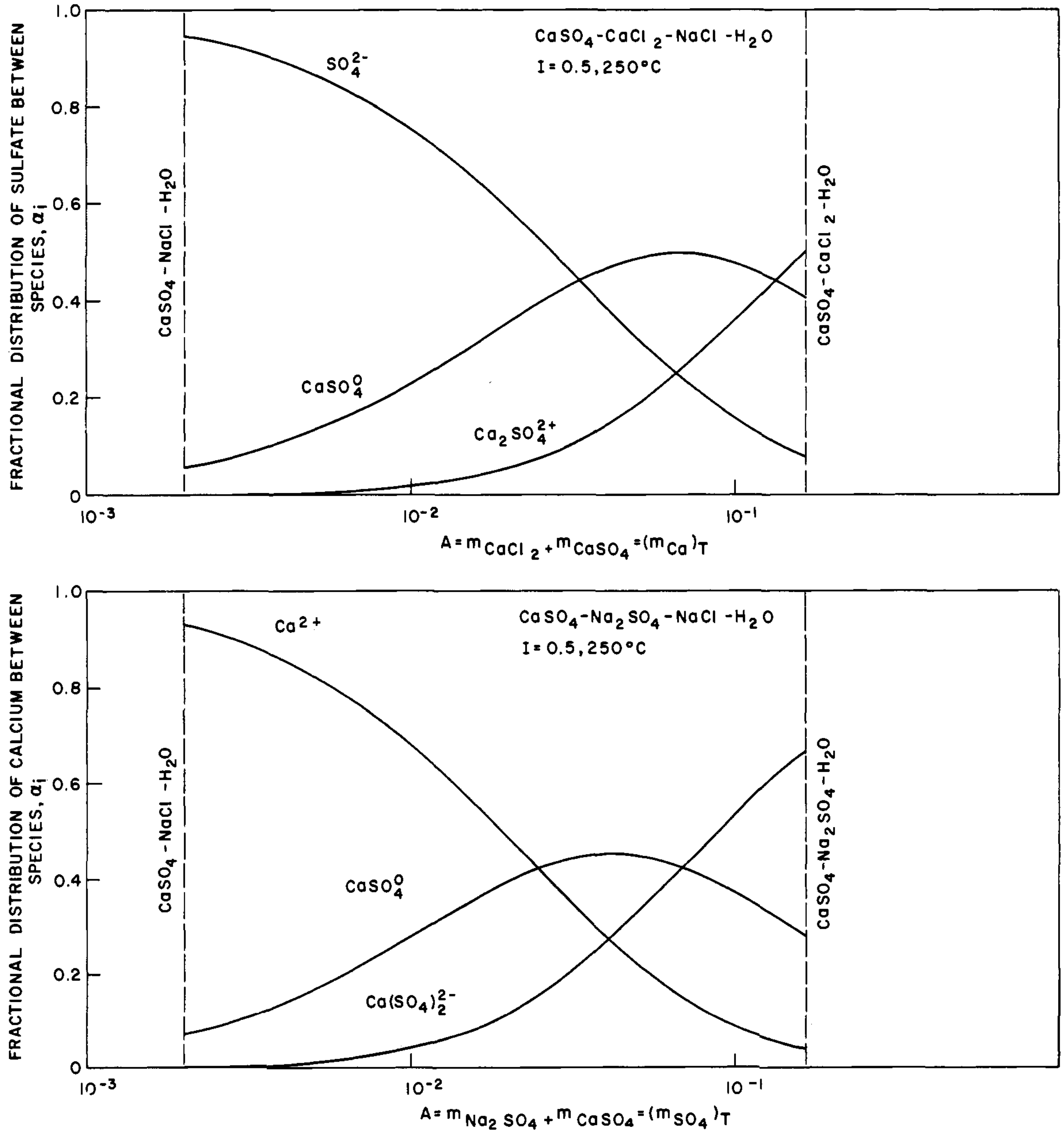

Figure 9. Distribution of calcium-sulfate complex species at I = 0.5 molal and 250° C., 012 case

Table VIII. Association Concentration Quotients for Ca_nSO_4 and $Ca(SO_4)_n$ Complexes

I, T	P	β_1	β_2
	$CaSO_4$-$CaCl_2$-NaCl-H_2O		
0.5 m; 250° C.	3.525×10^{-6}	30.52	229.5
0.9 m; 250° C.	9.72×10^{-6}	17.8	58.6
0.5 m; 300° C.	0.889×10^{-6}	63.5	325
0.9 m; 300° C.	3.094×10^{-6}	43.1	84.2
	$CaSO_4$-Na_2SO_4-NaCl-H_2O		
0.5 m; 250° C.	3.396×10^{-6}	41.2	597
0.9 m; 250° C.	9.34×10^{-6}	26.3	190
0.5 m; 300° C.	0.872×10^{-6}	74.4	1565
0.9 m; 300° C.	3.12×10^{-6}	39.7	590

Table IX. Fraction of Unassociated Ca^{2+} and SO_4^{2-} in Ternary Systems at Various Conditions

	$\frac{[SO_4^{2-}]}{[SO_4]_T}$		$\frac{[Ca^{2+}]}{[Ca]_T}$	
Conditions	$CaSO_4$-NaCl-H_2O	$CaSO_4$-$CaCl_2$-H_2O	$CaSO_4$-NaCl-H_2O	$CaSO_4$-Na_2SO_4-H_2
$I = 0.5$, 250° C.	0.945	0.080	0.928	0.044
$I = 0.9$, 250° C.	0.947	0.086	0.924	0.039
$I = 0.5$, 300° C.	0.943	0.048	0.934	0.018
$I = 0.9$, 300° C.	0.929	0.047	0.933	0.015

are little greater than the precision of the experimental points. Consequently, we will conclude that the 012 case, or complexes through $Ca_2SO_4^{2+}$ and $Ca(SO_4)_2^{2-}$, respectively, in calcium-rich and sulfate-rich solutions, is adequate to describe the present data. Values of P, β_1 and β_2 for the 012 case are collected in Table VIII.

Figure 9 has been drawn to show the predicted distribution of species in the companion $CaSO_4$-$CaCl_2$-NaCl-H_2O and $CaSO_4$-Na_2SO_4-NaCl-H_2O systems at I = 0.5 molal and 250° C. The ordinate of these plots shows the fractional distribution of sulfate between SO_4^{2-}, $CaSO_4^{\circ}$, and $Ca_2SO_4^{2+}$ in calcium-rich solutions, and of calcium between Ca^{2+}, $CaSO_4^{\circ}$, and $Ca(SO_4)_2^{2-}$ in sulfate-rich solutions, as a function of total calcium or sulfate molality, respectively. The concentrations of unassociated Ca^{2+} and SO_4^{2-} that exist in the boundary ternary systems can be compared as the fractions $[Ca^{2+}]/[Ca]_T$ and $[SO_4^{2-}]/[SO_4]_T$ (Table IX).

In the $CaSO_4$-NaCl-H_2O system $[Ca^{2+}]/[Ca]_T$ and $[SO_4^{2-}]/[SO_4]_T$ would be equal if only the ion-pair $CaSO_4$ were formed. In Table IX, $[SO_4^{2-}]/[SO_4]_T$ ranges from 0.947 to 0.929 for this system, and $[Ca^{2+}]/[Ca]_T$ ranges from 0.934 to 0.924. Therefore, $CaSO_4$ is 92 to 95% dissociated in sodium chloride solutions.

The data of Table IX also show that the complexing is more pronounced in the sulfate rich solutions than in the calcium-rich solutions. Thus in the $CaSO_4$-Na_2SO_4-H_2O system only 1.5 to 4.4% of the calcium ions remain free, while in the $CaSO_4$-$CaCl_2$-H_2O system 4.7 to 8.6% of the sulfate ions are free .

Association Quotients for Magnesium Sulfate Complexes. Table V contains m_{CaSO_4} data for the $CaSO_4$-$MgCl_2$-NaCl-H_2O system at I = 0.5 and temperatures of 250° and 300° C. Since β_1 and β_2 are known from calcium sulfate complexes at these conditions, it is possible to calculate β_1 values for $Mg_nSO_4^{2n-2}$ complexes from these data. The association quotients for the complexes $MgSO_4$ and $Mg_2SO_4^{2+}$ are defined as:

Table X. Values of β_{1Mg} and β_{2Mg}

I, Molal	T, ° C.	β_{1Mg}	β_{2Mg}
0.5	250	38.2	71.6
0.5	300	86.1	333.0

$$\beta_{1Mg} = \frac{[MgSO_4^{\circ}]}{[Mg^{2+}][SO_4^{2-}]} \qquad (29)$$

and

$$\beta_{2Mg} = \frac{[Mg_2SO_4^{2+}]}{[Mg^{2+}]^2[SO_4^{2-}]} \qquad (30)$$

By combining these definitions with material balances for magnesium, sulfate, and calcium, one can set up a computer program to calculate a least-mean-squares fit of β_{1Mg} and β_{2Mg} to all the points in Table V at a given ionic strength and temperature.

The best values determined for β_{1Mg} and β_{2Mg} are listed in Table X. Apparently, these values are of about the same magnitude as those of β_{1Ca} and β_{2Ca} at the same I and T.

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