Table III. Thermodynamic Activities and Activity Coefficients of Cadmium in Cadmium Amalgams, Calculated from Concentration Cell Potentials at Various Temperatures

Wt. % Cadmium	Atomic % Cadmium	e.m.f. mv.	Activity of Cadmium	Activity Coefficient of Cadmium
		50.0° C.		
9.710[a]	16.102	0.000	1.0000	6.210
9.435	15.677	0.502	0.9646	6.153
9.009	15.016	1.304	0.9106	6.064
8.005	13.442	3.419	0.7822	5.819
6.975	11.802	5.780	0.6602	5.594
5.860	9.998	8.745	0.5335	5.336
2.964	5.169	19.340	0.2492	4.821
1.488	2.665	28.935	0.1251	4.766
0.295	0.525	51.635	0.02449	4.760
0.0587	0.105	74.060	0.004890	4.657
		70.2° C.		
13.758[a]	22.161	0.000	1.0000	4.512
13.476	21.750	0.390	0.9740	4.478
12.990	21.038	1.082	0.9294	4.418
12.000	19.573	2.682	0.8341	4.261
9.999	16.546	6.934	0.6257	3.782
9.009	15.016	8.974	0.5450	3.629
8.005	13.442	11.258	0.4670	3.474
6.975	11.802	13.613	0.3983	3.375
5.860	9.998	16.655	0.3242	3.243
2.964	5.169	27.535	0.1553	3.004
1.488	2.625	38.000	0.07655	2.916
0.295	0.525	62.130	0.01497	2.851
0.0587	0.105	86.420	0.002896	2.758
		93.2° C.		
19.310[a]	29.927	0.000	1.0000	3.341
19.299	29.912	0.015	0.9990	3.340
18.500	28.831	1.161	0.9291	3.223
18.042	28.205	1.845	0.8897	3.154
18.000	28.148	1.851	0.8893	3.159
17.286	27.165	2.775	0.8387	3.087
15.739	25.001	5.411	0.7097	2.839
14.437	23.143	7.457	0.6234	2.694
12.000	19.573	11.821	0.4728	2.416
9.999	16.546	15.815	0.3671	2.219
9.009	15.016	17.950	0.3206	2.135
8.005	13.442	20.395	0.2746	2.043
6.975	11.802	22.900	0.2343	1.985
5.860	9.998	26.080	0.1915	1.915
2.964	5.169	37.750	0.09144	1.769
1.488	2.625	48.905	0.04510	1.718
0.295	0.525	74.630	0.008834	1.683
0.0587	0.105	100.030	0.001767	1.683

[a] Equilibrium solubility at temperature.

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Aqueous Systems at High Temperature. XIV.

Solubility and Thermodynamic Relationships for $CaSO_4$ in $NaCl–H_2O$ Solutions from 40° to 200° C., 0 to 4 Molal NaCl

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A SYSTEMATIC INVESTIGATION of the solubilities of $CaSO_4$ and its hydrates in $NaCl$-H_2O solutions at temperatures between 25° and 200° C. is of considerable interest in developing distillation processes for desalinating water. Calcium sulfate is a major constituent of scales which form on heat exchanger surfaces when sea water or other saline waters are distilled. Furthermore, a study of the solubility of a 2-2 salt in an electrolytic medium as a function of ionic strength provides a means for testing Debye-Hückel theory at high temperature. The purpose of this investigation was to obtain solubilities for application to desalination programs and to obtain data for testing solubility theory at temperatures above 25° C. Upon agreement with theory, the solubilities of $CaSO_4$ and its hydrates could then be estimated in electrolytic media other than in $NaCl$-H_2O solutions.

Solubilities of $CaSO_4 \cdot 2H_2O$ in $NaCl$-H_2O at 25° C. have been obtained by Shternina and Frolova (*15*), at 26° C. by several investigators (*4*), and recently of both $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ at 26°, 30°, 40°, and 50° C. by Bock (*2*). Solubilities of $CaSO_4 \cdot \frac{1}{2}H_2O$ and $CaSO_4$ in sea water concentrates at 100° C. have been determined by Langelier, Caldwell and Lawrence (*11*). Some solubilities of anhydrous $CaSO_4$ in $NaCl$-H_2O solutions at concentrations from 1 to 7.7 molal NaCl and at temperatures between 100° and 200° C., obtained by V.P. Il'inski, A.F. Sagaidachnyi, and others, have been compiled in graphical form by Zdanovskii (*17*). There have been extensive investigations of the solubilities of $CaSO_4$ and its various hydrates in H_2O beginning with the work of van't Hoff (*16*) and continuing until the present time (*3, 5*). A comprehensive review of studies prior to 1938, with presentation of some additional solubility data, is given by Posnjak (*13*), together with his conclusions on the nature of the solid phases. A very extensive evaluation of thermodynamic properties of the solids which further defines and correlates the distinct solid phases is given by Kelley, Southard, and Anderson (*10*).

This paper presents solubilities of metastable $CaSO_4 \cdot 2H_2O$ at 40° and 60° C., of metastable $CaSO_4 \cdot \frac{1}{2}H_2O$ [designated $\alpha CaSO_4 \cdot \frac{1}{2}H_2O$ by Kelley and coworkers (*10*)] at 125° C. and of $CaSO_4$ [designated anhydrite or "insoluble" anhydrite (*10*) or $\beta CaSO_4$ (*13*)] at 125° to 200° C. in $NaCl$-H_2O solutions, compares them with literature values, and interprets the results in terms of the Debye-

The solubility of metastable $CaSO_4 \cdot 2H_2O$ has been determined at 40° and 60° C., of metastable $CaSO_4 \cdot \frac{1}{2}H_2O$ at 125° C., and $CaSO_4$ (anhydrite) at 125°, 150°, 175°, and 200° C. in NaCl-H_2O solutions varying from 0 to 4 molal NaCl. These data, combined with additional literature values, agreed with Debye-Hückel theory at all temperatures and over the range of concentration (except at the highest concentrations at temperatures below 100° C.) when a function of the ionic strength, I, is $I^{1/2}/(1 + AI^{1/2})$, where $A = 1.5$, was used. This agreement lends confidence to the application of Debye-Hückel theory to this system at varying temperatures using a constant value for A. The solubility product, K°_{sp}, for the reaction, $CaSO_{4(solid)} \leftrightarrows Ca^{+2} + SO_4^{-2}$, decreased from $63.0\ \%\ 10^{-6}$ at 25° C. to $0.114\ \%\ 10^{-6}$ at 200° C., giving values of ΔF° varying from +5.75 to +15.0 kcal./mole, respectively. Values of ΔH° and ΔS° changed from −1.9 to −18 kcal./mole and from −26 to −70 cal. mole^{-1} deg.$^{-1}$, respectively, over the same range of temperature. For $CaSO_4 \cdot 2H_2O$ at 60° C., $K^{\circ}_{sp} = 35.7\ \%\ 10^{-6}$ was obtained and for $CaSO_4 \cdot \frac{1}{2}H_2O$ at 125° C., $K^{\circ}_{sp} = 9.49\ \%\ 10^{-6}$.

Hückel theory. Values of the thermodynamic solubility products, and of ΔF°, ΔH° and ΔS° are given for several temperatures from 25° to 200° C.

EXPERIMENTAL

Reagent-grade $CaSO_4 \cdot 2H_2O$ and NaCl were used as starting materials. Distilled water, passed through a mixed-bed exchange resin (Illinois Water Treatment Co., Rockford, Ill.), was used in the H_2O runs and to prepare NaCl-H_2O solutions of various concentrations. The experimental runs were carried out for the most part with the equipment and by the procedures described previously (*8*, *12*). The pressure vessels were modified, however, by substituting for the capillary sampling tube a 3-mm. diam. × 1-mm. thickness, porous-platinum filter-unit attached to the interior portion of the head of each vessel. This unit extended 10 mm. out from the flat portion of the head. The vessels were inverted before sampling the solution at various temperatures. Thus, liquid could be filtered through the porous platinum which would remove small particles of solid. In general, solution-solid mixtures were rocked at a particular temperature in pressure vessels for periods of time varying from one hour to five days before sampling the solution phases. Experiments at 40.0 ± 0.1 and 60.0 ± 0.1° C. were performed using 50 ml. Pyrex vessels (having plastic tops) which were rocked in a constant-temperature water bath. Solution phases at these two temperatures were sampled through a tube containing a porous glass filter tip. At all temperatures the concentrations found (until final equilibrium was attained) and the nature of the solid phases (whether or not metastable) were strongly dependent upon the temperature of the run and the length of time of rocking.

Selected solid phases were isolated after the high temperature runs in the manner described previously (*12*) and they were identified by a comparison of their x-ray diffraction patterns with known patterns. Usually the time required for cooling the pressure vessels and isolating the solid phases varied from five to fifteen minutes. The solid hydrates and $CaSO_4$ which were identified at 25° C. were not always those believed to be the stable forms at the high temperatures. Thus, the specified solid phases were deduced from the x-ray diffraction patterns and from their solubility behavior with respect to time at constant temperature, extrapolation to solubilities in H_2O found by others and found in this present investigation (Figures 1 and 2), and relative solubilities of the metastable and stable phases.

Solution phases were analyzed for calcium by flame photometry, the results of which were reproducible to approximately ± 2 to 4% depending upon concentration (at most, 1 to 2 cc. of sample were available for this analysis), and by colorimetric titration using EDTA as a complexing agent and using various colorimetric indicators (*7*). This latter method was reproducible from ± 1% on 1-cc. samples containing high concentrations of $CaSO_4$ to ± 4% for the lowest concentrations (~5 × 10^{-3} molal). The total concentration of cations was determined by adsorbing Na^+ and Ca^{+2} ions on a cation-exchange resin (Dowex-50) in the hydrogen form and titrating the eluent for total acid. The relatively small concentration of Ca^{+2} was then subtracted from the total cationic content to yield the number of moles of NaCl.

RESULTS AND DISCUSSION

The solubility of $CaSO_4 \cdot XH_2O$ in H_2O solution can be described by the equilibrium,

$$CaSO_4 \cdot XH_2O_{(solid)} \rightleftarrows Ca^{+2} + SO_4^{-2} + XH_2O, \qquad (1)$$

which can be expressed by the thermodynamic solubility product,

$$K^{\circ}_{sp} = [m_{Ca^{+2}}][m_{SO_4^{-2}}][\gamma_{Ca^{+2}}][\gamma_{SO_4^{-2}}][a_{H_2O}]^X, \qquad (2)$$

where X = number of moles of H_2O in the hydrate, $m_{Ca^{+2}}$ and $m_{SO_4^{-2}}$ are molal concentrations, $\gamma_{Ca^{+2}}$ and $\gamma_{SO_4^{-2}}$ are their respective activity coefficients, and a_{H_2O} is the activity of H_2O in the solution phase. Upon taking the logarithm of K°_{sp}, substituting $-4\ S\ I^{1/2}/(1 + A\ I^{1/2})$ from the Debye-Hückel theory both for $\log \gamma_{Ca^{+2}}$ and $\log \gamma_{SO_4^{-2}}$, and rearranging, the expression,

$$\log K_{sp} = \log K^{\circ}_{sp} + 8S \frac{I^{1/2}}{1 + A\ I^{1/2}} - X \log a_{H_2O}, \qquad (3)$$

is obtained where K_{sp} = the solubility quotient as a function of I, S = the limiting Debye-Hückel slope, A is a constant, and I = the ionic strength = $4m_{CaSO_4} + m_{NaCl}$. If $m_{Ca^{+2}}$ equals $m_{SO_4^{-2}}$, then $\log K_{sp} = 2 \log S$ and $\log K^{\circ}_{sp} = 2 \log S^{\circ}$; thus,

$$\log S = \log S^{\circ} + 4S \frac{I^{1/2}}{1 + A\ I^{1/2}} - \frac{X}{2} \log a_{H_2O} \qquad (4)$$

where S = the molal solubility of $CaSO_4$ at ionic strength, I, and S° = the hypothetical mola solubility at I = 0.

Figures 1 and 2 present the experimental data (given in Table I) for the solubilities in NaCl-H_2O solutions of $CaSO_4 \cdot 2H_2O$ (metastable) at 40° and 60° C., of $CaSO_4 \cdot \frac{1}{2}H_2O$ (metastable) at 125° C. and of $CaSO_4$ at 125°, 150°, 075°, and 200° C., plotted as $\log S + (X/2) \log a_{H_2O}$ against the Debye-Hückel function, $[(I^{1/2})/(1 + A\ I^{1/2})]$, where $A = 1.5$. This value of A, used frequently for this parameter, gave approximately the best fit to the data at 200° C. and provided a good fit at most of the other temperatures. Values of a_{H_2O} for NaCl-H_2O solutions at 25° C. were obtained from Robinson and Stokes' compilation (*14*). Since a_{H_2O} is directly related to the osmotic coefficients of

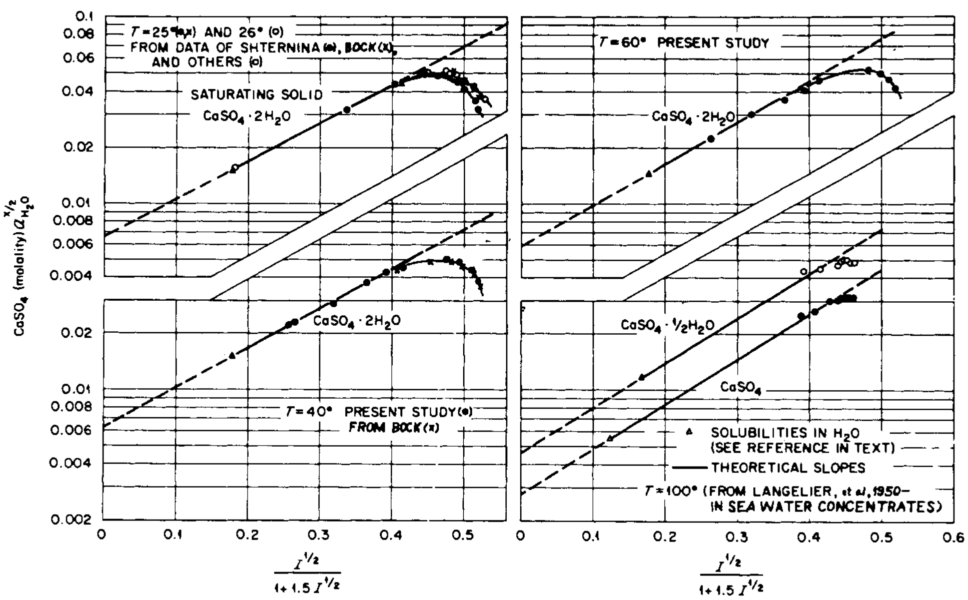

Figure 1. The solubilities of $CaSO_4$ and its hydrates in $NaCl$-H_2O solutions vs. $I^{1/2}/(1 + 1.5I^{1/2})$, 25–100° C.;

a_{H_2O} = activity of H_2O, X = number of moles of H_2O in solid phase

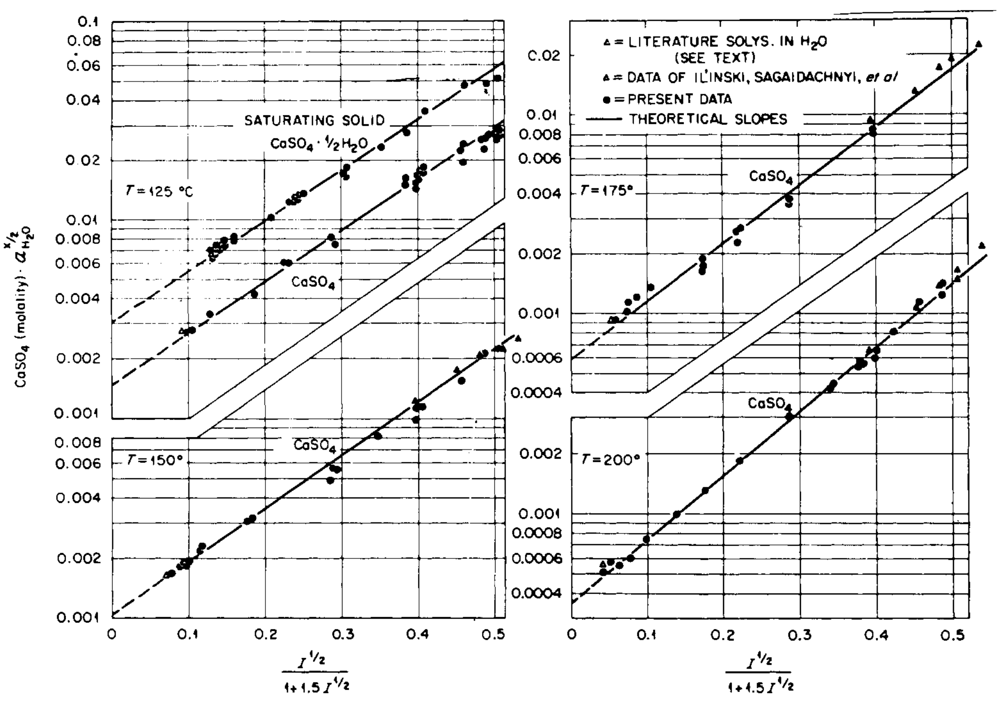

Figure 2. The solubilities of $CaSO_4 \cdot \frac{1}{2}H_2O$ (at 125° C.) and $CaSO_4$ in $NaCl$-H_2O solutions vs. $I^{1/2}/(1 + 1.5I^{1/2})$, 125–200° C.;

a_{H_2O} = activity of H_2O, X = number of moles of H_2O in solid phase = 0 for $CaSO_4$

electrolyte solutions, which are nearly temperature independent from 25° to 100° C., it was assumed that a_{H_2O} for purposes of estimation would be constant with temperature. The terms involving a_{H_2O} drop out of Equations 3 and 4 when $X = 0$, as for $CaSO_4$; thus the correction for a_{H_2O} is only made when the solids are $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot \frac{1}{2}H_2O$.

Solubilities of others (*2, 4, 11, 15, 17*) at the various temperatures [other than those of Il'inski and coauthors (*17*) at 100° and 125° C., which appeared to show variations in solubilities from those of metastable $CaSO_4 \cdot \frac{1}{2}H_2O$ to those of $CaSO_4$ at the highest concentration of NaCl] were converted to molal values and are plotted similarly in Figures 1 and 2. Our present results confirm and extend the previous studies. Solubilities of $CaSO_4 \cdot \frac{1}{2}H_2O$, and of $CaSO_4$ in H_2O at 125°, 150°, 175°, and 200° C. were obtained experimentally in this present investigation and were compared to those values taken from the smoothed curves given by Posnjak in his review (*13*) and from the data of Dickson, Blount, and Tunell (*5*). The values in H_2O at 25°, 40°, 60°, and 100° C. estimated from the same curves (*13*) are also shown. Our present solubilities in H_2O seem to show a negative deviation from literature values at 200° C. (*13*) but, when extrapolated to higher temperatures, are in agreement with those calculated by Dickson and coworkers (*5*) at temperatures up to 300° C. The straight lines drawn through the data at each temperature correspond to the theoretical Debye-Hückel limiting slope

Table I. The Solubility of $CaSO_4$ and Its Hydrates in $NaCl-H_2O$ Solutions, 40° to 200° C.

NaCl Molality	$CaSO_4$ Molality
$T = 40°$ C. $CaSO_4 \cdot 2H_2O$[a] 20[b]	
0	0.0156
0.0967	0.0227
0.243	0.0290
0.983	0.0455
2.81	0.0530
3.63	0.0519
4.48	0.0477
5.37	0.0436
68[b,c]	
0	0.0156
0.0967	0.0228
0.100	0.0227
0.243	0.0292
0.506	0.0378
0.762	0.0430
0.983	0.0461
2.81	0.0572
3.63	0.0563
4.48	0.0532
5.37	0.0492
$T = 60°$ C. $CaSO_4 \cdot 2H_2O$[a] 43[b]	
0	0.0149
0.0967	0.0219
0.243	0.0284
0.983	0.0455
2.81	0.0576
3.63	0.0573
4.48	0.0552
5.37	0.0523
72[b]	
0.506	0.0372
0.762	0.0422
$T = 125°$ C. $CaSO_4 \cdot \frac{1}{2}H_2O$[a] 1[b]	
0	0.00691
0	0.00711
0.100	0.0127
0.100	0.0130
0.100	0.0139
0.100	0.0132
0.100	0.0133
0.252	0.0173
0.252	0.0168
1.02	0.0355
2.09	0.0481
3.20	0.0495
4.38	0.0526
2[b]	
0.100	0.0139
0.252	0.0185
0.506	0.0239
0.763	0.0279
17[b]	
0	0.00703
0.100	0.0128
$T = 125°$ C. $CaSO_4 \cdot \frac{1}{2}H_2O$[a] 24[b]	
0.00134	0.00667
0.00244	0.00748
0.00479	0.00762
0.00856	0.00837
0.0457	0.0103
0.0901	0.0126
48[b]	
0.00065	0.00682
0.0031	0.00724
0.0050	0.00748
0.0106	0.00790
$T = 125°$ C. $CaSO_4$ Anhyd.[a] ~1.5	
0.763	0.0157
0.763	0.0163
1.02	0.0183
1.02	0.0177
1.09	0.0237
2.09	0.0227
3.20	0.0252
3.20	0.0261
4.38	0.0258
4.38	0.0256
2[b]	
3.20	0.0262
4.38	0.0265
17[b]	
1.02	0.0174
2.08	0.0191
3.20	0.0226
4.38	0.0283
24[b]	
0.223	0.00810
0.955	0.0172
48[b]	
0.0924	0.00628
0.965	0.0155
115[b]	
0.00128	0.00283
0.00377	0.00289
0.0108	0.00340
0.0489	0.00432
0.239	0.00754
0.965	0.0146
117[b]	
0.101	0.00613
0.958	0.0157
$T = 150°$ C. $CaSO_4$ Anhyd.[a] 17[b]	
0.252	0.0055
0.506	0.0081
1.02	0.0114
2.09	0.0152
3.20	0.0211
4.38	0.0224
$T = 150°$ C. $CaSO_4$ Anhyd.[a] 24[b]	
0.00436	0.00184
0.00614	0.00191
0.0106	0.00221
0.0492	0.00304
0.237	0.00575
0.962	0.0115
48[b]	
0.0011	0.00170
0.00360	0.00184
0.00591	0.00182
0.0107	0.00230
0.0479	0.00304
0.0239	0.00499
0.964	0.0101
$T = 175°$ C. $CaSO_4$ Anhyd.[a] 24[b]	
0.00276	0.00113
0.0483	0.00189
0.0488	0.00165
0.0966	0.00264
0.0974	0.00227
0.239	0.00378
0.961	0.00858
48[b]	
0.00053	0.000924
0.00298	0.000983
0.00516	0.00119
0.00976	0.00137
0.0483	0.00170
0.0968	0.00254
0.239	0.00359
0.962	0.00837
$T = 200°$ C. $CaSO_4$ Anhyd.[a] 1[b]	
0.763	0.00570
2.08	0.0119
3.20	0.0145
1.5[b]	
0.00071	0.00057
0.0249	0.00104
0.0485	0.00132
0.0950	0.00189
0.240	0.00323
0.481	0.00439
0.736	0.00554
0.965	0.00671
17[b]	
0.506	0.00455
0.763	0.00555
1.28	0.00822
3.20	0.0127
24[b]	
0.00049	0.000503
0.00288	0.000545
0.00511	0.000595
0.00982	0.000745
0.970	0.00621

[a] Saturating solid phase. [b] Rocking time (hours). [c] Essentially identical results were obtained after 44 hours.

at the particular temperature times a valency factor, $z^+ \cdot z^-$, which for $CaSO_4$ equals 4 (*9*). The limiting slopes, S, used were 0.5080, 0.5226, 0.5449, 0.6006, 0.6422, 0.6899, 0.7451, and 0.8097 at 25°, 40°, 60°, 100°, 125°, 150°, 175°, and 200° C., respectively, and were computed by M.H. Lietzke and R.W. Stoughton of this laboratory using the Akerlöf-Oshry equation for the dielectric constant (*1*) of H_2O, and selected values for the densities of H_2O (*6*).

Figure 3 shows all data plotted as:

$$\frac{1}{2}(S_{25}/S_T) \log \frac{K_{sp}\, a^X_{H_2O}}{K^\circ_{sp}} = -(S_{25}/S_T) \log \gamma_\pm \ vs.\ I^{1/2}/(1 + 1.5\, I^{1/2}).$$

All theoretical slopes thus are normalized to 4 times the Debye-Hückel slope at 25° C. shown by the straight line. Deviations at the low temperatures and high ionic strengths are observed. Nevertheless, the agreement with Debye-Hückel theory at all other ionic strengths and temperatures indicates that $CaSO_4$ in $NaCl-H_2O$ solution behaves as a strong electrolyte and does not associate or form complexes to any appreciable extent.

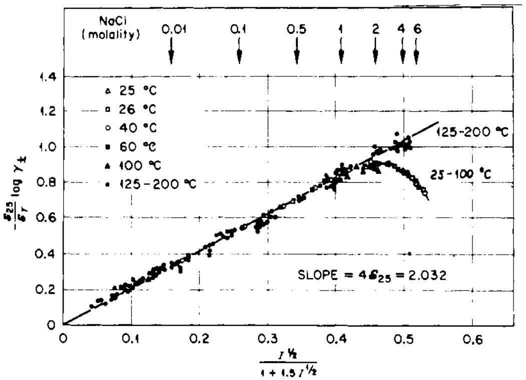

Figure 3. Variation of $-\log \gamma_\pm$ with $I^{1/2}(1 + 1.5I^{1/2}$ for solubility of $CaSO_4$ and its hydrates in $NaCl-H_2O$, 25–200° C.; Debye-Hückel slopes, S_T, normalized to the value at 25° C.

Smoothed values for the solubility of $CaSO_4$ and its hydrates in $NaCl-H_2O$ solutions were obtained by use of Equation 4 and the experimental data shown in Figures 1 and 2. The more recent results at 25° C. in concentrated $NaCl-H_2O$ appeared to be more self-consistent with temperature (*2*) than the earlier data (*15*) and were used to obtain the smoothed values. All values are given in Table II and were smoothed as a function of NaCl concentration but not as a function of temperature.

The thermodynamic solubility product, K°_{sp}, for the reaction, $CaSO_4 \cdot XH_2O_{solid} \rightleftharpoons Ca^{+2} + SO_4^{-2} + XH_2O$, was calculated at each temperature from the hypothetical molal solubilities at zero ionic strength, obtained with Equation 4 by the method of least squares. These values are given in Table III together with calculated values of ΔF°, ΔH°, and ΔS°. The quantity, ΔH°, was obtained from the slopes of the curves of Figure 4 at each temperature. Those values

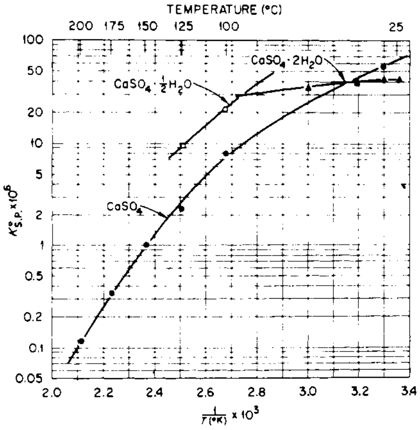

Figure 4. The thermodynamic solubility products, K°_{sp}, of $CaSO_4$ and its hydrates, 25–200° C.; K°_{sp} on logarithmic scale *vs.* ($1/T$, ° K.)

Table II. Solubilities of $CaSO_4$ and Its Hydrates in NaCl-H_2O Solutions at Selected Concentrations of NaCl, 20° to 200° C.[a]

T, ° C.: NaCl Molal.	25(1)	40(1)[b]	60(1)[b]	100(2)[b]	100(3)	125(2)[b]	125(3)	150(3)	175(3)	200(3)
0.0	0.0151	0.0156	0.0149	0.0113	0.00553	0.00680	0.00247	0.00154	0.000820	0.000498
0.01	0.0162	0.0167	0.0158	0.0124	0.00630	0.00780	0.00311	0.00201	0.00117	0.000718
0.03	0.0179	0.0184	0.0174	0.0141	0.00760	0.00935	0.00391	0.00269	0.00161	0.00104
0.06	0.0200	0.0205	0.0196	0.0165	0.00904	0.0112	0.00482	0.00333	0.00209	0.00141
0.1	0.0224	0.0228	0.0220	0.0195	0.0107	0.0133	0.00586	0.00409	0.00267	0.00181
0.3	0.0306	0.0310	0.0307	0.0287	0.0164	0.0207	0.00950	0.00692	0.00476	0.00344
0.6	0.0383	0.0390	0.0390	0.0376	0.0220	0.0282	0.0130	0.00979	0.00700	0.00524
1.0	0.0450	0.0458[c]	0.0464	0.0459	0.0272	0.0353	0.0166	0.0127	0.00918	0.00712
2.0	0.0545	0.0540[c]	0.0553	0.0510	0.0322	0.0471	0.0225	0.0175	0.0131	0.0106
3.0	0.0564	0.0558[c]	0.0577	0.0515	0.0340	0.0550	0.0265	0.0207	0.0159	0.0131
4.0	0.0542	0.0536[c]	0.0566	0.0505	0.0345	0.0612	0.0294	0.0232	0.0180	0.0150
6.0	0.0424	0.0440[c]	0.0490	0.045	0.033	0.0705	0.0340	0.0270	0.0213	0.0182
10.0[d]						0.0820	0.0394	0.0320	0.0256	0.0220

Solid Phases: (1) = $CaSO_4 \cdot 2H_2O$, (2) $CaSO_4 \cdot \frac{1}{2}H_2O$, (3) $CaSO_4$.

[a] Values at 25° and 100° have been derived from literature values (see test) and the Debye-Hückel limiting slope. [b] Metastable solid phase. [c] Values according to Bock's data (*2*) and present data after 20 hours. Results after 68 hours (Table I) give self-consistent concentrations but appear to be inconsistent with values at other temperatures. They were retained, however, since the difference could not be explained by any error in the experiments. [d] Extrapolated values; molality of NaCl at saturation in H_2O varies from 7.2 *m* at 25° to 7.9 *m* at 200° C.

for $CaSO_4 \cdot 2H_2O$ and for $CaSO_4$ were obtained by least-square fitting the data to a quadratic equation and differentiating to obtain $[d \log K^{\circ}_{sp}/d(1/T)]$. From the solubility results, in agreement with Debye-Hückel theory, it should be possible to estimate the solubilities of $CaSO_4$ and its hydrates at temperatures between 25° and 200° C. in electrolytes other than NaCl at ionic strengths up to 7.0. If the agreement with theory is observed for other 2-2 electrolytes, then their particular variations of solubility might also be calculated with ease in NaCl-H_2O and in other electrolyte solutions for which the ionic strengths can be determined.

Table III. Thermodynamic Values for the Equilibrium, $CaSO_4 \cdot XH_2O(\text{solid}) \rightleftarrows Ca^{+2} + SO_4^{-2} + XH_2O$

T, ° C.	K°_{sp}[a]	ΔF°[b] Kcal. Mole^{-1}	ΔH°[b] Kcal. Mole^{-1}	ΔS°[b] Cal. Mole^{-1} Deg.$^{-1}$
Solid Phase is $CaSO_4$				
25	63.0×10^{-6}	+5.75	−1.9	−25.7
30	54.5×10^{-6}	+5.88	−2.6	−28.1
40	47.8×10^{-6}[c]	+6.19	−4.0	−32.6
60	28.7×10^{-6}[c]	+6.92	−6.5	−40.3
100	7.73×10^{-6}	+8.78	−10.7	−52.2
125	2.25×10^{-6}	+10.2	−12.9	−58.0
150	1.00×10^{-6}	+11.7	−14.8	−62.7
175	0.336×10^{-6}	+13.3	−16.6	−66.6
200	0.114×10^{-6}	+15.0	−18.1	−70.0
Solid Phase is $CaSO_4 \cdot \frac{1}{2}H_2O$				
100	21.2×10^{-6}	+8.00	−9	−45.7
125	9.49×10^{-6}	+9.15	−10	−49.2
Solid Phase is $CaSO_4 \cdot 2H_2O$				
25	42.2×10^{-6}	+5.96	~+1.6	−14.6
30	43.6×10^{-6}	+6.05	~+0.6	−17.9
40	42.5×10^{-6}	+6.26	~−1.3	−24.1
60	35.7×10^{-6}	+6.77	−2.0	−26.3

[a] Obtained from best fit of experimental data at each temperature.
[b] Derived from least square fit of log K°_{sp} as a function of $(1/T, {}^{\circ}K.)$.
[c] Exception to footnote *a*; Calculated from least square fit according to footnote *b*.

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