Aqueous Systems at High Temperature

Solubility to 200° C. of Calcium Sulfate and Its Hydrates in Sea Water and Saline Water Concentrates, and Temperature-Concentration Limits

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The solubilities of calcium sulfate dihydrate (gypsum) at 60° and 95° C. and anhydrous calcium sulfate (anhydrite) at 100° to 200° C. have been determined in synthetic sea salt solutions at concentrations from zero to about ten times that of sea water. The values extend previous studies to include approximately the entire range of sea salt concentrations from 30° to 200° C. The formal solubility products at low concentrations were essentially the same at temperatures up to 100° C. as those previously determined in sodium chloride–water solutions of the same ionic strength, but about 70% higher at 200° C. With dissociation quotients for magnesium sulfate obtained from the comparative solubilities in sea salt and sodium chloride solutions, representative calculations for several natural waters, including sea water, were made of concentration and temperature limits to avoid precipitation of calcium sulfate or its hydrates. With the method used, limits of saturation can be estimated for saline waters in general.

IN THE DESIGN of distillation plants for purifying water, knowledge of temperature and concentration limits for avoiding scale formation by calcium sulfate, a common constituent of natural waters, is essential. Many somewhat restrictive methods based on experimental data have been presented for obtaining limits of saturation to avoid precipitation of this solid or its hydrates, particularly calcium sulfate dihydrate (gypsum) (*2, 4, 5, 6, 11, 16, 20, 24, 28*). In the present work, by using solubilities in NaCl-H_2O solutions given and referenced elsewhere (*15, 16*) and in sea water concentrates (*2, 7, 8, 11, 22, 25*) and the new solubilities in synthetic sea salt solutions from 60° to 200° C. presented here, a procedure believed to be of more general applicability has been developed. This (computer) procedure allows the rapid estimation of concentration and temperature limits for avoiding precipitation of $CaSO_4$ or its hydrates from saline waters in general, including those waters from which calcium (and/or magnesium) initially has been depleted.

EXPERIMENTAL

A concentrated stock (sea salt) solution (~5 molal total salt) was prepared that contained molal salt ratios of a synthetic sea water composition given by Spiegler (*27*) (Table III) but excluding stoichiometric $CaSO_4$. (In this paper, the term "sea salt" refers to this composition but with any amount of concentration or dilution with respect to water. The term "sea water concentrate" sometimes is used interchangeably, and refers also to solutions more dilute or more concentrated than sea water.) The salts used for the preparation of the stock solution, all of reagent grade purity, were NaCl, KCl, Na_2SO_4, $MgCl_2 \cdot 6H_2O$, $MgSO_4$, and NaBr. Before weighing, the salts, except $MgSO_4$, were dried at 100° to 110° C. for 4 to 24 hours. The formula, $MgCl_2 \cdot 6H_2O$, was verified by dehydrating a weighed sample at 200° C. to determine the loss of $6H_2O$ within 1%. Magnesium sulfate hydrate was dehydrated to $MgSO_4$ by drying at 400° C. for 24 hours.

The stock solution was quantitatively diluted with deionized water to give the many solutions of different concentrations in which the solubility of gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$), formed from gypsum within the solubility vessel, was determined. The washing of the reagent grade gypsum used in the solubility determinations, the addition of 2 cc. of 30% H_2O_2 (which decomposes to O_2 at high temperature) to 40 cc. of solution to prevent corrosion of the titanium alloy vessel, and the methods of equilibrating and sampling from the high pressure vessels have been described in detail (*14, 15, 16*). As in previous studies, solubilities of anhydrite at 100° and 125° C. were obtained by making runs first at 150° C. or higher to convert gypsum or hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) rapidly to anhydrite.

The solubility values at 60° C. were obtained by rocking bottles containing the solid-liquid mixtures in a constant temperature bath (± 0.3° C.) and withdrawing solution samples (through a porous glass tip sampling tube) for analysis after periods of time varying from 16 to 48 hours. Attainment of equilibrium was substantiated by agreement of analyses (to ± 1%) of samples obtained after 5 to 48 hours.

Since both calcium and magnesium were present, it was difficult to use a potentiometric titration for calcium [the end point potentials for the titration of calcium and magnesium with (ethylenedinitrilo)tetraacetic acid (EDTA) as a complexing titrant are relatively close]. Therefore, a titration with a standardized EDTA solution and Mallinckrodt analytical reagent hydroxynapththol blue as a colorimetric indicator was used as in the procedure of Patton and Reeder (*21*). The method was substantiated by analyses of known solutions in approximately the same ranges of calcium and additional salt concentrations.

The total salt concentration was obtained and verified by evaporating a weighed sample to dryness at 100° C. and weighing the total solid, knowing the dilution factor of the solution, and removing all metallic cations with a Dowex 50 cation exchange resin and titrating the eluent for total acid. The total sulfate concentration was obtained from the analysis for dissolved calcium sulfate, the total salt concentration, and the exact molal ratios of the salts in the diluted stock solution. The formal solubility product, $K'_{sp} = [m_{Ca}][m_{SO_4}]$, and the formal ionic strength, $I' = \frac{1}{2} \Sigma\, m_i z_i^2$, where m_i is the formal molality of ion i and

Table I. Negative Logarithm of Solubility Product Constants for Anhydrite (A), Hemihydrate (B), and Gypsum (G), and Several Other Constants for Evaluating Solubility Products at 0–300° C.

Temp., °C.	$-\text{Log } K^\circ_{sp}(A)$	$-\text{Log } K^\circ_{sp}(H)$	$-\text{Log } K^\circ_{sp}(G)$	A_{sp}	B_G	C_G	Debye-Hückel Slope[a] (for Molalities for 1-1 Electrolyte)
0	3.818	3.682	4.466	1.450	0.0880	0.0234	0.4875
25	4.192	3.734	4.373	1.500	0.0194	0.0134	0.5080
50	4.539	3.933	4.409	1.544	0.0000	0.0108	0.5337
75	4.884	4.236	4.514	1.575	0.0000	0.0068	0.5645
100	5.240	4.614	4.650	1.594	0.0000	0.0020	0.6006
125	5.617	5.044	4.792	1.600	0.0000	0.0000	0.6422
150	6.020	5.512	4.920	1.600	0.0000	0.0000	0.6900
175	6.453	6.007	5.025	1.600	0.0000	0.0000	0.7451
200	6.917	6.520	5.098	1.600	0.0000	0.0000	0.8097
250	7.941	7.576	5.130	1.600	0.0000	0.0000	0.9848
300	9.093	8.648	4.996	1.600	0.0000	0.0000	1.2870

[a] Debye-Hückel slopes for molar units multiplied by square root of density of water to convert for use with molal units.

z_i equals the charge on that ion, could then be obtained. For these values, m_{Ca} and m_{SO_4} represent the total molality of calcium and sulfate.

All samples were analyzed on a volume basis and were converted to molalities by using the densities at 25° C. of sodium chloride solutions of comparable salt concentration (*10*). Since sodium chloride is the predominant constituent of sea water, it was believed that this procedure was acceptable within the precision of the solubility determinations.

SOLUBILITY RELATIONSHIPS IN NaCl-H₂O SOLUTIONS

Solubilities of $CaSO_4$ and its hydrates in dilute and concentrated $NaCl\text{-}H_2O$ solutions at temperatures from 0° to 200° C., determined at this laboratory, have been published with references to earlier work (*15, 16*). A recent paper by Ostroff and Metler (*20*) presents additional solubilities of $CaSO_4 \cdot 2H_2O$ in $NaCl\text{-}H_2O$ solutions, 28° to 70° C., in very good agreement with both experimental and calculated (to ±1.5% at all ionic strengths) values (*15, 16*). A study by Madgin and Swales, not compared previously but also in good agreement, contains solubilities of $CaSO_4 \cdot 2H_2O$ and $CaSO_4$ in $NaCl\text{-}H_2O$ solutions at 25° and 35° C. (*12*). Previous work (*15, 16*) showed that the solubility of gypsum, hemihydrate, and anhydrite could be described at a particular temperature by the following equation (Debye-Hückel type with added terms),

$$\log K_{sp} = \log K^\circ_{sp} + 8S(I)^{1/2}/[1 + A_{sp}(I)^{1/2}] + BI - CI^2 \qquad (1)$$

where I is the (true) ionic strength of the solution defined in the experimental section in terms of the formal rather than the true ionic molalities, K_{sp} is the ionic (practical) solubility product, $[m_{\text{Ca}^{2+}}]\,[m_{\text{SO}_4^{2-}}]$, S is the theoretical limiting Debye-Hückel slope for a 1-1 electrolyte multiplied by the square root of the density of water to convert it for use with molal units, K°_{sp} is the solubility product constant at $I = 0$, and A_{sp}, B, and C are adjustable parameters. Values of A_{sp}, B_G, and C_G (subscripts G, H, and A are used here to designate application to gypsum, hemihydrate, and anhydrite, respectively) at several temperatures for gypsum are given elsewhere (*15*). Also given (*15*) is an equation for the variation with temperature (T, ° Kelvin) of K°_{sp} for gypsum, included as follows:

$$\log K^\circ_{sp}\ (\text{gypsum}) = 390.9619 - 152.6246 \log T$$
$$-12545.62/T + 0.0818493\,T \qquad (2)$$

In place of the equation for anhydrite given previously (*15*), an equation for K°_{sp} (anhydrite) that fitted the results somewhat better at temperatures from 100° to 200° C. (but

Table II. Experimental Values Obtained from the Solubility of Calcium Sulfate Dihydrate and Calcium Sulfate in Seawater Concentrates and Diluents, 30–200° C

Source[a]	I'[b]	$-\text{Log } K'_{sp}$[c]	$-\text{Log }[\text{Ca(m)}]$[d]
$T = 30^\circ C$, $(CaSO_4 \cdot 2H_2O)$[e]			
2	0.0599	3.631	1.862
2	0.443	2.992	1.557
2	0.791	2.783	1.487
2	1.506	2.573	1.440
2	2.202	2.471	1.438
2	2.613	2.433	1.446
2	3.64	2.403	1.507
2	4.00	2.411	1.541
3	0.598	2.883	1.519
3	1.866	2.489	1.418
3	3.94	2.416	1.540
3	6.68	2.559	1.849
4	0.708	2.810	1.491
4	2.111	2.488	1.442
4	4.20	2.432	1.573
$T = 60^\circ C$, $(CaSO_4 \cdot 2H_2O)$			
1	0.0599	3.636	1.865
1	0.0599	3.635	1.864
1	0.0805	3.559	1.785
1	0.0816	3.548	1.779
1	0.1370	3.394	1.714
1	0.1388	3.381	1.708
1	0.762	2.770	1.474
1	0.771	2.767	1.474
1	0.432	2.983	1.550
1	2.111	2.451	1.414
1	2.111	2.444	1.409
3	0.598	2.866	1.509
3	1.866	2.480	1.412
3	3.94	2.387	1.516
3	6.68	2.485	1.780
4	0.708	2.804	1.488
4	2.111	2.450	1.413
4	4.20	2.367	1.518
$T = 95^\circ C$, $(CaSO_4 \cdot 2H_2O)$			
1	0.0513	3.780	1.937
1	0.0513	3.772	1.933
1	0.0627	3.658	1.830
1	0.0696	3.706	1.859
1	0.1300	3.475	1.757
1	0.1300	3.475	1.757
1	0.422	3.055	1.591
1	0.427	3.046	1.587
1	0.762	2.815	1.503
1	2.111	2.417	1.390
1	2.141	2.338	1.336
1	3.42	2.246	1.366
1	5.89	2.378	1.636
1	5.89	2.301	1.568
3	0.598	2.907	1.534
3	1.866	2.498	1.424
3	3.94	2.402	1.529
3	6.68	2.400	1.701
$T = 100^\circ C$, $(CaSO_4)$			
1	0.0201	4.580	2.337
1	0.0401	4.413	2.222
1	0.2008	3.917	2.047
1	0.365	3.710	1.990
1	0.379	3.684	1.978
1	0.683	3.450	1.918
1	0.717	3.432	1.915
1	1.998	3.070	1.889
1	2.265	3.057	1.917
1	2.811	2.987	1.928
1	3.32	2.959	1.960
1	3.53	2.963	1.985
1	5.89	2.991	2.212
5	0.841	3.201	1.778
5	1.092	3.143	1.789
5	1.411	3.036	1.767
5	1.675	3.032	1.807
5	1.743	3.009	1.799
5	1.917	3.000	1.818
5	2.082	3.000	1.843
5	2.202	3.000	1.860
3	0.584	3.415	1.864
3	1.866	2.983	1.797
3	3.87	2.896	1.959
3	3.87	2.879	1.943
3	6.68	2.848	2.124
$T = 125^\circ C$, $(CaSO_4)$			
1	0.0129	4.971	2.532
1	0.0138	4.932	2.466
1	0.0138	4.917	2.461
1	0.0314	4.770	2.407
1	0.0314	4.757	2.400
1	0.0314	4.740	2.391
1	0.0314	4.717	2.378
1	0.0828	4.462	2.294
1	0.0840	4.387	2.250
1	0.0901	4.434	2.285
1	0.1817	4.187	2.207
1	0.1817	4.161	2.191
1	0.352	3.971	2.166
1	0.352	3.943	2.146
1	0.675	3.699	2.104
1	0.683	3.674	2.087
1	0.683	3.658	2.075
1	1.998	3.284	2.076
1	1.998	3.299	2.028
1	3.37	3.131	2.124
1	5.69	3.056	2.260
1	6.10	3.114	2.345
3	0.570	3.690	2.058
3	1.697	3.288	2.026
3	1.697	3.244	1.988
3	3.42	3.081	2.084
3	3.58	3.114	2.132
$T = 150^\circ C$, $(CaSO_4)$			
1	0.0065	5.562	2.828
1	0.0067	5.547	2.776
1	0.0246	5.244	2.661
1	0.0261	5.131	2.600
1	0.0717	4.900	2.550
1	0.1705	4.561	2.452
1	0.1705	4.481	2.397
1	0.332	4.294	2.396
1	0.344	4.264	2.381
1	0.635	3.951	2.291
1	0.651	3.921	2.273
1	1.305	3.614	2.226
1	1.944	3.450	2.216
1	1.970	3.427	2.201
1	2.690	3.310	2.207
1	3.32	3.244	2.225
1	3.32	3.225	2.208
1	5.89	3.125	2.342
3	0.556	3.943	2.248
3	1.697	3.514	2.227
3	1.720	3.456	2.179
3	1.720	3.426	2.152
3	3.81	3.237	2.273
3	6.68	3.131	2.400
$T = 175^\circ C$, $(CaSO_4)$			
1	0.0037	5.991	2.996
1	0.0040	5.914	2.957
1	0.214	5.611	2.866
1	0.214	5.516	2.809
1	0.214	5.511	2.807
1	0.706	5.164	2.722
1	0.727	5.244	2.782
1	0.1705	4.775	2.610
1	0.328	4.572	2.617
1	0.332	4.509	2.568
1	0.651	4.174	2.489
1	0.659	4.184	2.501
1	0.675	4.190	2.515
1	1.970	3.609	2.369
1	1.970	3.595	2.356
1	3.37	3.377	2.358
1	3.42	3.432	2.417
1	5.79	3.222	2.429
1	5.79	3.149	2.358
3	0.563	4.229	2.490
3	1.866	3.699	2.433
3	3.94	3.398	2.442
$T = 200^\circ C$, $(CaSO_4)$			
1	0.0018	6.489	3.287
1	0.0022	6.462	3.232
1	0.0206	5.842	3.002
1	0.0706	5.276	2.799
1	0.1621	5.068	2.827
1	0.1621	5.046	2.809
1	0.1621	4.987	2.762
1	0.328	4.733	2.754
1	0.643	4.398	2.685
1	0.643	4.347	2.639
1	1.305	4.007	2.585
1	1.970	3.764	2.516
1	2.613	3.602	2.473
1	3.37	3.437	2.415
1	5.79	3.108	2.318
3	0.563	4.475	2.708

[a] 1 = Marshall-Slusher (Present-1967), 2 = Posnjak (1940), 3 = Hara et al. (1934), 4 = Shaffer (1967), 5 = Langelier et al. (1950).

[b] Formal ionic strength (molal units).

[c] K'_{sp} = Formal Soly. Prod. of Satg. Solid (molal basis).

[d] $[\text{Ca(m)}]$ = Molality of calcium (= molality of Satg. Solid).

[e] Saturating solid phase.

essentially the same at lower temperatures) was obtained and used in this work,

$$\log K^{\circ}_{sp}\ (\text{anhydrite}) = -215.509 + 85.685 \log T + 6075.2/T - 0.070707\,T \qquad (3)$$

From the solubilities of hemihydrate (*16, 23, 24, 26*) (25° to 125° C.), most of them in H_2O, and those referenced by Smith (*26*) (90° to 125° C.), we have estimated the values of K°_{sp} for hemihydrate as a function of temperature (° K.) from 0° to 200° C., and have obtained the following equation similar to that for gypsum and anhydrite (*15*) to describe its behavior,

$$\log K^{\circ}_{sp}\ (\text{hemihydrate}) = 154.527 - 54.958 \log T - 6640.0/T \qquad (4)$$

The A_{sp} parameter at each temperature was assumed the same for expressing the behavior of each of the three salts, since it should not be a function of the hydration state of the saturating solid. From the previous relationships (*15*), it was shown that $B_A = B_G - 0.020$ and $C_A = C_G + 0.0030$. The difference, $(B_G I - C_G I^2) - (B_A I - C_A I^2)$, is attributable to the hydration of $CaSO_4 \cdot 2H_2O$ and corresponds to $2 \log a_{H_2O}$, where a_{H_2O} is the activity of H_2O in the solution phase. By analogy, Equations 5 and 6 for B_H and C_H were derived:

$$B_H = B_A + 0.25\,(B_G - B_A) \qquad (5)$$

$$C_H = C_A + 0.25\,(C_G - C_A) \qquad (6)$$

The BI and CI^2 terms of Equation 1 are important only at very high ionic strengths (above 2 molal) and at low temperatures; they become very small or drop out entirely at temperatures above about 50° to 100° C. For convenience, some values for the several constants, calculated with Equations 2 to 4, and parameters are given in Table I.

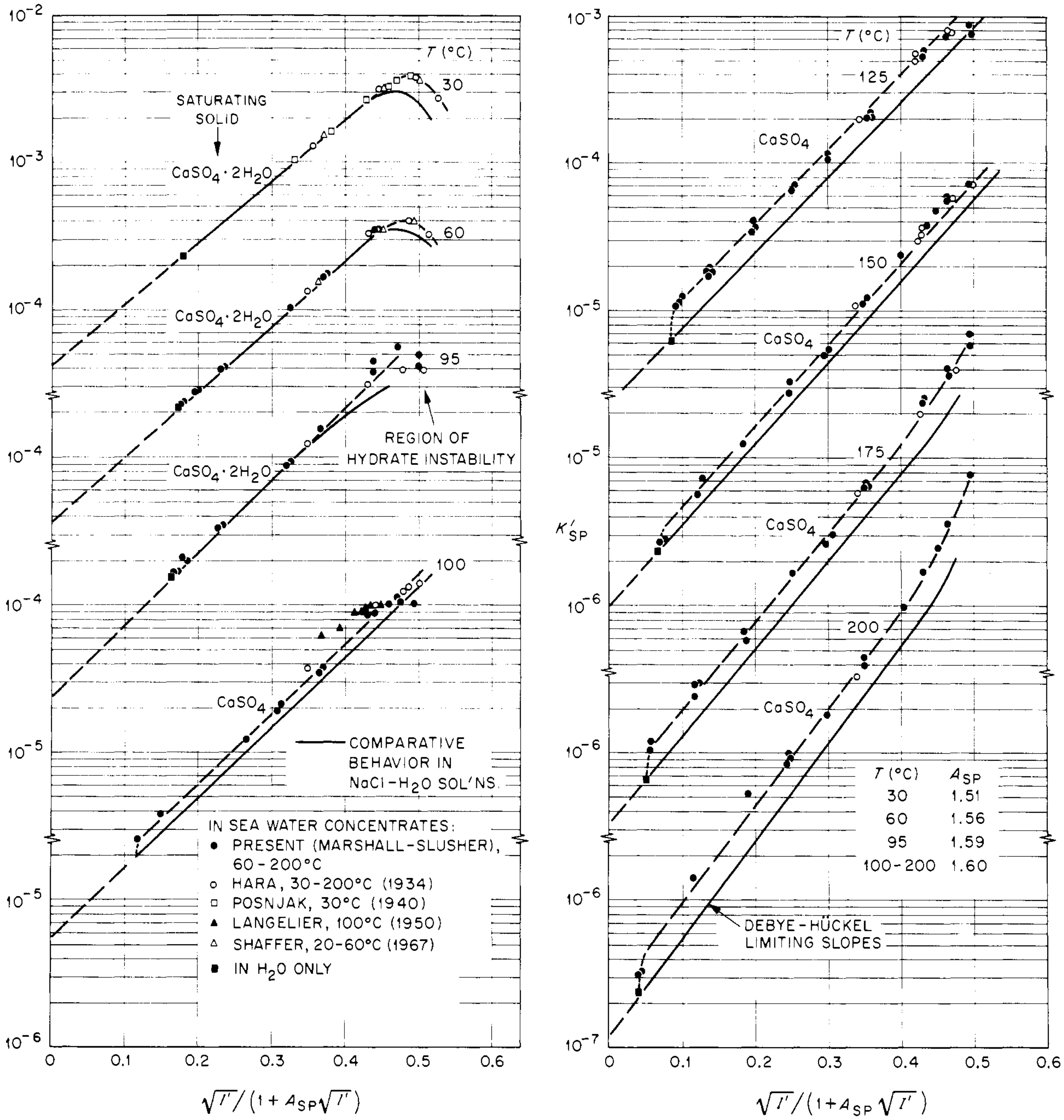

Figure 1. Solubility products, K'_{sp}, vs. $[I']^{1/2}/(1 + A_{sp}[I']^{1/2})$ of $CaSO_4 \cdot 2H_2O$ and $CaSO_4$ in sea water concentrates compared with their behavior in $NaCl\text{-}H_2O$ solutions from 30° to 200° C.

With the use of the above equations and constants at the several temperatures the solubility of gypsum in NaCl-H_2O from 0° to 110° C. is believed to be described to within about ±3% (*15*), and for hemihydrate and anhydrite to 200° C., within about ±6%.

SOLUBILITY PRODUCTS IN SEA WATER CONCENTRATES

The experimentally determined solubility products, K'_{sp}, of anhydrite at 100° to 200° C. in synthetic sea water concentrates and diluents, expressed as $-\log K'_{sp}$ and obtained as described above, are given in Table II. Included also are the experimentally determined negative logarithms of the molal concentration of calcium (the solubility value). The logarithm of the total sulfate concentration is equal to the difference, $\log K'_{sp} - \log[m_{Ca}]$. The values for K'_{sp} are plotted in Figure 1 as $\log K'_{sp}$ *vs.* $(I')^{1/2}/[1 + A_{sp}(I')^{1/2}]$ where the A_{sp} values are the same as those used earlier for $CaSO_4$ in NaCl solutions (*15*) and are included in Table I. Values in H_2O are given elsewhere (*15*, *16*). The solid lines on Figure 1 correspond to the behavior of K_{sp} derived from the previously determined solubilities in NaCl-H_2O solutions. Although at 100° C. there are no solubility measurements of anhydrite in NaCl-H_2O solutions, the solid line is consistent with extrapolated solubility products from both lower and higher temperatures [K°_{sp} (anhydrite) is calculated with Equation 3], and is believed to represent closely the equilibrium solubility behavior. Thus, our own values at 100° C. in sea salt solutions are believed to represent equilibrium values (they were obtained by approaching 100° C. from higher temperatures) while those values of Langelier *et al.* at 100° C., obtained by approaching 100° C. from lower temperatures, appear to be somewhat high.

Included also in Figure 1 and Table II are those values of K'_{sp} in sea water concentrates at 30° C. calculated from the solubilities of Posnjak (*22*), at 30° and 60° C. obtained from some very recent measurements of Shaffer (*25*), at 100° C. given by Langelier *et al.* (*11*) in molal units, and at the several temperatures calculated from the solubilities of Hara *et al.* (*8*). Values of K'_{sp} from the results of both Posnjak and Hara *et al.* were obtained by multiplying the analyzed saturation concentration of calcium [Tables I and II of Posnjak (*22*); solubilities of Posnjak's Table II, incorrectly listed as grams per 100 grams of H_2O, are in grams per 100 grams of solution; Tables II and III of Hara *et al.* (*8*)], converted to molal units, by the molality of total sulfate ($m_{CaSO_4} + m_{excess\ sulfate}$). Posnjak's series of synthetic concentrates before saturation with $CaSO_4 \cdot 2H_2O$ did not contain calcium. Therefore, total sulfate was calculated from his values by adding the concentration of sulfate in the stock concentrate to that obtained by analysis for saturation calcium (= $CaSO_4$). To obtain total sulfate from the measurements of Hara *et al.* (which in the stock concentrates contained analyzed small amounts of calcium), the molal excess of sulfate over that of calcium in the stock concentrate [evaluated from Table II (*7*)] was added to the analyzed total calcium after saturation; this amount corresponded to total sulfate after saturation. The methods of conversion are stated in detail, since the data of Hara are misinterpreted elsewhere (*2*), but interpreted correctly later (*25*). The agreement of the present results with previously published solubilities is good (except at 100° C.) and is within the range of scatter of the individual solubility measurements.

The solubility products of gypsum in synthetic sea water concentrates at 30° and 60° C. are essentially identical with those in NaCl-H_2O solutions when compared at the same ionic strength, except at the highest ionic strengths. At 100° to 200° C. the solubility products of anhydrite are greater in sea salt than in sodium chloride solutions, and at a constant temperature the logarithmic difference, $\log (K'_{sp}/K_{sp})$, is approximately constant over a very wide range of ionic strength. This difference (Figure 2) is a function of both K°_{sp} and the dissociation constant(s) of any associated species present in the sea salt solutions. Thus, values in Figure 2 could be used for correcting differences in solubility in the solution compositions (sea

Table III. Molal Compositions of Several Representative Saline Waters

Component	Saline Water Code[a] A	B	C	D	E	F	G
Sodium	0.4758	0.1463	0.2196	0.0147	0.00401	0.02756	0.0459
Calcium	0.01034	0.00915	0.01490	0.00513	0.00551	0.01150	0.01878
Magnesium	0.0542	0.0309	0.00672	0.00222	0.00420	0.00813	0.01539
Potassium	0.01007	0.0025	0.00065	0.00046	...	0.000229	0.06574
Iron	...	...	...	0.000023	...	...	...
Manganese	...	...	...	...	...	...	...
Chloride	0.5544	0.1529	0.2303	0.00235	0.00054	0.0371	0.1156
Sulfate	0.02856	0.03238	0.01575	0.01262	0.00893	0.01107	0.03097
Bicarbonate	0.00241	0.0028	0.00341	0.00286	0.00534	0.00605	0.00250
Carbonate	...	0.0004	...	...	...	...	...
Bromide	0.00084	0.0140[b]	...	...	...	...	...
Fluoride	...	...	0.00004	0.00013	...	...	...
Nitrate	...	...	0.000035	...	...	0.00084	...
Silicon dioxide	...	...	0.00022	0.00023	...	0.00053	0.00023
Boron	...	...	0.000060	0.00017	...	0.00020	...
I'(original)[c]	0.7080	0.2979	0.3018	0.0501	0.0422	0.0975	0.2452
R (original)[c]	2.763	3.539	1.057	2.461	1.622	0.959	1.649
I'(revised)[d]	0.7092	0.2993	0.3035	0.0515	0.0449	0.1003	0.2464
R(revised)[d]	2.878	3.692	1.171	2.741	2.105	1.220	1.716

[a] A. Standard sea water (*27*) based on chlorinity of 19.00 grams per kg. of solution. B. Caspian Sea, analysis of water obtained near Baku, U. S. Geol. Survey analysis (*29*). C. Deep well, Roswell, N. M., Jan. 14, 1965 (*1*). D. West well, Miller, S. D., depth 1245 feet, sampled Oct. 31, 1955 (U. S. Geol. Survey analysis) (*18*). E. Deep well No. 5, Webster, S. D. (*17*). F. Irrigation well, Buckeye Irrigation Co., Buckeye, Ariz., sampled April 23, 1955 (U. S. Geol. Survey analysis) (*18*). G. Pecos River below Grandfalls, Tex., sampled April 1951; U. S. Geol. Survey Water Supply Paper 1199 (*18*). [b] Bromide added arbitrarily to achieve electroneutrality; could be any other monovalent ion. [c] Ionic strength (I') and molal ratio SO_4^{2-}/Ca^{2+} (R), of original saline water. [d] Ionic strength (I') and molal ratio SO_4^{2-}/Ca^{2+} (R) after removal of CO_3^{2-} and HCO_3^- by addition of H_2SO_4.

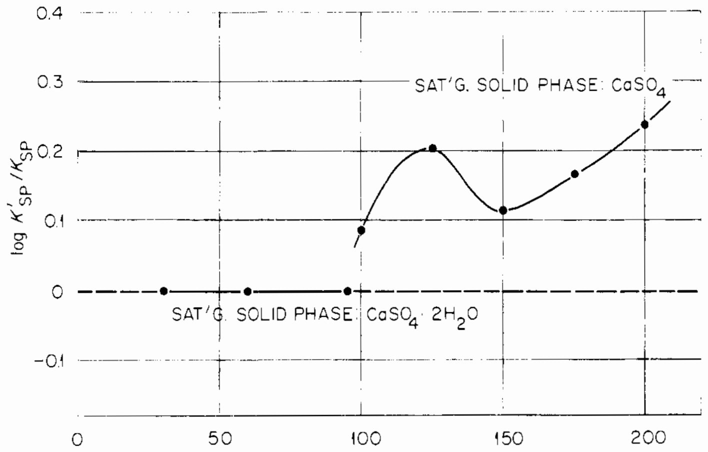

Figure 2. Correction for $K_{sp}(CaSO_4)$ to obtain apparent solubility product, K'_{sp}, in sea water concentrates

salt solutions) and for the solid phase from which they were obtained but not in other saline water compositions.

As a sea salt solution approaches infinite dilution (solubility of $CaSO_4$ or its hydrates approaches that in water), the value of K'_{sp} must approach K_{sp}; Figure 1 shows this convergence occurring only at total salt concentrations below about 0.04 molal. Figure 3 shows schematically how the curve must approach the same Debye Hückel limiting slope and solubility product in water upon dilution of either sea salt or NaCl solutions.

CALCULATION OF SOLUBILITY LIMITS

Assumptions: Dissociation Constant of Magnesium Sulfate. The increase in solubility in sea salt solutions over that in sodium chloride solutions can be attributed essentially to the formation of a neutral species, $MgSO_4^0$, which removes part of the concentration of sulfate ion and thereby allows the solubility of $CaSO_4$ (or its hydrates) to increase in order to satisfy its solubility product, K_{sp}. The existence of neutral $CaSO_4^0$ was not expected to interfere appreciably with this assumption (except in extreme cases mentioned below), since its concentration (in solutions saturated with $CaSO_4$) should be nearly independent of ionic strength and is incorporated into the values of K_{sp} used in this study (*13, 15*).

From the solubility results in sea salt solutions given in this paper and from those solubilities in sodium chloride solutions, values for the dissociation quotient, K_d, of the equilibrium,

$$MgSO_4 \overset{K_d}{\rightleftharpoons} Mg^{2+} + SO_4^{2-} \quad (7)$$

and constant, K_d^0, at $I = 0$ were calculated and are presented elsewhere (*13*), where $\log K_d$ was estimated by the following Debye-Hückel equation,

$$\log K_d = \log K_d^0 + 8S(I)^{1/2}/[1 + (I)^{1/2}] \quad (8)$$

and $\log K_d^0$ varied with temperature according to the equation,

$$\log K_d^0 = -158.540 + 62.160 \log T + 4810.6/T - 0.046298T \quad (9)$$

[4810.6 given incorrectly as 4180.6 elsewhere (*13*)].

Calculated *vs.* Observed Solubilities, 25° to 200° C. By using the several equations for solubility products of calcium sulfate and its hydrates and the dissociation quotients of magnesium sulfate, with their respective constants (Table I), solubilities were calculated for direct comparisons with saturated solution compositions given in Table II and with other published, experimentally observed values in mixed electrolyte systems (*4, 5, 12, 20*). The formal ionic strengths were corrected slightly for the calculated amount of neutral species, $MgSO_4^0$. The entire procedure was similar to that for obtaining concentration factors, described below, except that I' in Equation 11 was kept always equal to the initial, formal ionic strength. CF in Equation 12 then represented the molal solubility ratio, calculated to an observed, rather than a concentration factor, where formal ionic strength changes with concentration. When I' was corrected for this change the differences usually were less than 0.1 to 0.2% for ratios (calculated to observed) between 0.9 and 1.1, and were never greater than 0.7% for those of 0.6 to 0.9 and 1.1 to 1.4.

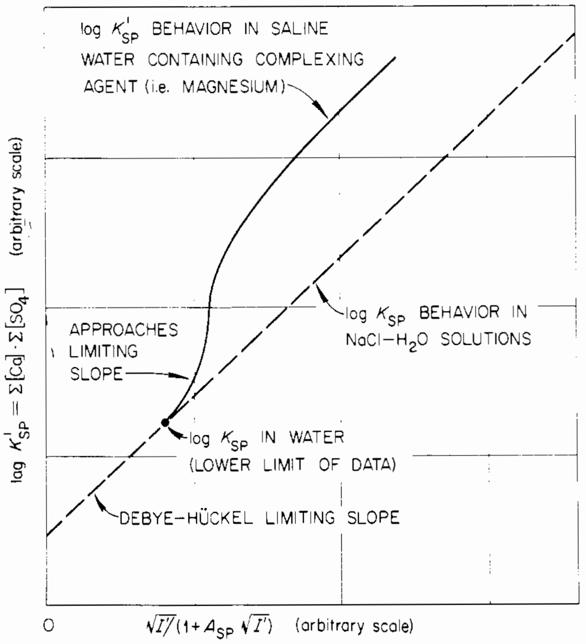

Figure 3. Schematic behavior of apparent solubility product, K'_{sp}, of $CaSO_4$ in magnesium containing saline waters

Figure 4 compares the calculated with observed solubilities from 25° to 95° C. in sea water solutions for all the (observed) results presented in Table II. Included also are comparisons with observed solubilities in mixed electrolytes obtained by several investigators (*5, 12, 20*). Comparisons with observed solubilities in NaCl-H_2O other than those in Figure 4 have been given (*15*).

The use of a dissociation constant for $CaSO_4^0$, roughly estimated from data up to 200° C. (*15*), may well account for the positive deviations from those values of Ostroff and Metler (Figure 4) where m_{MgCl_2}/m_{NaCl} equals 0.5 to infinity, and also for the negative deviations from those of Madgin and Swales containing similarly high values (0.5 to infinity) of $m_{Na_2SO_4}/m_{NaCl}$. The presence of some neutral $CaSO_4^0$ in solution would yield calculated deviations in the directions shown for these two extreme types of solutions. From a solubility study in progress (*30*), we hope to obtain sufficiently accurate values for the dissociation constant and quotients of $CaSO_4^0$ that can be applied as a refinement to these calculations for the extreme deviations.

In Figure 5 are shown the comparative calculations for sea salt solutions at temperatures from 100° to 200° C. The drop in the calculated values at 175° and 200° C. at ionic strengths above 1 molal can be attributed to the deviation from the relationship of Equation 8 in calculated

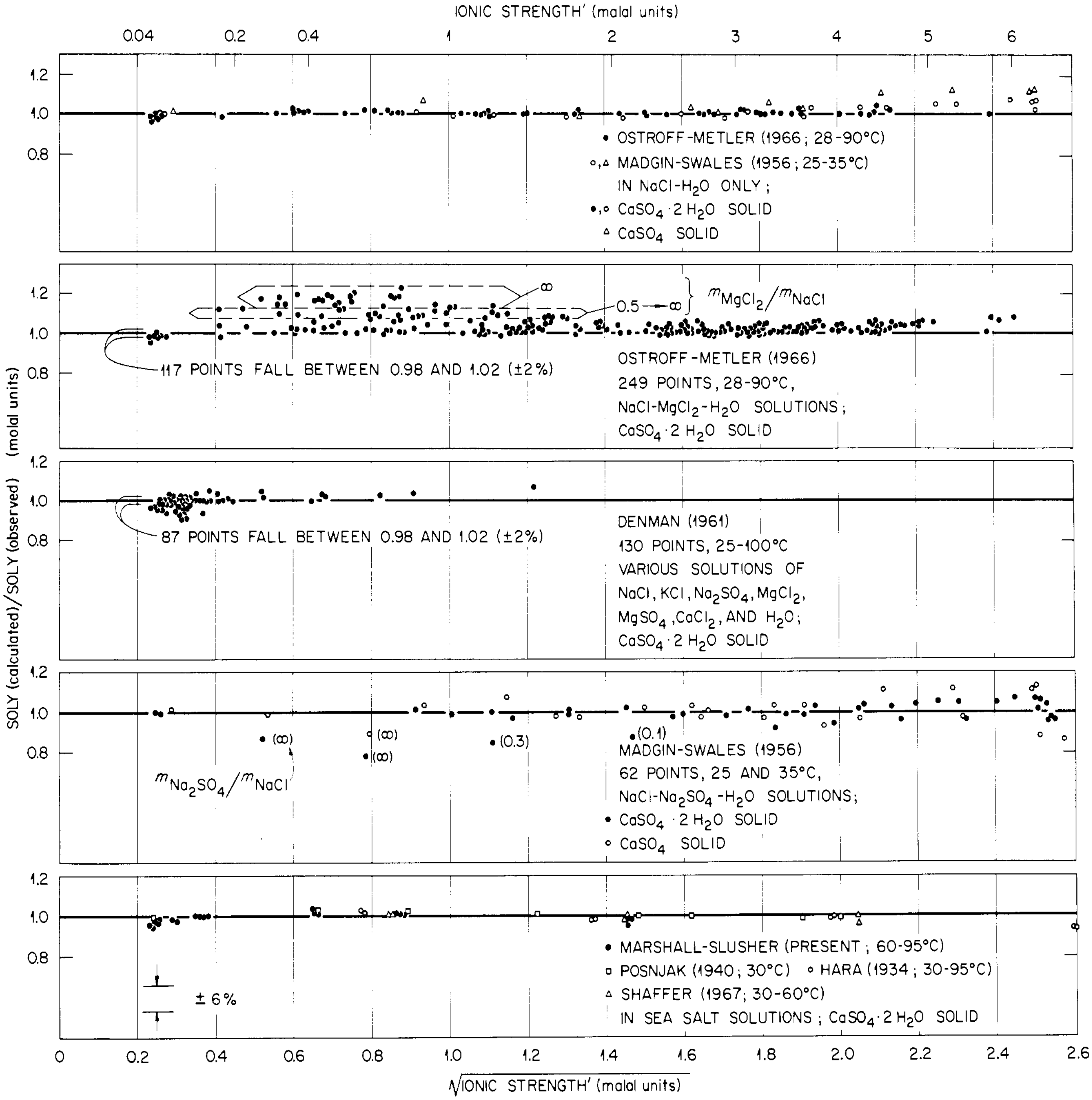

Figure 4. Representative comparison of calculated and observed solubilities of $CaSO_4 \cdot 2H_2O$ and $CaSO_4$ in sea salt solutions and other mixed electrolytes at 25° to 95° C.

dissociation quotients of magnesium sulfate at these high ionic strengths (*13*). Additional terms could be added to Equation 8 to account for this deviation but, with the lack of any other solubility data to substantiate their inclusions, this was not done.

Comparisons of calculated with observed solubilities of Clampett and Fowler (*4*) for $CaSO_4 \cdot \frac{1}{2}H_2O$ at temperatures from 100° to 150° C. (not included in Figure 5) were not within reasonable agreement. Their values do not agree with those of Langelier *et al.* (*11*) at 100° C. for $CaSO_4 \cdot \frac{1}{2}H_2O$ nor with our own values (*16*) at 125° C. except in water and unconcentrated sea water. In view of the extrapolated, reasonable agreement between our own values (at 125° C.) and those of Langelier *et al.* (at 100° C.), we suspect an error in the measurements of Clampett and Fowler for the concentrated solutions.

The method of calculation and the assumptions used thus appear satisfactory for calculating solubilities in saline waters in general at temperatures from 25° to 200° C.; but for maximum reliability, it should be applied to waters containing a predominance of a 1-1 electrolyte.

Calculation of Concentration Factors. It can be shown that (*13*)

$$[MgSO_4^0] = (\Sigma[Mg])K_{sp}/(K_d[Ca^{2+}] + K_{sp}) \qquad (10)$$

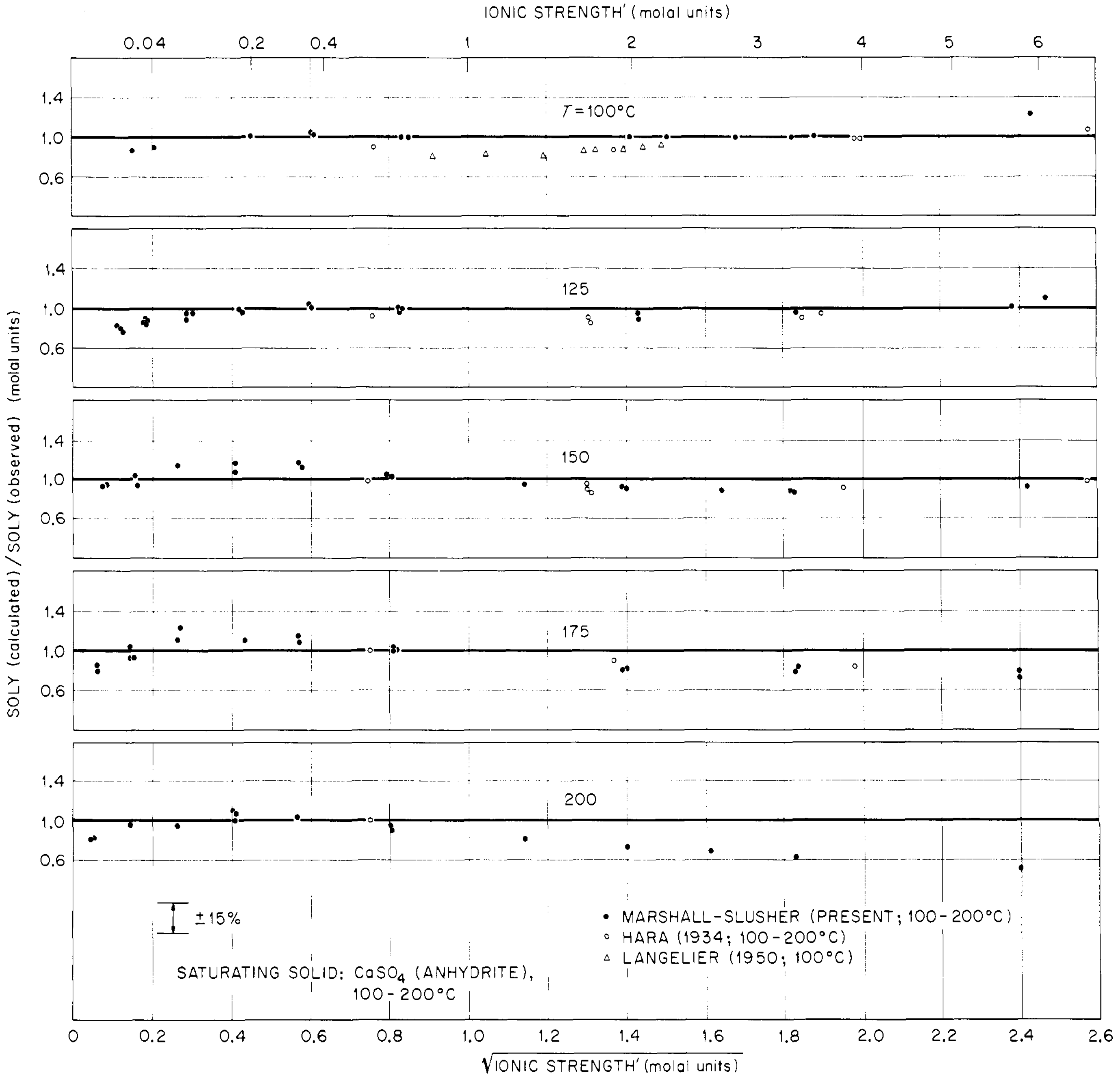

Figure 5. Representative comparison of calculated and observed solubilities of $CaSO_4$ (anhydrite) in sea salt solutions at 100° to 200° C.

$$I = I' - 4[\mathrm{MgSO_4^0}] \tag{11}$$

from which

$$CF = \{(K_{\mathrm{sp}} + [\mathrm{Ca^{2+}}]\cdot[\mathrm{MgSO_4^0}])/FP_1\}^{1/2} \tag{12}$$

In Equations 8 to 12, T is in degrees Kelvin, I and I' are the true and formal (molal) ionic strengths, respectively, FP_1 is the formal product $[m(\text{total calcium})\cdot m(\text{total sulfate})]$ in the initial (unconcentrated) saline water, $\Sigma[\mathrm{Mg}]$, $[\mathrm{Ca^{2+}}]$, and $[\mathrm{MgSO_4^0}]$ are the molal concentrations of total magnesium, calcium ion, and $\mathrm{MgSO_4^0}$, respectively, and CF is the concentration factor on a molal basis $[= I'$ (concentrate)$/I'$ (original solution)$]$.

By first using I' (initial), $\Sigma[\mathrm{Ca}]$ (initial) for $[\mathrm{Ca^{2+}}]$, and $\Sigma[\mathrm{Mg}]$ (initial), preliminary values of K_{sp}, K_d, $[\mathrm{MgSO_4^0}]$, I, and CF were calculated. By iterative calculations a final value of CF (and thus of I' for the concentrate) was obtained that differed less than 0.5% from the previously calculated value. Equations 1 to 6 and 8 to 12 were used for the calculations.

Use of Computer Program for Obtaining Concentration Factors. A computer program was written to perform the above calculations. After values of the Debye-Hückel slopes and the A_{sp}, B_G, and C_G parameters from Table I are included in the "Read In" data for each of a series of temperatures, only the original, formal ionic strength, I', the analytical molalities of calcium and of magnesium, and the molal

COMPUTER PROGRAM

Computer Program for Calculating Concentration Factors (*CF*) to Avoid Precipitation of $CaSO_4$ and Its Hydrates from Saline Waters. [Program written in FORTRAN IV (International Business Machines Co.). For interpretation and use, a basic knowledge of the FORTRAN languages is necessary.]

The *READ* Values:

NST = No. of separate temperatures for evaluation; maximum value of subscript, *I*.
TEMP = temperature (° C.).
DHS = limiting Debye-Hückel slope [x (density of $H_2O)^{1/2}$] for 1-1 electrolyte.
A = A_{sp} parameter.
B = B_G parameter (for gypsum only) for solubility product calculations for gypsum.
C = C_G parameter (for gypsum only) for solubility product calculations for gypsum. (Above quantities are read in once for $I = 1$ to NST for evaluation of all saline water compositions.)
TITLE = title for the particular saline water composition.
*AI*1 = molal ionic strength of the saline water.
*CAL*1 = molal concentration of calcium in the saline water.
R = molal ratio, SO_4/Ca in the saline water.
*TMG*1 = total molality of magnesium in saline water. (Calculations are repeated for each additional TITLE card and different values of *AI*1, *CAL*1, *R*, and *TMG*1.)

The *WRITE* Values:

A. TITLE, *AI*1, *CAL*1, *R*, *TMG*1, the *A* parameter used for the variation of $K_d(MgSO_4)$.
B. For each solid: TEMP, concentration factors (*CF*) on molal, molar, and weight fraction bases, ionic strengths at saturation, K°_{sp}'s and number of iterative calculations (NIT) to obtain values of *CF*.
C. Some particular constants used to obtain values of *CF*: *DHS*, $K^\circ_d(MgSO_4)$, A_{sp} parameters for K_{sp} variations with ionic strength, and *A*, *B*, and *C* parameters for anhydrite, hemihydrate, and gypsum.

An Alternate Equation to Substitute into Program for Specific Use with Sea water:
$WF1/AI1 = 0.04790 - 0.002194 * AI1 + 0.00006900 * AI1**2$ (= wt. fraction/ionic strength)

FORTRAN IV Computer Program for Calculating Temperature-Solubility Limits of Calcium Sulfate and Its Hydrates in Saline Waters and Their Concentrates

```
C  CALCN, TEMP-SOLY LIMITS(CASO4+HYDRATES IN SALINE WATERS), MARSHALL (1967)
C  W. L. MARSHALL (1967)-OAK RIDGE NATL. LAB., TENN., U.S.A.
C  PROGRAM IN FORTRAN IV LANGUAGE (READ IN TAPE 5, READ OUT TAPE 6), (1967)
     0DIMENSION TITLE (10), DHS(100), TEMP(100), TA(100), A(100), B(100,3),
     1C(100,3), JJ(100,3), XKDISO(100), SOLPO(100,3), AIF(100,3),
     2CFML(100,3), CFMR(100,3), CFWF(100,3)
      READ (5,1)NST
    1 FORMAT (I10)
      READ (5,2) (TEMP(I), DHS(I), A(I), B(I,3), C(I,3), I=1, NST)
    2 FORMAT (5E10.0)
      DO21 I = 1, NST
      B(I,1)=(I,3)-0.020
      C(I,1)=C(I,3)+0.0030
      B(I,2)=B(I,1)+0.25*(B(I,3)-B(I,1))
      C(I,2)=C(I,1)+0.25*(C(I,3)-C(I,1))
      TA(I)=TEMP(I)+273.16
     0SOLPO(I,1)=10.**(-215.509+85.685*ALOG10(TA(I))
     1+6075.2/TA(I)-0.070707*TA(I))
      SOLPO(I,2)=10.**(154.527-54.958*ALOG10(TA(I))-6640.0/TA(I))
     0SOLPO(I,3)=10.**(390.9619-152.6246*ALOG10(TA(I))
     1-12545.6/TA(I)+0.0818493*TA(I))
   210XKDISO(I)=10.**(-158.540+62.160*ALOG10(TA(I))
     1+4810.6/TA(I)-0.046298*TA(I))
   22 READ (5,3) TITLE, AI1, CAL1, R, TMG1
    3 FORMAT (10A4, 4E10.0)
      SOLP1=R*CAL1**2
      WF1=AI1*(0.05838-0.003260*AI1+0.00012489*AI1**2)
      FMR1=AI1*(0.9970-0.01883*AI1)
      DO 25 K=1,3
      DO 25 I=1, NST
      ASSMG=0.0
      CFML(I,K)=1.
      DO 23 J=1, 100
      CAL=CAL1*CFML(I,K)
      TMG=TMG1*CFML(I,K)
      AI=AI1*CFML(I,K)-4.*ASSMG
     0SOLP=SOLPO(I,K)*10.**(8.*DHS(I)*SQRT(AI)/(1.+A(I)*SQRT(AI))
     1+B(I,K)*AI-C(I,K)*AI**2)
      XKDIS=XKDISO(I)*10.**(8.*DHS(I)*SQRT(AI)/(1.+SQRT(AI)))
      ASSMG=TMG*SOLP/(XKDIS*CAL+SOLP)
      X=SQRT((SOLP+ASSMG*CAL)/SOLP1)
      IF(ABS(X-CFML(I,K))/X-.001)24,24,23
   23 CFML(I,K)=X
   24 JJ(I,K)=J
      AIF(I,K)=CFML(I,K)*AI1
     0CFWF(I,K)=AIF(I,K)*(0.05838-0.003260*AIF(I,K)+0.00012489*
     1AIF(I,K)**2)/WF1
   25 CFMR(I,K)=AIF(I,K)*(0.9970-0.01883*AIF(I,K))/FMR1
      WRITE(6,4)TITLE
    4 FORMAT(1H1,10A4)
      WRITE(6,5)AI1
    5 FORMAT(27H0IONIC STR OF SALINE WATER=E12.4)
      WRITE(6,6)CAL1
    6 FORMAT(26H INITIAL CONCN OF CALCIUM=E12.4)
      WRITE(6,7)R
    7 FORMAT(20H MOLAL RATIO SO4/CA=E12.4)
      WRITE(6,8)TMG1
    8 FORMAT(28H INITIAL CONCN OF MAGNESIUM=E12.4)
      WRITE(6,9)
    9 FORMAT(28H A PAR FOR KDISS(MGSO4)=1.0)
      WRITE(6,10)
   100FORMAT(65H0CONCN FACTORS FOR CASO4(ANHYDRITE),CF=CONCN(SATD)/CONCN
     1(INITIAL))
      WRITE(6,11)
   110FORMAT(112H0 TEMP(C)         CF(MOLAL)         CF(MOLAR)         CF(WT
     1FRACT)    ION STR(MOLAL-SATD)       SOLY PD(ZERO)        NO ITER)
     0WRITE(6,12)(TEMP(I),CFML(I,1),CFMR(I,1),CFWF(I,1),AIF(I,1),
     1SOLPO(I,1),JJ(I,1),I=1,NST)
   12 FORMAT(1H ,F6.0,5E18.3,I12)
      WRITE(6,13)
   130 FORMAT(60H0CONCN FACTORS FOR HEMIHYDRATE,CF=CONCN(SATD)/CONCN(INIT
     1IAL))
      WRITE(6,11)
     0WRITE(6,12)(TEMP(I),CFML(I,2),CFMR(I,2),CFWF(I,2),AIF(I,2),
     1SOLPO(I,2),JJ(I,2),I=1,NST)
      WRITE(6,14)
   140FORMAT(65H0CONCN FACTORS FOR CASO4 DIHYDRATE),CF=CONCN(SATD)/CONCN
     1(INITIAL))
      WRITE(6,11)
     0WRITE(6,12)(TEMP(I),CFML(I,3),CFMR(I,3),CFWF(I,3),AIF(I,3),
     1SOLPO(I,3),JJ(I,3),I=1,NST)
      WRITE(6,15)
   15 FORMAT(52H0PARTICULAR CONSTANTS USED IN THE ABOVE CALCULATIONS)
      WRITE(6,16)
   160FORMAT(119H0 TEMP(C)     D H SLOPE           K-DIS(0)(MGSO4)      A PARA
     1 B(ANHYD)    B(HEMI)     B(GYPS)      C(ANHYD)       C(HEMI)       C(GYPS))
     0WRITE(6,17)(TEMP(I),DHS(I),XKDISO(I),A(I),B(I,1),B(I,2),B(I,3),
     1C(I,1),C(I,2),C(I,3),I=1,NST)
   17 FORMAT(1H ,F6.0,F13.4,E20.3,F13.3,6F11.4)
      GO TO 22
      END
```

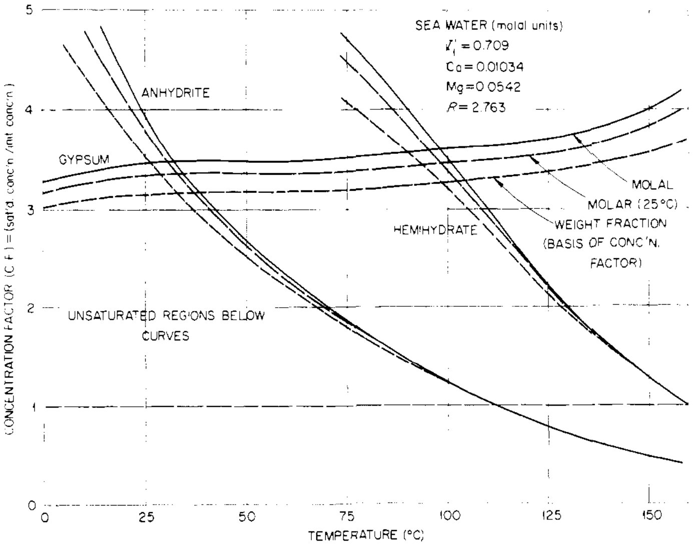

Figure 6. Calculated limits of solution stability to avoid precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 1/2H_2O$), and anhydrite ($CaSO_4$) from sea water concentrates

I_1'. Molal ionic strength of sea water
Ca, Mg. Original molalities of Ca and Mg
R. Molal ratio, SO_4/Ca

ratio (R), sulfate/calcium, are needed for calculating separately the temperature-concentration limits for anhydrite, hemihydrate, and gypsum. The program contains the equations for the temperature variation of the solubility product constants of anhydrite, hemihydrate, and gypsum, of the dissociation constants of magnesium sulfate, and the conversion expression for the B and C parameters for anhydrite and hemihydrate. The calculation is based on the assumption that natural waters will behave generally like sea water, and the neutral species, $MgSO_4^\circ$, will be the predominant species contributing to the increase in solubility over that in sodium chloride solutions (of the same, formal ionic strength).

Equations are included in the program for the variation of molarity/molality and weight fraction/molality ratios with molal ionic strength of sodium chloride solutions; molarities were obtained from densities given elsewhere (*10*). With these equations, the CF values were estimated also with molar (at 25°C.) and weight fraction units based on the variations (with ionic strength) of density and weight fraction of NaCl, the predominant salt constituent in most natural waters. All three values of CF approach unity for the original water but diverge by as much as 10% at CF values of 5 to 6. [As an option for substitution, an equation for the variation of weight fraction/molality *vs.* molality specifically for sea water is included with the program. This equation gives CF(weight fraction) values only slightly different from those obtained with the equation for $NaCl\text{-}H_2O$ solutions.]

Calculations for Representative Saline Waters. For representative calculations, a "standard composition" for sea water (*27*) was selected together with those for several other natural waters. The reported analyses were converted to molal units, and are given in Table III together with each source and reference. The (molal) ionic strengths (I') of the original waters were obtained and are included in Table III. In distillation practices, a stoichiometric amount of H_2SO_4 is usually added to replace and allow removal of bicarbonate and carbonate ions. With this substitution, a revised set of values for I' and R is given in Table III. For addition of HCl to remove carbonate and bicarbonate, R does not change from the original value. I' changes slightly if carbonate, in addition to bicarbonate, is present.

Figure 6 shows the calculations for sea water. The concentration factor, CF, represented by $I'_{\text{soln.}}/I'_{\text{orig.}}$, which corresponds to the molal or molar (at 25°C.) ionic strength or the weight fraction of the salt solution saturated with $CaSO_4$ (or one of its hydrates) divided by the corresponding molality (or molarity or weight fraction, respectively) of the unconcentrated saline water, is plotted against temperature. A calculated molar CF value of 3.3 for hemihydrate at 102°C. (the approximate boiling point of sea water of this CF at 1 atm.) compares well with 3.2 obtained with Marineland, Calif., sea water by Glater, Ssutu, and McCutchan (*6*) by a boiling concentration method (at sea level). The small difference could be due to slight differences between our standard composition (Table III) and their Marineland water. At temperatures below 95°C. and at moderately low ionic strengths, $CaSO_4 \cdot 2H_2O$ (gypsum), although metastable above about 40° to 60°C., is the usual precipitating phase, and therefore the boundary curve for this solid (below 95°C.) is the most important (*5, 15, 23, 24, 25*). [Controversy still exists over the true transition temperature of conversion of $CaSO_4 \cdot 2H_2O$ to $CaSO_4$. Recently, two papers have appeared, one of which (Zen) estimates the transition temperature in water to be 46° ± 25°C. (*31*) and the other (Ostroff) decides that gypsum will not convert to anhydrite at temperatures below 97°C. (*19*). The curve for the solubility product constant (K°_{sp}) of anhydrite obtained with our Equation 3 intersects that for gypsum obtained with Equation 2 at about 41°C. and is based on our own and other measurements for gypsum and the solubility measurements of Hill (*9*) and later of Bock (*3*) and of Power *et al.* (*24*) for anhydrite. The difficulty in obtaining complete agreement on this transition temperature lies in the sluggishness of the transition to anhydrite below about 90°C.] Above 95°C., the transient solubility of metastable $CaSO_4 \cdot \frac{1}{2}H_2O$ (hemihydrate) (*23, 24*) and the equilibrium solubility of $CaSO_4$ (anhydrite) (*16*) are the significant equilibria; these curves (above 95°C.) therefore become the more useful.

Some concentration factors were obtained by plotting experimental values of $(K'_{sp})^{1/2}$ against I' and determining the intersection with a straight line representing the formal ion product in solution concentrates [like the method used by Langelier *et al.* (*11*)]. These experimentally derived values are compared to calculated values in Table IV. The agreement is good.

In Figure 7, concentration factors for anhydrite, hemihydrate, and gypsum are given for the several representative natural waters listed in Table III, where carbonate and bicarbonate are not removed. It is believed that they approach the solubility behavior reasonably closely in view

Table IV. Comparison of Some Calculated Concentration Factors (CF) on a Molal Basis with Smoothed, Experimentally Observed Values for Sea Salt Solutions

t, °C.	CF Exptl.	CF Calcd.	Saturating Solid Phase
30	3.53	3.46	$CaSO_4 \cdot 2H_2O$
60	3.56	3.51	$CaSO_4 \cdot 2H_2O$
100	1.20	1.24	$CaSO_4$
125	0.74	0.78	$CaSO_4$
150	0.47	0.48	$CaSO_4$
175	0.25	0.27	$CaSO_4$
200	0.15	0.16	$CaSO_4$

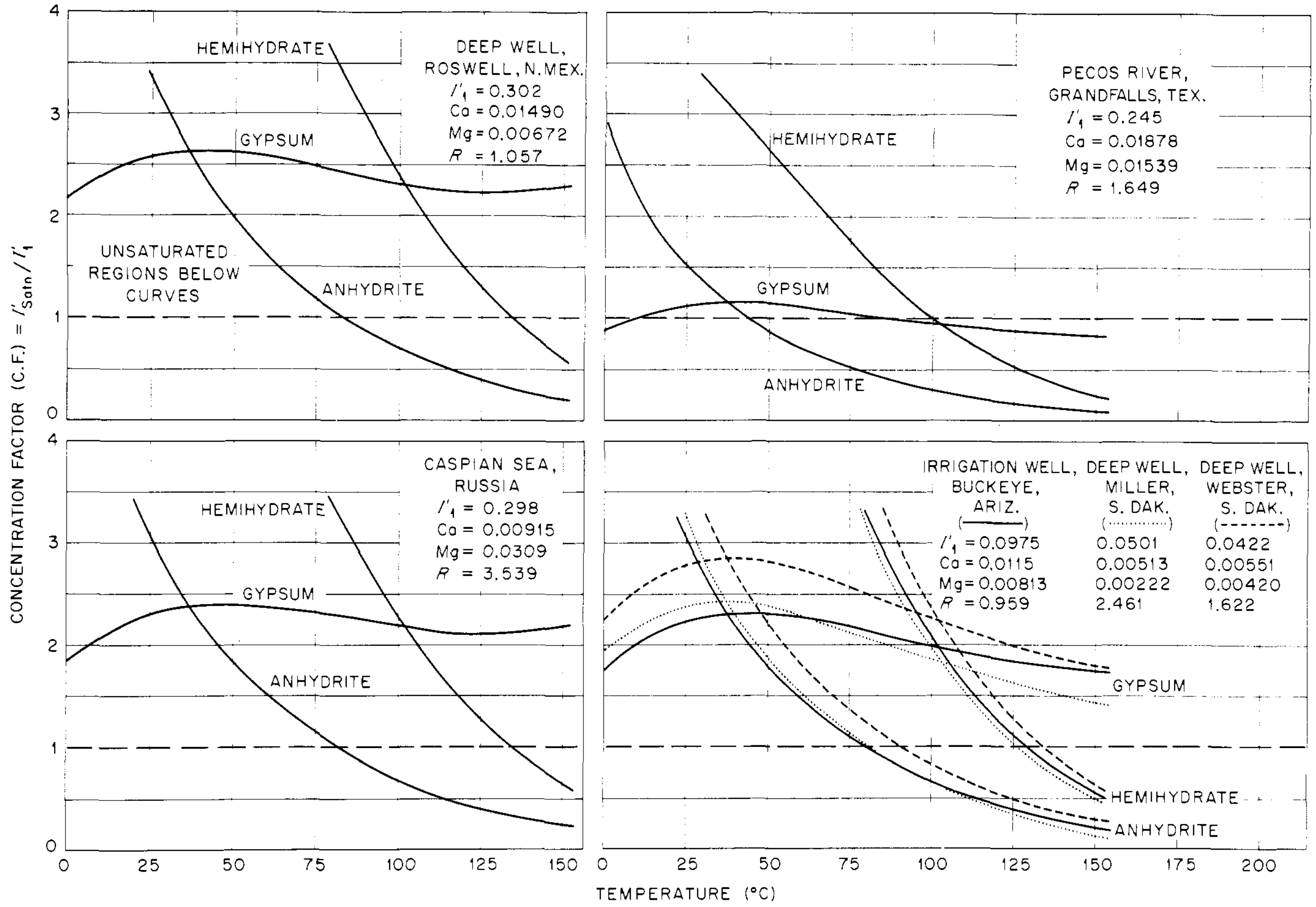

Figure 7. Calculated limits of solution stability to avoid precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 1/2H_2O$), and anhydrite ($CaSO_4$) from representative saline waters

I'_1. Molal ionic strength of original water
I'. Molal ionic strength of concentrate
Ca, Mg. Original molalities of Ca and Mg
R. Molal ratio, SO_4/Ca

of the good agreement in sea salt and other mixed electrolyte solutions (Figures 4 and 5).

The composition for the Pecos River (Grandfalls, Tex.) represented in Figure 7 appears to be saturated or nearly saturated with gypsum at 25° C. For this water, the concentration factor for anhydrite falls below 1.0 at a temperature much below 100° C. Therefore, a rather large amount of calcium must be removed to prevent precipitation of anhydrite at a temperature somewhat above 100° C. or to increase the concentration factors for gypsum at lower temperatures. In contrast, sea water is considerably undersaturated with respect to gypsum (a metastable phase above 30° to 60° C.) at temperatures at least above 160° C.

REMOVAL OF CALCIUM AND MAGNESIUM FROM SALINE WATERS

Temperature and Concentration Limits. If calcium (and/or magnesium) is removed from a saline water and replaced by an equivalent amount of sodium—for example, by an ion exchange process—then either the temperature limits (at a concentration factor of 1.0) or concentration factors at a particular temperature can be calculated easily with the computer program. In Figure 8, the calculated saturation limits for gypsum at 90° C., expressed as concentration factors, are plotted against the percentage depletion of calcium (by substitution of sodium) only and of both calcium and magnesium for several of the representative saline waters. In Figure 9, the temperature limits for precipitation of anhydrite from the several waters are plotted against the percentage removal of calcium (and also with simultaneous and equivalent removal of magnesium). When magnesium is depleted simultaneously, the rise is less than with calcium alone because of the removal of the complexing agent, magnesium.

CONCLUSIONS

The examples shown in Figures 6 to 9 are representative calculations. While we believe that the analyses for the several natural waters were reliable at the time of sampling, the compositions may vary with time and particular location (excluding a near-constancy for sea water). For rapid evaluations of other saline waters, the computer program can be used, together with constants given in Table I. This procedure should prove very valuable where the input water composition of a desalination plant varies with time; rapid evaluation could allow immediate adjustment in operating conditions.

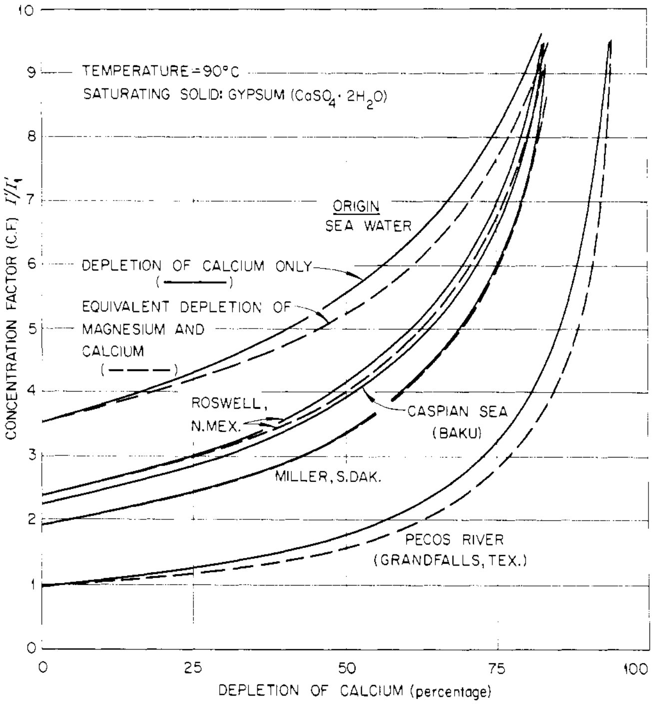

Figure 8. Effect at 90° C. of calcium and magnesium depletion on allowable concentration of representative saline waters before precipitation of gypsum

I'_1. Molal ionic strength of original water

I'. Molal ionic strength of concentrate

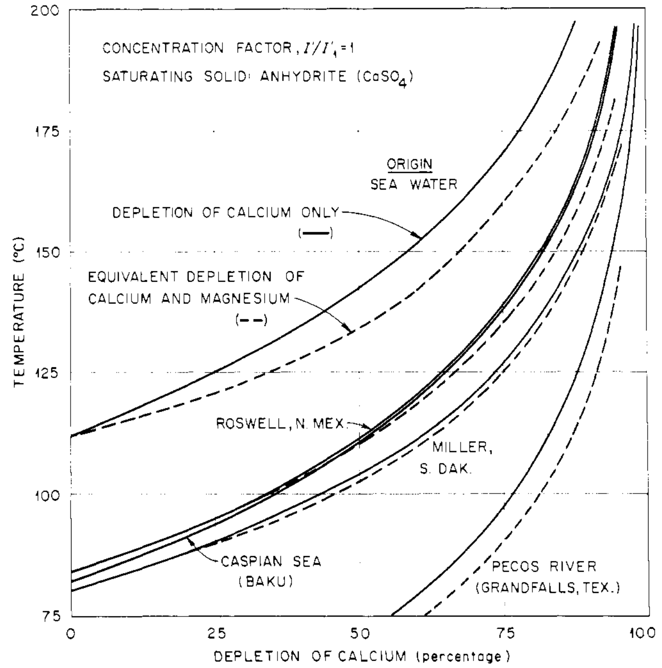

Figure 9. Effect of calcium and magnesium depletion on temperature of precipitation of anhydrite from representative saline waters

Unconcentrated

ACKNOWLEDGMENT

The many helpful discussions with K.A. Kraus, H.F. McDuffie, J.E. Ricci, and George Scatchard during the course of this research are greatly appreciated.

LITERATURE CITED

(1) Alary, Lewis, U. S. Geol. Survey analysis, Jan. 14, 1965.

(2) American Machine and Foundry Co., Research and Development Division, "Investigation of the Solubility of Calcium Sulfate in Sea Water Concentrates at Temperatures from Ambient to 65° C.," Office of Saline Water, U. S. Dept. Interior, Res. Dev. Rept. **191** (May 1966).

(3) Bock, E., *Can. J. Chem.* **39**, 1746 (1961).

(4) Clampett, J.B., Fowler, R.T., *J. Appl. Chem.* **14**, 81 (1964).

(5) Denman, W.L., *Ind. Eng. Chem.* **53**, 817 (1961).

(6) Glater, J., Ssutu, L., McCutchan, J.W., *Environmental Sci. Tech.* **1**, 41 (1967).

(7) Hara, R., Nakamura, K., Higashi, K., *Tech. Repts. Tohoku Imp. Univ.* **10**, 433 (1932).

(8) Hara, R., Tanaka, Y., Nakamura, K., *Ibid.*, **11**, 199 (1934).

(9) Hill, A. E., *J. Am. Chem. Soc.* **59**, 2242 (1937).

(10) "International Critical Tables," E. W. Washburn, editor in chief, 1st ed., Vol. **III**, p. 79, McGraw-Hill, New York, 1928.

(11) Langelier, W. F., Caldwell, D. H., Lawrence, W. B., Spaulding, C. H., *Ind. Eng. Chem.* **42**, 126 (1950).

(12) Madgin, W. M., Swales, D. A., *J. Appl. Chem.* **6**, 482 (1956).

(13) Marshall, W.L., *J. Phys. Chem.* **71**, 3584 (1967).

(14) Marshall, W.L., Jones, E.V., *Ibid.*, **70**, 4028 (1966).

(15) Marshall, W. L., Slusher, R., *Ibid.*, **70**, 4015 (1966).

(16) Marshall, W. L., Slusher, R., Jones, E. V., J. CHEM. ENG. DATA **9**, 187 (1964).

(17) Mason and Hanger-Silas Mason Co., Inc., and Rust Engineering Co., "First Annual Report of Saline Water Conversion Plant, Webster, S. Dak.," Office of Saline Water, U. S. Dept. Interior, Rept. **PB 181680**, Res. Dev. Rept. **101**, Part II, p. 19 (March 1964).

(18) Office of Saline Water, U. S. Dept. Interior, staff report, "Standardized Procedure for Estimating Costs of Saline Water Conversion," Rept. **PB 161375**, 45 (March 1956).

(19) Ostroff, A. G., *Geochim Cosmochim. Acta* **28**, 1363 (1964).

(20) Ostroff, A. G., Metler, A. V., J. CHEM. ENG. DATA **11**, 346 (1966).

(21) Patton, J., Reeder W., *Anal. Chem.* **28**, 1026 (1956).

(22) Posnjak, E., *Am. J. Sci.* **238**, 559 (1940).

(23) Power, W. H., Fabuss, B. M., Satterfield, C. N., J. CHEM. ENG. DATA **9**, 437 (1964).

(24) *Ibid.*, **11**, 149 (1966).

(25) Shaffer, L. H., *Ibid.*, **12**, 183 (1967).

(26) Smith, G. C., Ph.D. dissertation, "Heterogeneous Nucleation of Calcium Sulfate," Dept. Chemical and Mechanical Eng., College of Engineering, Univ. of Michigan, Ann Arbor, Mich., March 1965.

(27) Spiegler, K. S., "Salt Water Purification," Wiley, New York, 1962.

(28) Stiff, H. A., Davis, L. E., *Trans. Am. Inst. Mining Met. Engrs.* **195**, 25 (1952).

(29) Williams, W. W., U.S. Atomic Energy Commission, private communication, 1965.

(30) Yeatts, L. B., Marshall, W. L., research in progress, 1967.

(31) Zen, E-An, *J. Petrol.* **6**, 124 (1965).

RECEIVED for review April 3, 1967. Accepted August 28, 1967. Work sponsored by the Office of Saline Water, U. S. Department of Interior, and performed at the Oak Ridge National Laboratory, operated by Union Carbide Corp. for the U. S. Atomic Energy Commission. Symposium on Water Desalination, Annual Meeting, Southwestern Division, American Chemical Society, Albuquerque, N. M., November 30-December 2, 1966. No. XIX in a series on aqueous systems at high temperature. The preceding paper (No. XVIII) is by L.B. Yeatts and W.L. Marshall, "Activity Coefficient Behavior of Calcium Hydroxide in Aqueous Sodium Nitrate to the Critical Temperature of Water," *J. Phys. Chem.* **71**, 2641 (1967).