(12) Herington, E.F.G., *Nature* **160**, 610 (1947).
(13) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951).
(14) Herington, E.F.G., Coulson, E.A., *Trans. Faraday Soc.* **44**, 629 (1948).
(15) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(16) Kretschmer, C.B., Wiebe, R., *J. Am. Chem. Soc.* **76**, 2579 (1954).
(17) Lambert, J.D., Roberts, G.A., Rowlinson, J.S., Wilkinson, V.J., *Proc. Roy Soc. (London) Ser. A* **196**, 113 (1949).
(18) Lu, B.C-Y, *Chem. Eng.* **67**, 105 (1960).
(19) Lu, B.C-Y, Spinner, I.H., Ho, J.G.K., *Can. J. Chem. Eng.* **40**, 16 (1962).
(20) Margules, M., *Sitzber. Akad. Wiss. Wien. Math-Naturw. Klasse* **11**, 104, 1243 (1895).
(21) McDermott, C., Ellis, S.R.M., *Chem. Eng. Sci.* **20**, 293 (1965).
(22) Pike, K.A., Ph.D. thesis, Loughborough University of Technology, 1965.
(23) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(24) Rowlinson, J.S., *Trans. Faraday Soc.* **45**, 974 (1949).
(25) Scatchard, G., Raymond, C.L., *J. Am. Chem. Soc.* **60**, 1278 (1938).
(26) Severns, W.H., Sesonske, A., Perry, R.H., Pigford, R.L., *A.I.Ch.E. J.* **1a**, 401 (1955).
(27) Van Laar, J.J., *Z. Physik. Chem.* **72**, 723 (1910); **185**, 35 (1929).
(28) Weltner, W., Pitzer, K.S., *J. Am. Chem. Soc.* **73**, 2606 (1951).
(29) Wohl, K., *Trans. Am. Inst. Chem. Engrs.* **42**, 215 (1946).
(30) Wohl, K., *Chem. Engr. Pragt.* **49**, 218 (1953).

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Solubility of Gypsum in Sea Water and Sea Water Concentrates at Temperatures from Ambient to 65° C.

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When strong brines derived from decarbonated sea water are evaporated at temperatures from 35° to 60° C., gypsum, $CaSO_4 \cdot 2H_2O$, forms in the bulk of the liquid. In sea water of normal concentration, the solubility product of this substance is nearly independent of temperature; in the interval 20° to 60° C., the average value is 1.57×10^{-3} (mole)^2/(kg. solvent)^2. In strong brines, six times normal concentration, the solubility product is much greater; it increases from 3.58×10^{-3} (mole)^2/(kg. solvent)^2 at 20° C. to 4.41×10^{-3} (mole)^2/(kg. solvent)^2 at 60° C.

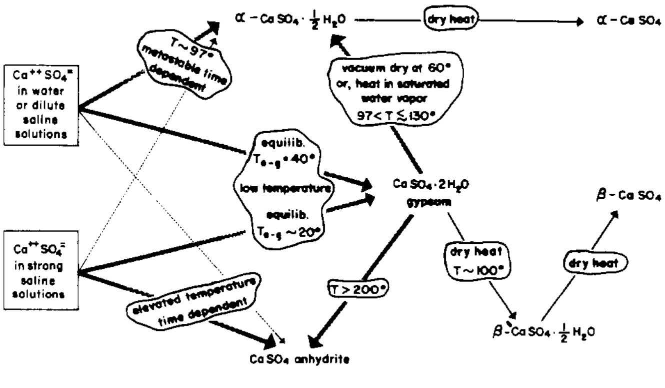
THE FURTHER CONCENTRATION of the brines discharged from conventional evaporator cycles has been studied as part of a continuing program to lower the cost of desalinated water. Tests conducted in 1961 showed that low temperature evaporation would permit the concentration of sea water from a total dissolved solids of 31,000 p.p.m. to over 300,000 p.p.m. without scale formation on the evaporator heat transfer surfaces. These findings have been reported by Fisher and Gilbert (*3*), who also described the triple-effect superconcentrator that was used for further engineering evaluation of the concentration process.

The triple-effect flash evaporator was designed to operate using either sea water or the blowdown from a conventional evaporator as feed. When the evaporator was operated under conditions such that the minimum concentration of the brine circulating in the system was never less than five times sea water, and the maximum temperature was below 65° C., a nonfouling precipitate formed in the brine. This type of operation is achieved through the use of a feed and bleed system in each effect.

The precipitate appeared to be a form of calcium sulfate, and the author thought that the ability to prepare this salt reproducibly would be useful in terms of scale control cycles and by-product recovery schemes. Therefore, the nature of this precipitate has been determined, and the conditions under which it formed have been investigated.

EXISTING DATA

Because of the technological importance of calcium sulfate, a considerable number of papers on this substance have appeared. To put our program in perspective, it is useful to mention briefly some of the more important reviews and sources of data. Posnjak reviewed the material published prior to 1938 (*10*) and, in 1941, Kelly, Southard, and Anderson (*7*) published a comprehensive review dealing with gypsum ($CaSO_4 \cdot 2H_2O$) and its dehydration products. By way of orientation, we have prepared Figure 1, which summarizes the relationships among the various forms of calcium sulfate. Only three—gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate (α-hemihydrate), and anhydrite ($CaSO_4$)—can coexist with aqueous systems. The equilibrium temperatures shown for the interconversions between these phases are based on thermodynamic analyses—that is, on the crossing points of the solubility or vapor pressure curves of the various solids; they do not necessarily imply that the transition will occur at the stated temperature. These thermodynamic transition temperatures should be a function of water activity; we found, for example, that gypsum dehydrated to form the hemihy-



all forms convert to anhydrite at temperatures ≳ 200° C., but rapidly only at T ~ 900°

Figure 1. Conversion diagram for various forms of calcium sulfate

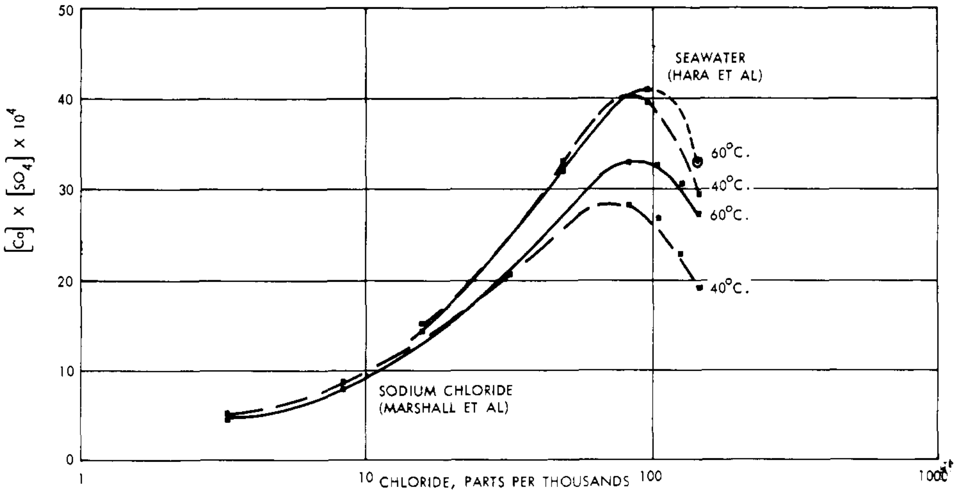


Figure 2. Solubility of gypsum in sea water and sodium chloride solutions

drate readily when heated in a vacuum at 60° C. Recent data obtained by Bock (*1*) show that the transition temperature of gypsum to anhydrite is as low as 20° C. in 5 molal NaCl. The solubility of gypsum in water is nearly independent of temperature. However, Bock's data show that in strongly saline solutions the solubility of gypsum increases slightly with temperature, at least below 50° C. Anhydrite, on the other hand, shows retrograde solubility in either pure water or saline solutions. More recently, Marshall, Slusher, and Jones (*9*) published the results of an additional study which extends our knowledge of the $CaSO_4 - H_2O - NaCl$ system to temperatures as high as 200° C. The smoothed solubilities given in their summary are based on a combination of their own work and appropriate data from the literature. Some of the measurements reported by Marshall *et al.* are summarized in Figure 2, where some of Marshall's results are compared with similar data for sea water and sea water concentrates derived from a study published by Hara *et al.* (*5, 6*). There is a considerable discrepancy between the data reported for sea water and those that apply to pure sodium chloride.

The studies that are well known and generally available deal mainly with solubility in either plain water or sodium chloride solutions. Langelier (*8*) has given a limited amount of data on the hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$) in sea water, but little is known about the solubilities of the various forms of calcium sulfate in sea water and sea water concentrates. However, a little known study of the solubility of calcium sulfate in sea water brines was made by Hara, Tanaka, and Nakamura (*6*) during the early 1930's. To measure solubility, they used an optical technique which used as a reference a solution that contained substantial amounts of calcium and sulfate. Because of this, it is not possible to relate calcium sulfate solubility "per cent," which they reported, to "solubility products" as usually defined. However, the measurements were based on four stock solutions which were carefully analyzed by chemical methods, and the information given on the brines permits calculation of solubility products from the data.

Hara's "% calcium sulfate in solution" can be converted to solubility product by recalculating "solubility" as moles per kilogram of solvent and then adding the change in calcium concentration during a saturation run to the sulfate concentration reported for the starting stock solution.

$$K_{sp} = (Ca^{+2})_f \times \{(SO_4^{-2})_i + (Ca^{+2})_f - (Ca^{+2})_i\}$$

The recalculated data of Hara for both anhydrite and gypsum are summarized in Figure 3. The general trends of the solubility data—increasing solubility with increasing salinity, retrograde solubility behavior for anhydrite at all salinities, and gypsum solubility increasing with increasing temperature at high salinities—are consistent with what has already been reported for calcium sulfate in sodium chloride solutions. However, there is a very real discrepancy between the data given by Hara and those given by Marshall.

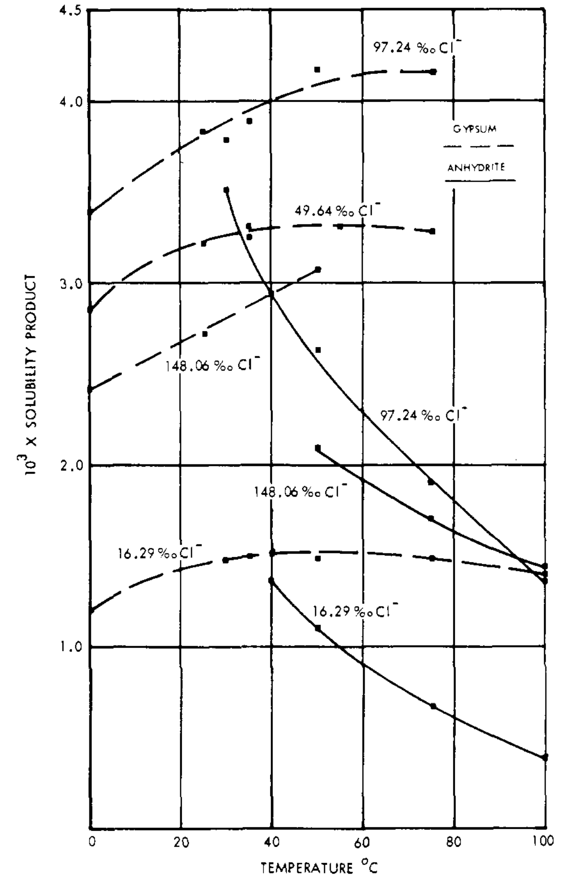


Figure 3. Calcium sulfate solubility products (5, 6)

EXPERIMENTAL

Solubility of Gypsum in Sea Water and Strong Brines. Because the solid phase which formed during low temperature evaporation of sea water was gypsum, measurements were made on this substance. Three fluids were used: an actual sample of sea water (nominal sea water), a brine that was nominally sea water concentrated three times, and a brine that was nominally sea water concentrated six times. Analytical data obtained on these fluids are summarized in Table I.

Table I. Analyses of Sea Water and Brines

	% Solids	% Cl	% Ca	% SO_4	Density	pH
1. Samples from Millstone Point Test Station. Sea water acidified with 100 p.p.m. H_2SO_4 and stripped of CO_2						
Nominal 10X brine, 9652A-48A & B	...	15.09	...	1.599	...	...
Nominal 6X brine, 9533A-42A & B	19.45	11.10	0.0733	1.207	1.1523	5.6
Nominal 3X brine, 9652A-49	8.89	4.96	...	0.577	...	...
Nominal sea water, 9630A-25	3.01	1.66	0.0354	0.236	1.0209	5.6
2. Oceanographer's "normal" sea water (*13*)						
	3.45	1.898	0.0400	0.265	1.0243	~8.2

Solubility Runs. The nominal sea water was withdrawn from the feed stream normally used for our test evaporators. Prior to being withdrawn from the stream, it had been acidified by the addition of 100 p.p.m. of H_2SO_4 and passed through a CO_2 stripper. The pH of the water after this treatment was 5.6. The nominal 6X brine was the product obtained by operating our experimental three-stage superconcentrator with the normal (acidified, CO_2-stripped) feed. The nominal 3X brine was prepared by diluting a 10X brine made in the superconcentrator with a quantity of the nominal sea water described above. The general procedure was as follows: A series of borosilicate glass pressure bottles was charged with about 300 grams of sea water or brine. To each bottle was added 0.5 to 3.0 wt. % of gypsum (calcium sulfate powder, reagent grade, General Chemical Co. catalog No. 1537). The bottles were then sealed and placed on a rotating rack in a constant temperature bath. The times varied from 17 hours at the highest temperatures to 13 days at the lowest temperature.

The bath was a large polymerization apparatus originally manufactured by the American Instrument Co. We added a sensitive mercury thermometer (±0.05° C.), and, to improve the stirring, a recirculating pump. The temperature during the saturation runs was monitored by a multipoint recorder connected to 6 thermocouples placed at different points in the bath. The temperatures in different parts of the bath remained within ±0.25° C. of each other, and, with one exception, the bath temperature did not fluctuate more than ±0.50° C. during any run.

At the end of each run, the motion of the rack was stopped and the sample bottles were rotated to a position such that the neck was above the surface of the fluid in the bath. The top of the bottle was dried and then opened, and the saturated fluid was sampled using the fixture shown in Figure 4. Air pressure was used to force the liquid through a medium (10- to 15- micron) fritted glass filter into a suitable sample bottle. The liquid samples were later analyzed for calcium and sulfate. A few check runs were made using fine (4- to 6- micron) fritted glass. There was no significant difference in the results.

On one or two occasions, the saturating bottles leaked during the run. This was easy to spot because the chromate rust inhibitor used in the bath imparted a yellow color to the sample. The "leakers" were, of course, discarded. Samples of the solids remaining in one or more of the bottles at the end of each run were obtained by removing the saturating bottle from the bath and quickly filtering the residue. Such samples were identified by x-ray analysis and were shown to be the same as the gypsum originally used to saturate the fluid.

Analytical. Calcium was determined in the presence of magnesium using a selective complexing agent EGTA [ethylene glycol bis-(β-aminoethyl ether)-N,N,N',N'-tetraacetic acid]. After trying several procedures, we adopted a modification of the method described by Burg and Conaghan (*2*). They used Calcon as the indicator and carried out the titration under conditions which held both the calcium and the magnesium in solution throughout. This produced poorly defined end points; but when the procedure was altered to produce a magnesium hydroxide precipitate before the beginning of the titration, sharp, reproducible end points were obtained (*12*).

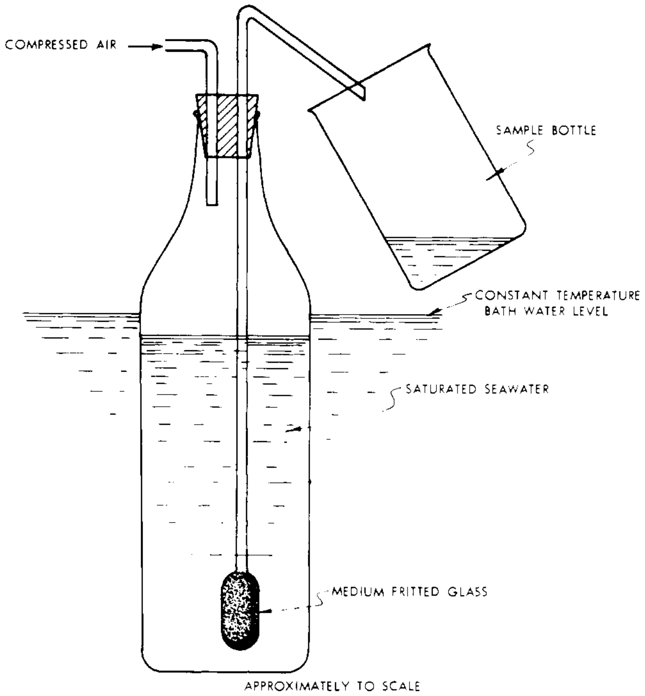


Figure 4. Arrangement for sampling liquids from saturation runs

Because calcium coprecipitates with the magnesium, an empirically determined calibration curve is needed in interpreting the results obtained when the titration is carried out in the presence of a magnesium hydroxide precipitate. The curve which gives the relationship between the EGTA titer and the calcium concentration is easily determined; and, over a limited range of calcium concentrations, it can be approximated as a straight line with a positive intercept on the calcium concentration axis. A least squares analysis of a series of test titrations indicated that we could expect an accuracy of ±1% (*12*). However, it is apparent from the data actually obtained (Table II) that

Table II. Detailed Results of Saturation Experiments on $CaSO_4 \cdot 2H_2O$ in Brines

Gypsum Added to Brine, %	Saturation Time, Hr.	X-Ray Report on Residual Solids	Ca^{+2}, G./Kg. Sat. Soln.	SO_4^{-2}, G./Kg. Sat. Soln.	Remarks
			Nominal 6X Brine	Runs at 60° C.	
1	24	Gypsum	0.882	12.38	See text
3	24	...	0.903	12.39	See text
3	60	Gypsum	...	...	No reliable analysis
3	17	...	0.899	12.83	Diluted brine on sampling
3	17	...	0.881	12.27	Diluted brine on sampling
...	...	...	0.880	...	Undiluted comb. of A and B
			...	12.28	Rerun of C diluted
					K_{sp} (molal units)
			0.89 ± 0.03	$12.3_5 \pm 0.1$	4.41×10^{-3}
			Nominal 6X Brine	Runs at 40° C.	
0.5	53.5		0.795	12.15	
0.5	53.5		0.798	12.03	
			0.832	...	Rerun of D diluted
3	53.5		0.794	12.09	
3	53.5		0.792	12.05	
0.5	66		0.803	12.14	
			0.786	...	Rerun of E diluted
0.5	66		0.782	12.13	
3	66		0.788	12.10	
3	66		0.792	12.10	
3	72		0.829	12.24	Diluted brine on sampling
3	72		0.815	12.17	Undiluted sample of A
0.5	120	Gypsum	0.796	12.11	
3.0	120	Gypsum	0.829	12.06	
			0.794	...	Rerun of F diluted
					K_{sp} (molal units)
			0.80 ± 0.02	12.1 ± 0.1	3.85×10^{-3}
			Nominal 6X Brine	Runs at 20° C.	
1	5 days	Gypsum and NaCl	0.736	12.06	Wt. % Cl^- 11.041
1	13 days		0.739	12.07	11.012
3	5 days		0.742	12.11	11.082
3	13 days		0.739	12.08	11.044
					K_{sp} (molal units)
			0.74 ± 0.02	12.1 ± 0.1	3.58×10^{-3}
			Nominal 3X Brine	Runs at 60° C.	
1	36	Gypsum	1.374	8.05	
1	36	...	1.391	8.06	
3	36	...	1.383	8.04	
3	36	...	1.383	8.05	
					K_{sp} (molal units)
			1.38 ± 0.04	8.05 ± 0.1	3.48×10^{-3}
			Nominal 3X Brine	Runs at 40° C.	
1	28	Gypsum	1.358	7.99	
1	28	...	1.371	7.94	
3	28	...	1.378	7.98	
3	28	...	1.356	7.97	
					K_{sp} (molal units)
			1.37 ± 0.04	7.97 ± 0.1	3.42×10^{-3}
			Nominal Sea Water	Runs at 60° C.	
1	25	Gypsum	1.321	4.35	
1	25	...	1.336	4.34	
3	25	...	1.291	4.42	
3	25	...	1.327	4.43	
1	70	Gypsum	1.278	4.38	
1	70	...	1.269	4.36	
3	70	...	1.277	...	Sulfate anal. discarded because of inconsistent results
3	70	...	1.246	...	
					K_{sp} (molal units)
			1.29 ± 0.04	4.38 ± 0.05	1.56×10^{-3}

(*Continued on page 187*)

Table II. Detailed Results of Saturation Experiments on $CaSO_4 \cdot 2H_2O$ in Brines *(Continued)*

Gypsum Added to Brine, %	Saturation Time Hr.	X-Ray Report on Residual Solids	Ca^{-2}, G./Kg. Sat. Soln.	SO_4^{-2}, G./Kg. Sat. Soln.	Remarks
			Nominal Sea Water	Runs at 40° C.	
0.5	69.5		1.296	4.40	
1	53.5		1.331	4.34	
1	53.5		1.431	4.34	
1	34		1.341	4.37	
1	34		1.412	4.42	
			1.36 ± 0.07	4.37 ± 0.05	K_{sp} (molal units) 1.64×10^{-3}
			Nominal Sea Water	Runs at 20° C.	
1	5 days	Gypsum	1.249	4.37	
1	13 days	...	1.251	4.33	
3	13 days	...	1.257	4.34	
			1.25 ± 0.04	4.36 ± 0.05	K_{sp} (molal units) 1.51×10^{-3}

Table III. Detailed Results of Additional Saturation Experiments

Gypsum Added to Brine, %	Saturation Time, Hr.	X-Ray Report on Residual Solids	Ca^{-2} G./Kg. Satd. Soln.	SO_4^{-2} G./Kg. Satd. Soln.	Remarks
			Nominal 6X Brine	Runs at 60° C.	
1	24		0.863		Diluted brine on sampling
1	24		0.880		
1	24		0.883		
1	24	Gypsum	0.899	12.78	
1	24		0.895		
1	72	Gypsum	0.870		
1	72		0.911		
1	72		0.901	12.81	
1	72		0.894		
			0.89 ± 0.01	12.8 ± 0.1	K_{sp}(molal units) 4.57×10^{-3}
			Nominal 6X Brine	Runs at 40° C.	
1	24	Gypsum	0.845		Undiluted sample
1	24		0.850		
1	24		0.835		
1	24		0.840		
1	72		0.835		
1	72		0.840		
1	72		0.845		
1	72		0.839		
1	72	Gypsum		12.58	Diluted brine on sampling
			0.84 ± 0.01	12.6 ± 0.1	K_{sp}(molal units) 4.23×10^{-3}

duplicate experiments agree to no better than ±3% and it is believed that this is a fairer estimate of the accuracy of our over-all procedure.

Sulfate analyses were performed using Scott's standard gravimetric method (*4*).

RESULTS

Identity of the Solid Phase. Because of the many forms in which calcium sulfate may appear, it was important to identify the solids formed during typical operation of the superconcentrator. Samples were taken from the third effect. The operating conditions ranged from 32° C. and approximately 16.0% chloride to 35° and 12.7% chloride. One sample was prepared by filtering the hot brine from the evaporator and then washing the precipitate with alcohol. A second sample which consisted of the crystals in a brine slurry was also obtained. X-ray diffraction showed that the first of these was pure gypsum ($CaSO_4 \cdot 2H_2O$) and that the second was gypsum contaminated with about 20% common salt.

As a check on these observations, samples of decarbonated sea water were evaporated at both 40° and 60° C. until solids began to form in the bulk of the liquid. These were filtered immediately and the superficially dry solids were then x-rayed. One sample taken from sea water evaporated at 40° C. was reported to contain 85% gypsum and about 15% salt. In another case, a sample evaporated rapidly and nearly completely at 40° C. was found to contain salt and gypsum in the proportion 95 to 5. Slow evaporation of sea water at 60° C., observed carefully and stopped just when the first crystals formed, produced a precipitate that was identified as gypsum, $CaSO_4 \cdot 2H_2O$.

Solubility of Gypsum in Sea Water and Strong Brines. Complete detailed results from the saturation runs are given in Tables II and III. Most of these analyses were performed in duplicate; and although remarkable precision was obtained, we feel that a reasonable estimate of the error in our determinations is ±1% or ±0.05 gram per kg., whichever is greater. There was never any indication of a trend in the data which might be a function of the time of shaking or the amount of solids placed in the saturating bottle. Therefore, we averaged all the data obtained at each temperature and used these averages to calculate the solubility products. Average values, standard deviations, and the molal solubility products calculated from the averages are given in Table V and are summarized in graphical form in Figure 5. Check runs made at a later date (Table IV) on similar brines agree with the original

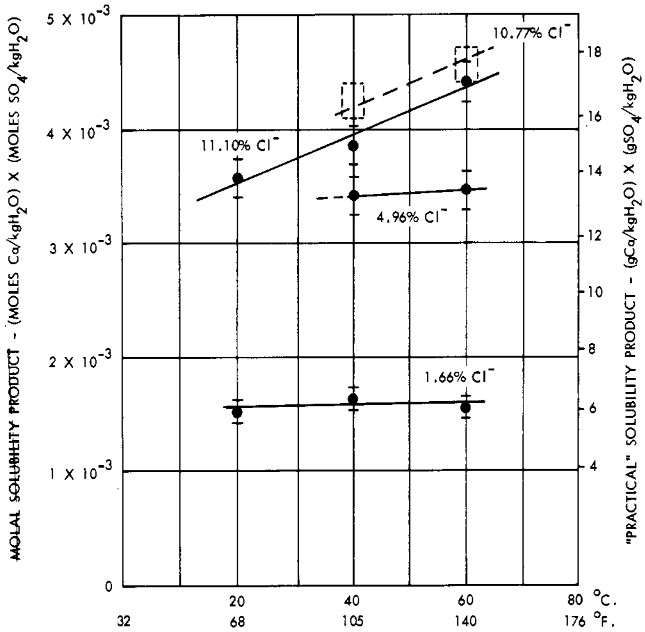


Figure 5. Solubility of gypsum in sea water and sea water concentrates
—— Brines obtained April 22, 1965, Tables I and II
— — — Brine obtained Oct. 20, 1965, Table III

data within the stated limits of error. However, the latest results suggest that the solubility product originally obtained for 6X brine saturated at 40° C. may be lower than the true value. This is consistent with internal evidence in the tabulation of detailed results. Careful analysis of our first set of data indicates that the value obtained is probably at the lower limit of the stated error; and we now believe that the correct solubility product for gypsum in the nominal 6X brine must be $\sim 4.0 \times 10^{-3}$ in molal units (moles^2/kg. solvent^2).

In Table V, in addition to our averaged data, there are also recorded for comparison: results recalculated from the data of Hara, and representative points from data obtained by Marshall and by Posnjak (*11*). The values obtained in the present work are in generally good agreement with the data reported by Hara *et al.* However, in terms of the "scale formation" problem, the trend of the solubility curve with temperature is of utmost

Table IV. Comparative Results on Saturation Experiments in Nominal 6X Brine

	% Solids	% Cl$^-$	% Ca^{-2}	% SO$_4^{-2}$	% Mg^{-2}	Density	pH
9533A-42A & B							
4/22/65	19.45	11.10	0.0733	1.207	0.725	1.152	5.6
9701A-10							
10/26/65	19.53	10.77	0.0748	1.235	0.715	1.152	3.8

Saturation Time, Hr.	Temp., ° C.	Ca^{-2} G./Kg. Satd. Soln.	SO$_4^{-2}$ G./Kg. Satd. Soln.	K_{sp} (Molal Units) x 10^3
9533A-42A & B				
starting brine		0.73	12.07 ± 0.1	
17-24	60	0.89 ± 0.03	12.35 ± 0.1	4.41
54-120	40	0.80 ± 0.02	12.1 ± 0.1	3.85
3-13(days)	20	0.74 ± 0.02	12.1 ± 0.1	3.58
				Est. accuracy ± 4%
9701A-10				
starting brine		0.75 ± 0.01	12.35 ± 0.1	
24-72	60	0.89 ± 0.01	12.80 ± 0.1	4.57
24-72	40	0.84 ± 0.01	12.58 ± 0.1	4.23
	20 not run			Est. accuracy ± 3%

Table V. Summary of Saturation Experiments

Molal solubility products [(Ca^{-2})(SO$_4^{-2}$) x 10^3] for gypsum (CaSO$_4$·2H$_2$O) in sea water and sea water concentrates at various temperatures

6X brine	20° C.	30° C.	40° C.	60° C.	
11.10% Cl	3.58		3.85	4.41	This work
9.72% Cl	3.75		3.97	4.14	(*5, 6*)
5.5X Syn. S.W.		2.93			(*10, 11*)
3X brine					
4.96% Cl			3.42	3.48	This work
4.96% Cl	3.12		3.29	3.28	(*5, 6*)
3.0X Syn. S.W.		2.86			(*10, 11*)
Sea water					
1.66% Cl	1.51		1.64	1.56	This work
1.63% Cl	1.42^a		1.52	1.48	(*5, 6*)
Syn. S.W.		1.54			(*10, 11*)
2*M* NaCl			2.92	3.06	(*9*) (At ionic strength, approx. comparable with 3X brine)

^{a} Estimated from cross plot of data.

importance. In sea water, both sets of data show that over the temperature range 20° to 60°C. the solubility of gypsum is essentially independent of temperature. In the 6X brines, on the other hand, our data show a slightly steeper solubility-temperature slope than is indicated by Hara's work.

DISCUSSION

The increase in the solubility of gypsum with increasing temperature in strong brine seems to account for the formation of a calcium sulfate precipitate which does not foul heat transfer surfaces. However, our observations raise several problems. First, why does gypsum form? Even at 40°C. the data of Bock indicate that the stable form in strong brine should be anhydrite. Second, why is gypsum more soluble in sea water brine (this work) than in sodium chloride solutions (*9*)? It is our feeling that the answer to both of these questions may be connected with the presence of magnesium sulfate in the sea water brine.

A third problem which requires exploration is the rate at which gypsum converts to anhydrite in the temperature range 40° to 60°C. or a little above. This may be very important in terms of scale control in practical sea water conversion plants.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Bock, E., *Can. J. Chem.* **39**, 1746 (1961).
(2) Burg, R.A., Conaghan, H.F., *Chemist-Analyst* **29**, 100 (1960).
(3) Fisher, D.A., Gilbert, F.W., Division of Water, Air, and Waste Chemistry, 149th Meeting, ACS, Detroit, Mich., April 1965.
(4) Furman, N.H., "Scott's Standard Methods of Chemical Analysis," p. 2483, Van Nostrand, New York, 1962.
(5) Hara, R., Nakamura, K., Higashi, K., *Tech. Repts. Tohoku Imp. Univ.* **10**, 433 (1932).
(6) Hara, R., Tanaka, Y., Nakamura, K., *Ibid.*, **11**, 199 (1934).
(7) Kelly, K.K., Southard, J.C., Anderson, C.T., U. S. Bur. Mines, Tech. Paper **625** (1941).
(8) Langelier, W.F., Caldwell, D.H., Lawrence, W.B., Spaulding, C.H., *Ind. Eng. Chem.* **42**, 126 (1950).
(9) Marshall, W.L., Slusher, R., Jones, E.V., J. CHEM. ENG. DATA **9**, 187 (1964).
(10) Posnjak, E., *Am. J. Sci.* **35A**, 247 (1938).
(11) *Ibid.*, **23**, 559 (1940).
(12) Shaffer, L.H., Knight, R.A., Smith, D.A., "Desalination," in press.
(13) Sverdrup, H.U., Johnson, M.W., Fleming, R.H., "The Oceans," p. 173, Prentice-Hall, New York, 1942.

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Multiphase and Volumetric Equilibria of the Methane–*n*-Decane Binary System at Temperatures between −36° and 150° C.

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Vapor-liquid equilibria are presented at seven temperatures between −25° and 150° C. at pressures up to 100 atm. The data are tabulated as vapor and liquid compositions, fugacity–mole fraction ratios, and liquid molar volumes as functions of temperature and pressure. The vapor-liquid data indicate that Henry's Law expressed as fugacity–mole fraction ratio holds as a reasonably accurate approximation at pressures below 30 atm. Data along the solid-liquid-vapor three-phase line are tabulated as pressure, liquid composition, and liquid molar volume as functions of temperature. The solid data lead to a value of the heat of fusion of *n*-decane in good agreement with the literature value.

THE STUDIES of Lavender, Sage, and Lacey (*7*) and of Reamer *et al.* (*10*) have furnished valuable vapor-liquid equilibrium behavior in the methane–*n*-decane system at temperatures higher than 21°C. and at elevated pressures. The present study presents additional vapor-liquid data in the lower methane concentration region, at temperatures down to −25°C. and presents three-phase vapor-liquid-solid information.

The volumetric behavior of methane has been reported in several studies (*2, 3, 6, 8, 9*). Matthews and Hurd (*8*) and Canjar (*2*) have evaluated the thermodynamic properties of methane from pressure, volume, temperature data. Data on the liquid density, vapor pressure, heat of fusion and other physical properties of *n*-decane have been reported by Rossini *et al.* (*11*).

EXPERIMENTAL

The equipment and experimental techniques have been adequately described and were identical to those used in other studies involving methane in binary systems (*1, 4, 5, 12, 13*). Briefly, the experimental technique involved accurate additions of methane gas to a 12-ml. internal volume borosilicate glass equilibrium cell which contained a known amount of *n*-decane. The equilibrium cell had an inside diameter of approximately 7.5 mm. and a working length of 230 mm. Temperatures were taken on a platinum resistance thermometer which was believed to be accurate to within 0.02°C. of the International Platinum Scale. Pressures were taken on bourdon tube gages which were accurate to ±0.07 atm. Each bourdon gage was checked at the start of an experimental run by use of an accurate dead weight gage. Liquid volumes were taken from calibra-

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