A Contribution to the Equilibrium of the System of Sea Salts at 110°C*

By Yasuo TANAKA, Shozo TAKASAGO and Takashi KOMATSU

(Received June 21, 1949)

Introduction It is expected from the phase diagram of the system of sea salts at 110°C obtained by D'Ans(1) that, on concentrating the bittern at higher temperatures, the majority of sulfate radicals should easily be removed as kieserite, $MgSO_4 \cdot H_2O$, together with NaCl, leaving chlorides of potassium and magnesium in the mother liquor. In practice, however, a difficulty lies in the formation of a muddy precipitate, called "earthy sulfate" or "high-temperature crystal," at this stage.(2) This precipitate contains a certain potassium salt; its treatment is difficult, and its formation causes the loss of potassium.

In this respect, since the above-mentioned isothermal contains rough estimations in certain respects and, particularly, as seen from Table 1, the points *K* and *X* of D'Ans are too far from the observed values, further experiments are desirous. Another problem to be considered in this connection is the phenomenon of supersaturation. Since sulfates especially kieserite, are liable to be supersaturated in the system of sea salts(3) and, further, actual bittern has a colloidal nature, containing inorganic and organic suspensions, the influence of supersaturation in both pure and actual solutions must be clarified.

In the present report, the determination of the point *K* and a preliminary experiment concerning the point *X* in the system of sea salts at 110°C have been made with pure substances, supersaturation being taken into consideration. The summary of the results has also been shown in Table 1.

Materials and Experimental Procedure. The materials used were the products of E. Merk. Sodium- and magnesium chlorides were used after recrystallization. From their analyses, all the materials were regarded as sufficiently pure with definite waters of crystallization.

The apparatus adopted for the experiment was similar to what was used by Tschugäff and

Table 1

Pt*	Literature	Temp. (°C)	Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	Solid phases
			(mol/1000 mol H_2O)				
I	Leimbach(4)	100	16	—	26	10	NaCl, Vant., Lõw.
	D'Ans(1)	110	34	—	27	11	
I, K	D'Ans(1)	111	33.5	—	27.5	10.5	Lõw.+Vant.→Kies. (+NaCl)
K	Leimbach(4)	100	16	—	49	11	NaCl, Lõw., Kies.
	Maeda(5)	105	21.298	—	44.08	11.32	
	D'Ans(1)	110	33.0	—	28	11	
	Tanaka	〃	17.5	—	49.5	13.5	
X	Leimbach(4)	105	26.8	9.1	31.45	11.86	NaCl, Lõw., Kies., Lang.
	Tanaka	110	20	12	41	8	Lõw,+Vant.→Kies.
*X, V****	D'Ans(1)	108	26.5	29.6	14.0	16.0	(+Lang.+NaCl)
V	„	110	26.1	30.2	14.3	15.7	NaCl, Vant., Lõw., Lang.

* Notions are followed after D'Ans. However, the point *Y* of him is denoted here as *X*, because the point has been expressed him by as *X* below 83°. Below 83°, *X* is the coexisting point of NaCl, kieserite, langbeinite and kainite.

** The values of D'Ans are estimated, and the others are observed ones.

*** According to the diagram of D'Ans, since this transition takes place at 108°, lõweite does no more coexist with langbeinite at 110°. A new bivariant point, NaCl, Vant., Kies. and Lõw., must be given at this temperature, although the point is abridged in his diagram.

---

* Phase-Rule Studies on the Sea-Salt Industry. II. Presented at the meeting of the Kinki-Section of the Chemical Society of Japan at Kyoto on May 7, 1949.

(1) J. D'Ans, "Die Lõsungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Berlin (1933)

(2) Cf., T. Nishimura, *J. Soc. Chem. Ind. Japan.* **20.** 384, 587 (1917); **22.** 255 (1919); S. Oka, *J. Electrochem. (Japan)*, **11,** 186 (1943)

(3) Cf., for instance, H.L. Robson, *J. Am. Chem. Soc.*, **49,** 2772 (1927); V.G. Kuznetsow, *Bull. acad. sci., U.R.S.S., Classe sci. math. nat., Ser. Chim.* **1937,** 385

(4) G. Leimbach, *Mitt. K.F.A*, **4.** 11 (1925); G. Leimbach and A.Pfeiffenberger, *Caliche*, **11,** 428 (1930)

(5) T. Maeda, *J. Soc. Chem. Ind., Japan*, **23,** 573, 954 (1920). It is regrettable Maeda's research is neglected by D'Ans. D'Ans seems to have extrapolated these two points chiefly from the data at lower temperatures.

Chlopin(6) and by Maeda.(5) The principle of the method is to maintain the system without evaporation at constant temperature and, at the same time, to stir the system by boiling the solution with a reflux condenser under a proper reduced pressure.* Portions of the solution were taken out for analysis by means of a pipette fitted with a filter of cotton wool. The determinations of the solid phase were omitted.

The analyses were carried out after the usual analysis of the bittern.(7) Chloride ion was determined volumetrically by the Vorhard's method, sulfate and magnesium by the usual gravimetric methods and potassium gravimetrically as $NaK_2Co(NO_2)_6 \cdot H_2O$. Sodium was estimated by the difference.** The results were expressed as mols of radicals per 1000 mols of water.

The System, $MgCl_2$-$MgSO_4$-H_2O To know the general conception of the crystallization velocity of kieserite at higher temperatures, this two-salt system was studied at first. The experiments were carried out under various conditions, and the solutions were analysed from time to time. The results are arranged in Table 2.

Table 2

Expt. No.	Time (hr.)	Mg	Cl_2	SO_4	Initial conditions and remarks
		(mol/1000 molH_2O)			
1	5	86.2	73.5	12.6	No precitate at room temp. It was formed after heating 3.5 hrs.
	7.5	83.5	73.7	9.8	
	12.5	81.9	74.7	7.2	
	15	81.6	74.6	7.0	
2	2.5	74.5	65.9	8.6	With some precipitate at room temp. (The sample in 1 was used after dilution.)
	4.5	75.7	67.3	7.3_5	
	6	75.6	68.2	7.3_5	
3	1	125.4	121.7	3.6_5	An excess of $MgSO_4$ was presented at room temp.
	2	125.8	122.1	3.7	
	4	125.9	122.3	3.6	
4	2	84.9	73.8	11.1	With a slight precipitate at room temp.
	4	83.4	74.4	9.0	
	6	84.4	75.9	8.5	
5	1	113.1	107.3	5.8	The solution was concentrated by boiling, and the measurement was commenced after some precip. was observed.
	2	116.6	111.1	5.5	
	4	119.1	115.0	4.1	
	6	120.6	116.7	3.9	
6	2	70.4	58.3	12.1	As in 5.
	4	68.4	57.9	10.5	
	6	69.2	58.9	10.3	
7	2	84.5	73.9	10.6	Some $MgSO_4 \cdot 7H_2O$ was added at high temp. It was once dissolved, and the precip. was observed again after 0.5 hr.
	4	83.1	73.5	9.6	
	6	83.2	74.4	8.8	

Our results agree rather better with those of Maeda at 105°C(5) than with Campbell's at 100°C,(8) and the solid phase may be regarded as consisting always of kieserite. The discontinuity, which is observed in Campbell's result and is considered by him as the transition point from kieserite to anhydrous $MgSO_4$, is never seen in the results of the others. His data, particularly those near the transition point of him, seem to be too high.

As for the crystallization velocity, it may be concluded from the results that the formation of the nuclei of kieserite is very difficult, and, when they are once formed to a certain amount, further crystallization takes place smoothly and the system reaches to an equilibrium within several hours.

Determination of the point K in the System, NaCl-$MgSO_4$-$MgCl_2$-H_2O As the general tendency of the crystallization velocity in the system of sea salts at higher temperatures could be seen from the above experiment, the present experiments were executed under the following procedure: a mixture with a certain composition, nearly saturated or with a precipitate, was concentrated step by step by boiling, and for each step the solution was analysed after keeping the system at 110°C for 5 hours. The results are shown in Table 3 and Fig. 1.* Considering from the composition of the start-

Table 3

Ser.	Expt. No.	Na_2	Mg	Cl_2	SO_4	Total salts	Solid phases
		(mol/1000		mol		H_2O)	
A	—	(25	50	60	15	75)	(initial composition)
	11	23.3	54.3	64.9	12.7	77.6	NaCl, Lŏw.
	12	20.5	58.5	65.9	13.1	79.0	〃 〃
	13	15.4	66.3	68.2	13.5	81.7	〃 〃 (metastable)
	14	10.9	73.0	70.1	13.8	83.9	〃 〃 (metastable)
	15	11.7	68.0	69.5	10.2	79.7	NaCl, Lŏw., Kies. (not in equil.)
B	—	(14	54	35	33	68)	(initial composition)
	16	9.4	70.2	54.4	25.2	79.6	Lŏw., Kies.
	17	15.1	64.9	62.9	17.1	80.0	〃 〃
	18	19.3	60.9	71.1	9.0_5	80.2	〃 〃 (metastable)
C	—	(16	53	53	16	69)	(initial composition)
	19	16.7	62.9	65.8	13.7_5	79.6	Lŏw. (near K-point)
	20	14.7	64.5	71.6	7.6	79.2	NaCl, Kies
	21	11.8	69.3	75.5	5.6	81.1	〃 〃
D	22	9.7	75.0	79.2	5.5	84.7	NaCl, Kies.
	23	5.2	87.4	89.5	3.1	92.6	〃 〃
	24	0.4	109.0	107.1	2.3	109.4	〃 〃
	25	0.1	119.0	117.4	1.7	119.1	〃 〃

---

* In the present case, as the solutions boil at 110° under a pressure not so far from 1 atm., the effect of pressure on the solubility may be neglected.

** In the case of the partial system, $MgCl_2$-$MgSO_4$-H_2O, magnesium was also estimated by the difference, because its direct determination was not so accurate when it existed in large quantities.

(6) L.A. Tschugäff and W. Chlopin, *Z. anorg. Chem.* **86,** 154 (1914)

(7) Cf., N. Naito and T. Mizuno, "Method of Inorganic Analyses and Tests," Dairen (1944)

* As for the graphical representation of the system used here, see I of this report (this Bulletin, **23,** 11 (1950)

(8) A.N. Campbell, K.W. Downes and C.S. Samis, *J. Am. Chem. Soc.*, **56,** 2507 (1934)

ing mixtures, these solutions are well explained as being in contact with the solid phases described in the table, respectively.

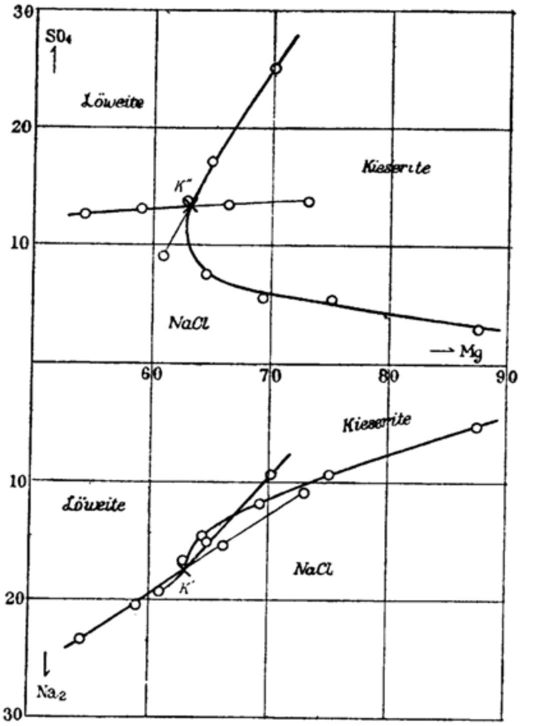

Fig. 1

In the figure, three boundary curves cross each other quite well at one point, and so it can be regarded as the point *K*. The fact that the curves of series A and B extend beyond this point may be explained as due to the existence of meta-stable equilibrium owing to the difficulty of transformation of the crystals once deposited, or to the phenomenon of supersaturation. The composion of the point is near to

Na_2 17.5, Mg 63, Cl_2 67 and SO_4 13.5
mols per 1000 mols of H_2O.

To compare the result with the data in Table 1, our result coincides quite well with that of Leimbach at 100°C. Maeda's result at 105°C also lies not so far from them. The magnesium content of the point by D'Ans is obviously too small. Consequently, the point *K* of D'Ans at 110°C should be revised, and löweite should have a considerably larger field of existence at higher tempetatures.

Preliminary Experiment on the System, $NaCl$-KCl-$MgSO_4$-$MgCl_2$-H_2O The solubility determinations in the five component system of sea salts, particularly those of the boundary curve between the points *X* and *R* at 110°C have been undertaken. Although the experiment is not yet completed, it is concluded at least that the potassium contents of the results are smaller and the magnesium contents are larger, particularly in the vicinity of the point *X*, than what are expected from the diagram of D'Ans. The point *X* seems to lie at about

Na_2 20, K_2 12, Mg 49, Cl_2 73 and SO_4 8
mols per 1000 mols of H_2O, and the point agrees pretty well with that of Leimbach at 105°C (cf., Table 1). The point *X* of D'Ans, too, seems to be revised, and langbeinite may have a larger field.

However, even if the point *X* lies where it is found in the present result, the crystallization path in concentrating sea water at higher temperatures is to pass through the kieserite field as well, and there is no possibility of depositing langbeinite or other salts on the way. Extensive studies in this concern is desirous, and, at the same time, supersaturation in the actual evaporation of the bittern must be examined carefully.

Summary

1. The solubility of magnesium sulfate in magnesium chloride solution at 110°C has been studied with a special reference to the crystallization velocity. In this system, it seems that the formation of the nuclei of kieserite is very difficult, and, when they are once formed, further crystallization takes place smoothly.

2. In the system, $NaCl$-$MgSO_4$-$MgCl_2$-H_2O, at 110°C, it has been found that the point *K* lies at about

Na_2 17.5, Mg 63, Cl_2 67 and SO_4 13.5
mols per 1000 mols of H_2O. The content of magnesium is much larger than what has been estimated by D'Ans, and, accordingly, the löweite field of him should be enlarged.

3. Preliminary experiment on the five component system of sea salts at 110°C has shown that langbeinite may have a larger field than expected from the diagram of D'Ans.

Central Laboratory, Dairen