

Equilibria in the system containing chloride and sulphates of potassium and magnesium

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Abstract. Reciprocal salt-pair system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ has been studied at 35°C to eliminate the discrepancies reported by different workers and for correlating the experimental data with natural evaporation of brine (without NaCl) so as to recover potash salts.

Keywords. Schoenite ; leonite ; kainite ; kieserite.

1. Introduction

The various processes employed for the production of potassium salts from sea water concentrates depend upon the equilibria existing in the reciprocal salt-pair system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at the desired temperature. Van't Hoff (1918) studied the system at 25°C and 83°C and pointed out the existence of leonite and kainite at 25°C , but the boundaries of these salts were not clear. Autenrieth (1954) studied both stable and metastable equilibria to establish the transition from schoenite to leonite. Further work was carried out by D'Ans (1933) and Campbell (1934) at other temperatures such as at 0°C , 55°C and 100°C . Campbell did not report the existence of kainite at 100°C , but Van't Hoff pointed out its existence at 83°C . When the above data were used to interpret the extraction process of potassium and magnesium salts from brine and bittern, considerable variations were observed.

In tropical countries like India, bittern gets evaporated between 30° to 45°C and therefore an understanding of the above system is necessary. To establish the various equilibria the above reciprocal salt-pair system has been studied at 35°C .

2. Experimental methods

For studying the reciprocal salt-pair system at 35°C , a constant temperature water bath maintained at the above temperature was used. For establishing the time for various equilibrium stages, the contents of the system were allowed to stir

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continuously for about 48, 72 hrs and after repetitive experiments and concurrence of the two successive results only further progress was made in studying the system.

The common methods of analysis such as magnesium by EDTA, chloride by Mohr's method, potassium by tetraphenylborate, sulphate by gravimetric estimation of BaSO_4 were used. The BEL flamephotometer was used to check the analysis of potassium by the above method.

In the preliminary stages the equilibria in the various connected binary systems were obtained. The compositions of various binary solutions of the salts—potassium chloride, magnesium chloride hexahydrate, magnesium sulphate heptahydrate and potassium sulphate were noted. A saturated solution of one salt was then added to a second solid salt having a common ion to get the invariant point as represented by the composition of the solution where the solid in contact with the solution showed the presence of both the salts. In the more complicated system, the third salt was added to a system where the solution was in equilibrium with two salts. This gave the various invariant points on the diagram with respect to the solid phase with which three salts were in equilibrium. The various fields or boundaries were established for the double salts—schoenite, leonite, kainite, kieserite etc.

In all the above cases the solid phase compositions have been obtained by chemical methods of analysis and were confirmed by using x-ray diffraction and differential thermal methods of analysis (DTA). This enabled checking and establishing the nature of various equilibria in the system and information about the nature of the solid phase at each stage.

3. Results and discussion

The above system, *i.e.*, $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C formed a reciprocal salt-pair. The analytical results obtained are given in table 1 and diagrammatically shown in figures 1 and 2 by Löwenherz's and Jänecke's method of projection. In figure 1 the horizontal axis was used to represent 2KCl (or K_2Cl_2) and MgSO_4 and the vertical ordinate to represent K_2SO_4 and MgCl_2 and the results were expressed in moles/1000 moles of water. In Jänecke's method of projection (figure 2) the compositions of the solutions were expressed in mole per cent of the dissolved salts. The composition of various solutions occurring at different invariant points is given in alphabetical order of names.

3.1. Critical points consisting of one or two salts with a common ion

In all the points A, B, C and D where KCl , K_2SO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are in equilibrium, the results fairly agree with previous data (Autenrieth 1954). The same is true for the points E, F, G, H, I, J, K and L where the solutions were saturated with respect to the salts having a common ion.

3.2. Critical points representing solutions in equilibrium with three salts

As mentioned above, all the points have been obtained by starting the experiments with a solution saturated with respect to two salts. Starting from point G and adding the magnesium sulphate heptahydrate to the system in increments

Table 1. Solubility data in the system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C

Point	Composition of the liquid phase									Solid Phase
	in moles/1000 moles of H_2O			in mole % of the dissolved salts						
	K_2Cl_2	MgCl_2	K_2SO_4	MgSO_4	K_2Cl_2	MgCl_2	K_2SO_4	MgSO_4		
A	46.86	100.0	8	KCl
B	15.32	100.00	..	8	K_2SO_4
C	59.26	..	100.00	8	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
D	..	108.2	100.00	..	8	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
E	6.15	73.18	7.75	92.25	8	KC + Carnallite
F	0.39	106.10	0.36	99.64	8	Carnallite + $\text{MgCl}_2 - 6\text{H}_2\text{O}$
G	45.83	..	1.64	..	96.46	3.54	8	KCl + K_2SO_4
H	..	72.97	..	11.35	..	86.54	8	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
I	..	103.61	..	8.05	..	92.79	..	7.21	8	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{MgSO}_4 \cdot \text{H}_2\text{O}$
J	..	103.66	..	4.92	..	95.47	..	4.53	8	$\text{MgSO}_4 \cdot \text{H}_2\text{O} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
K	17.29	27.45	38.65	61.37	8	K_2SO_4 + Schoenite
L	6.91	62.91	9.94	90.07	8	Schoenite + $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
M	15.24	25.33	..	14.84	27.50	45.71	..	26.78	8	K_2SO_4 + Schoenite + Leonite
N	10.57	47.25	..	15.07	14.50	64.82	..	20.67	8	KCl + Leonite + Schoenite + Kainite
O	5.39	71.3	..	5.27	6.58	86.99	..	6.43	8	KCl + Carnallite + Kainite
P	8.03	48.00	..	17.53	11.16	65.10	..	23.78	8	Kainite + $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} +$ Schoenite
Q	4.54	67.50	..	11.83	5.41	80.48	..	14.11	8	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} +$ Kainite
R	0.53	74.99	..	9.19	0.63	88.53	..	10.65	8	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O} +$ Kainite + Kieserite + Carnallite
S	1.34	99.95	..	6.79	1.24	92.48	..	6.28	8	Carnallite + Kieserite + $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
T	16.37	32.24	..	13.16	29.1	57.5	..	23.4	8	KCl + K_2SO_4 + Leonite

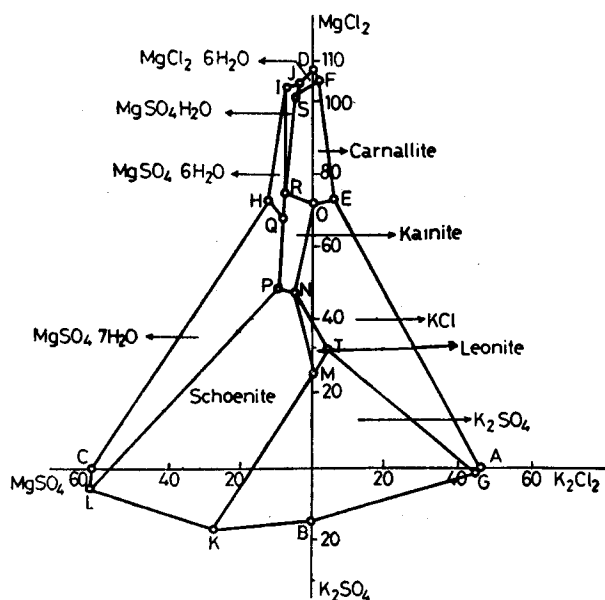


Figure 1. Study of the system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C (Löwenherz's method)

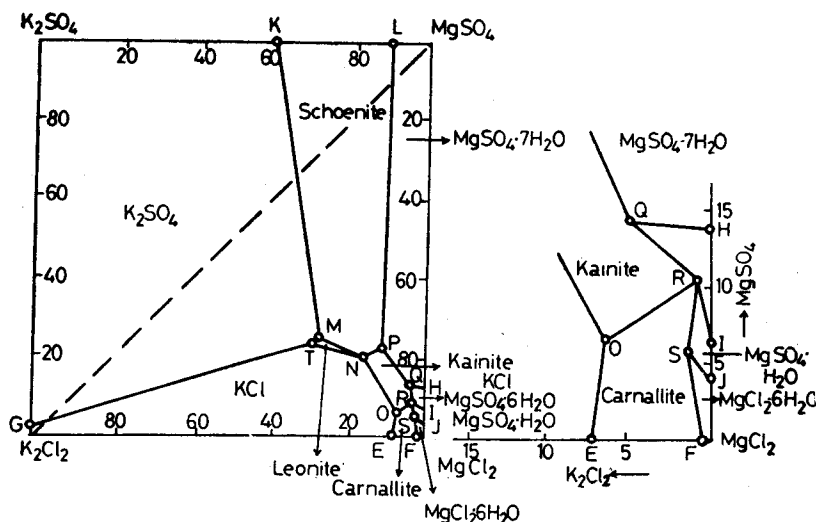


Figure 2. Study of the system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C (Jänecke's projection).

with a little addition of magnesium chloride hexahydrate, a situation arose where the solution was in equilibrium with three salts, the analysis of the solid phase showed the presence of leonite alongwith KCl and K_2SO_4 . This was represented by point T in the diagram. The continued addition of MgCl_2 to the system reached the composition of the solution to the point N where kainite was present alongwith KCl, schoenite and leonite. This is a peculiar case of invariant point where the solution is in equilibrium with four salts namely schoenite, leonite,

KCl and kainite. Either decrease or increase of temperature for disturbing the equilibrium brought slight changes in the equilibrium but when brought back to the original conditions (*i.e.*, at 35° C), it showed the presence of four salts in the solid phase. The experiments were repeated to confirm the above equilibria. The phenomena of supersaturation and metastable equilibrium can be ruled out by the above studies. This has been confirmed by the kainite formation which takes place at higher temperatures. Further addition of $MgCl_2$ produced another invariant point where carnallite was in equilibrium with kainite and KCl. By the small addition of magnesium chloride hexahydrate the formation of keiserite takes place as a fine light yellow powder. Thus again the existence of four salts takes place, *viz.*, carnallite, kieserite, kainite and $MgSO_4 \cdot 6H_2O$. The same procedure, as discussed earlier was observed. This is represented by point R in the diagram. Finally, continued addition of the $MgCl_2 \cdot 6H_2O$ brought the system to the crystallization point S where the solution was in equilibrium with solid salts carnallite, keiserite and $MgCl_2 \cdot 6H_2O$.

The experiments were carried out by starting with point K where the solid salts were K_2SO_4 and schoenite. By adding $MgCl_2 \cdot 6H_2O$ to the system, a condition was reached when the composition of the solution was represented by M on the diagram, which was in equilibrium with salts schoenite, leonite and K_2SO_4 . Successive addition of $MgCl_2 \cdot 6H_2O$ to the system shifts the equilibrium to the point N where four salts (KCl + Leonite + Schoenite + Kainite) are in equilibrium. This establishes the earlier experiment.

Addition of both $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 6H_2O$ was necessary to bring variations in the equilibrium and to reach the point P where the solid phase showed the existence of $MgSO_4 \cdot 7H_2O$ schoenite and kainite. The continued addition of both further produced another invariant point Q in the system. The solid phase consisted of $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 6H_2O$ and kainite. The enhanced increase of $MgCl_2 \cdot 6H_2O$ concentration in the system dehydrated $MgSO_4 \cdot 6H_2O$ to kieserite giving rise to the point R where kieserite, kainite, $MgSO_4 \cdot 6H_2O$ and carnallite were in equilibrium. This confirms the earlier result.

The points N and R where four salts in equilibrium were bound by starting with the point L and I in the diagram respectively. The other points P, Q, S and O were confirmed by starting with the invariant points of the respective systems, *i.e.*, L, H, J and E.

4. Conclusions

This study establishes the various equilibria existing in the system at 35° C. It is hoped that the various discrepancies observed in the earlier data have now been eliminated and the data when applied to the recovery of potassium salts could help in understanding the above complicated system, *i.e.*, recovery of potassium as schoenite, leonite and kainite etc. The transition of schoenite and leonite at 32.5° C and at higher temperatures has been established conclusively.

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