EQUILIBRIA IN THE SYSTEMS CONTAINING WATER AND CHLORIDES OF IRON, COBALT AND NICKEL AT 25.0°.[1]

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Iron, cobalt and nickel form one of the three triads in the eighth group of the periodic system of the chemical elements and they have many similarities in their chemical behaviours. We have undertaken to study the equilibria in the systems of their chlorides and water, as, so far as we know, there has been no systematic study about them.

As to the equilibrium of the system of ferrous chloride, nickel chloride and water at 25°, we have found that they form two series of solid solutions, one on the side of ferrous chloride with four molecules of water of crystallisation and the other on the side of nickel chloride with six molecules of it, and have reported the result lately in the "Cohen-Festband" of the *Zeitschrift für physikalische Chemie.*[2]

In this article we will report on the equilibria in the following systems at 25.0°:

1. $FeCl_3$, $CoCl_2$, and H_2O,
2. $FeCl_3$, $NiCl_2$, and H_2O,
3. $CoCl_2$, $NiCl_2$, and H_2O,
4. $FeCl_3$, $CoCl_2$, $NiCl_2$, and H_2O.

Materials. Ferric chloride from C. Merck was twice recrystallised after Roozeboom.[3] Of cobalt chloride and nickel chloride, the purest preparations (each free from the other) of Kahlbaum was directly used. The ordinary distilled water was used.

Procedure. The usual procedure as ordinarily carried out in our laboratory and reported in several previous papers was employed.

Analysis. The *total chlorine* was determined by Volhard's method modified by V. Rothmund and A. Burgstaller.[4] When the solution was faintly pink coloured by an excess of the cobalt salt, it was removed by an addition of a proper quantity of nickel nitrate, and vice versa, and the titration could be carried out in the presence of cobalt and nickel.

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(1) The experimental work of this article was performed in the Physico-chemical Department of the Chemical Institute, Kyoto Imperial University, in 1926.

(2) *Z. physik. Chem.*, **130** (1927), 480.

(3) *Z. physik. Chem.*, **10** (1892) 477.

(4) Treadwell-Hall, "Analytical Chemistry." Vol. 2. 4th ed., p. 703.

The *nickel* was determined by the Tschugaeff's reaction between nickel salt and dimethyl glyoxime.[1]

The *iron*. The ferric salt was first reduced to the ferrous salt with stannous chloride and after proper treatments was finally titrated with potassium permanganate.[2]

The *cobalt* was estimated from the total chlorine and the quantities of iron and nickel.

Results.

1. The System: $FeCl_3$—$CoCl_2$—H_2O.

The result is given in Table 1.

TABLE 1.

No.	Solution.			Wet residue.			Dry residue.
	$FeCl_3$	$CoCl_2$	H_2O	$FeCl_3$	$CoCl_2$	H_2O	
1	0.00	36.08	63.92	—	—	—	$CoCl_2.6H_2O$
2	7.77	29.36	62.87	3.65	44.86	51.49	〃
3	19.08	20.95	59.97	4.95	46.09	48.96	〃
4	35.52	10.13	54.35	8.79	44.32	46.89	〃
5	41.07	7.99	50.94	12.20	41.04	46.76	〃
6	43.28	7.40	49.32	50.07	6.61	43.32	$CoCl_2.6H_2O$ and $FeCl_3.6H_2O$
7	43.34	7.45	49.21	45.22	11.89	42.89	
8	43.95	6.58	49.47	55.46	2.03	42.51	$FeCl_3.6H_2O$
9	44.50	5.99	49.51	54.37	2.03	43.59	〃
10	47.17	2.47	50.36	56.04	0.48	43.48	〃
11	51.57	4.74	43.69	16.36	54.48	29.16	$oCl_2.2H_2O$] $FeCl_3.6H_2O$
12	49.42	0.00	50.58	—	—	—	

In this and the following tables the compositions are give in gram percentages. A labile residue is enclosed in brackets. The result is graphically represented in Fig. 1.

(1) E. Grossmann, "Die Bestimmungsmethoden des Nickels and Cobalts und ihre Trennung von der anderen Elementen." Pp. 91, 120; O. Brunk, *Z. angew. Chem.*, **20** (1907) 834.

(2) Treadwell-Hall, *loc. cit.*, p. 610.

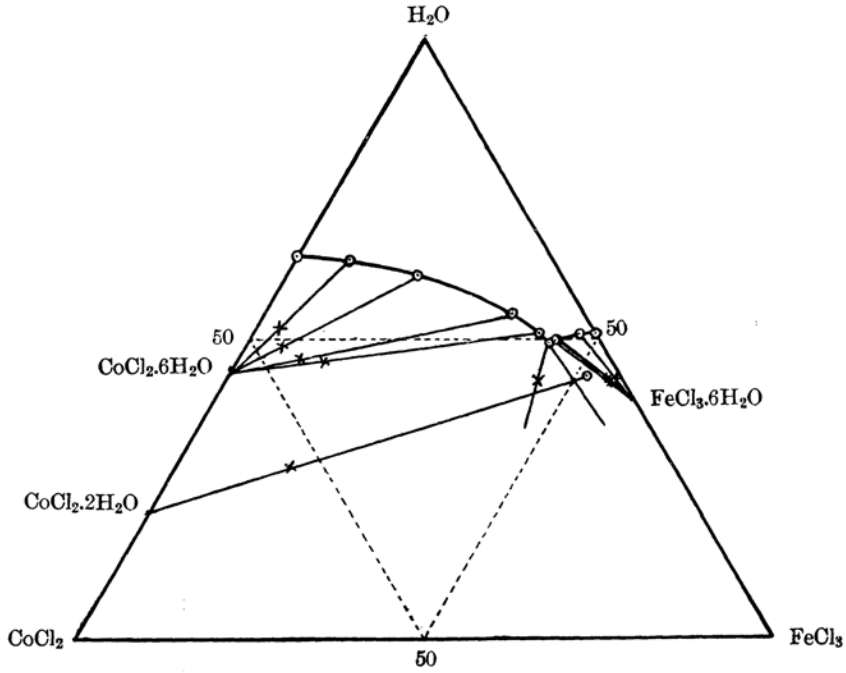

Fig. 1.

These chlorides do not form any double salt nor any solid solution as may be expected. Each forms only the hexahydrates even in the saturated solution of the other. The existence of a labile dihydrate was observed.

2. The System: $FeCl_3$—$NiCl_2$—H_2O.

The result is given in Table 2 and graphically in Fig. 2.

TABLE 2.

No.	Solution.			Wet residue.			Dry residue.
	$FeCl_3$	$NiCl_2$	H_2O	$FeCl_3$	$NiCl_2$	H_2O	
1	0.00	38.88	61.12	—	—	—	$NiCl_2.6H_2O$
2	10.24	30.89	58.87	2.36	49.07	48.57	〃
3	22.68	22.21	55.11	5.47	46.98	47.55	〃
4	26.33	19.86	53.81	7.81	47.18	45.01	$NiCl_2.6H_2O$ and
5	26.49	19.75	53.76	9.14	47.62	43.19	$NiCl_2.4H_2O$
6	29.77	18.11	52.12	9.19	43.90	46.91	[$NiCl_2.6H_2O$]
7	31.35	16.43	52.22	9.94	49.68	40.38	$NiCl_2.4H_2O$
8	37.47	11.88	50.65	13.40	45.55	41.05	
9	40.65	10.73	48.62	32.32	27.36	40.31	$NiCl_2.4H_2O$ and
10	40.61	10.69	48.72	44.22	15.59	40.19	$FeCl_3.6H_2O$
11	42.22	9.89	47.89	15.29	44.34	40.37	[$NiCl_2.4H_2O$]
12	46.24	7.33	46.43	16.04	44.52	39.44	[〃]
13	41.01	10.01	48.98	54.33	2.80	42.87	$FeCl_2.6H_2O$
14	43.39	6.80	49.81	—	—	—	〃
15	46.08	4.37	49.55	54.86	1.11	44.03	〃
16	49.42	0.00	50.58	—	—	—	〃

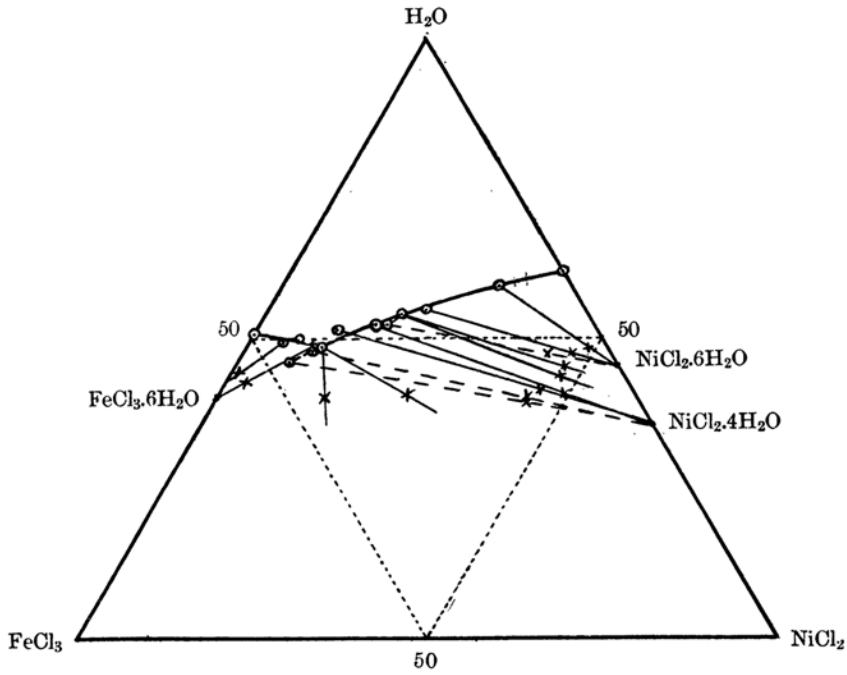

Fig. 2.

In this table the labile residues are enclosed in brackets. In this case also no double salt nor solid solution was observed as may be expected. The both chlorides are hexahydrated, but when the concentration of ferric salt is increased, nickel chloride becomes tetrahydrated.

3. The System: $CoCl_2$—$NiCl_2$—H_2O.

The result is given in Table 3 and graphically in Fig. 3.

TABLE 3.

No.	Solution.			Wet residue.			Dry residue.
	$NiCl_2$	$CoCl_2$	H_2O	$NiCl_2$	$CoCl_2$	H_2O	
1	38.88	0.00	61.12	54.75	0.00	45.25	$NiCl_2.6H_2O$
2	34.36	4.38	61.26	41.54	12.20	46.26	(Ni, Co) $Cl_2.6H_2O$
3	31.91	6.28	61.81	34.37	19.67	45.96	〃
4	30.63	7.66	61.71	32.74	21.14	46.12	〃
5	26.13	11.83	62.04	25.32	28.71	45.97	〃
6	22.51	14.87	62.52	18.99	34.80	46.31	〃
7	13.39	23.42	63.19	9.87	44.21	45.92	〃
8	10.45	26.17	63.38	7.63	46.13	46.22	〃
9	4.31	32.06	63.93	1.83	51.88	46.29	〃
10	0.00	36.08	63.92	0.00	54.59	45.41	$CoCl_2.6H_2O$

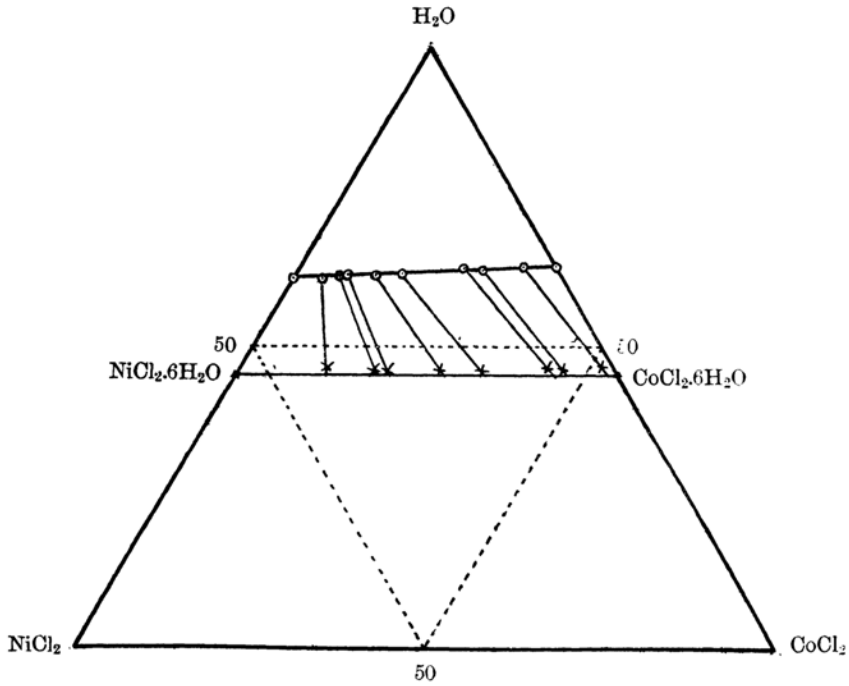

Fig. 3.

These chlorides form a complete series of solid solutions with six molecules of water of crystallisation.

4. The System : $FeCl_3$—$CoCl_2$—$NiCl_2$—H_2O.

The result is given in Table 4.

TABLE 4.

No.	Solution.				Wet residue.			
	$FeCl_3$	$NiCl_2$	$CoCl_2$	H_2O	$FeCl_3$	$NiCl_2$	$CoCl_2$	H_2O
1	40.63	10.75	0.00	48.62	—	—	—	—
2	40.61	9.79	0.50	49.10	35.22	20.85	3.61	40.32
3	40.02	8.76	1.53	49.69	32.18	17.13	8.94	41.15
4	40.71	7.50	2.90	48.89	12.62	27.52	20.58	39.28
5	40.78	5.84	4.03	49.35	29.36	9.95	16.49	44.20
6	40.44	5.92	4.89	48.75	34.61	8.85	15.38	41.16
7	41.23	4.54	5.25	48.98	21.07	9.18	28.81	40.94
8	41.31	3.98	6.00	48.71	27.38	6.58	24.55	41.49
9	40.87	3.53	6.63	48.97	11.19	8.06	34.72	46.03
10	40.71	2.98	7.58	48.73	20.97	4.81	28.53	45.70
11	41.80	1.86	7.62	48.72	33.93	1.66	20.90	43.51
12	42.35	1.29	7.31	49.05	26.82	1.16	25.33	46.69
13	40.30	0.00	7.40	52.30	—	—	—	—

The residues as analysed contained some mother liquor adhering and it was impossible to find the composition of dry residues from the data we had, but they may serve at least to ascertain that the residues contained all the three chlorides. From the Phase Theory it may be easily seen that the residues consist of two solid phases, and from what we have seen in the cases of the three component systems it is certain that one of the solid phases is ferric chloride hexahydrate and the other a solid solution of cobalt and nickel chlorides. As to the water of crystallisation in the solid solutions, we may presume that on the side of nickel chloride they contain four molecules of water of crystallisation and on the side of cobalt chloride six molecules of it, for these chlorides crystallise from the solutions saturated with ferric chloride with four and six molecules of water of crystallisation respectively.

To represent the result in a triangular diagram in the terms of the three chlorides with no regard to water, we have calculated the following table:

TABLE 5.

No.	Solution.			Solid solution.	
	$FeCl_3$	$NiCl_2$	$CoCl_2$	$NiCl_2$	$CoCl_2$
1	79.07	20.93	0.00	100.00	0.00
2	79.79	19.24	0.97	85.25	14.75
3	79.95	17.08	2.97	65.88	34.12
4	79.69	14.67	5.64	57.22	42.78
5	80.50	11.53	7.97	37.63	62.37
6	78.98	11.55	9.47	36.55	63.46
7	80.79	8.89	10.32	24.16	75.84
8	80.56	7.75	11.69	21.13	78.87
9	80.08	6.91	13.02	18.84	81.16
10	79.41	5.80	14.79	14.43	85.57
11	81.50	3.63	14.87	7.34	92.66
12	83.12	2.53	14.35	4.38	95.62
13	84.48	0.00	15.52	0.00	100.00

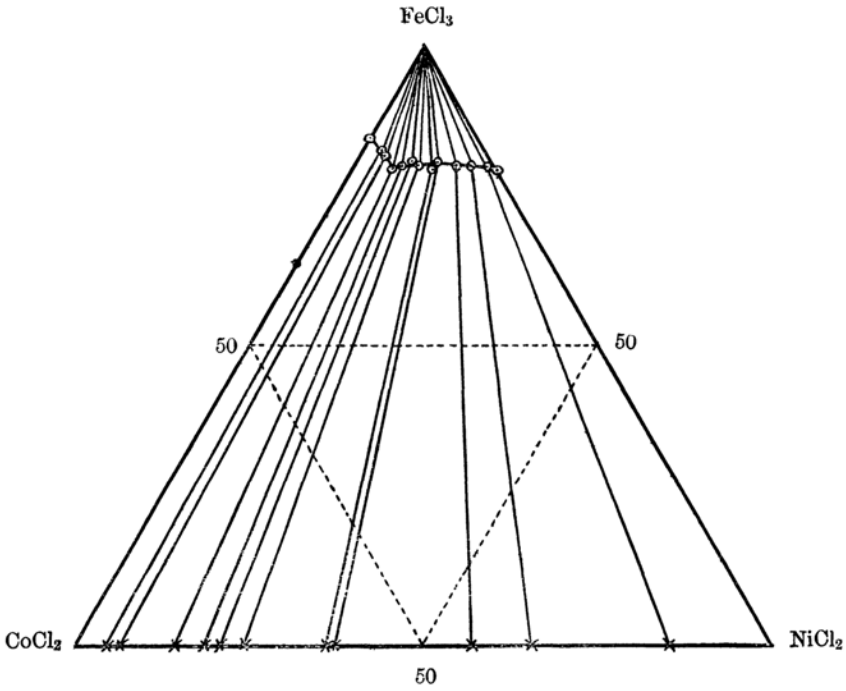

Fig. 4.

The result is graphically represented in Fig. 4. As above stated the residues are not pure, but to see an approximate relation between the solutions and the residues they were assumed to be pure in the plotting.

Summary.

The equilibria in the following systems at 25.0° have been studied:

1. $FeCl_3$—$CoCl_2$—H_2O,
2. $FeCl_3$—$NiCl_2$—H_2O,
3. $CoCl_2$—$NiCl_2$—H_2O,
4. $FeCl_3$—$CoCl_2$—$NiCl_2$—H_2O,

and the results have been given in tables and diagrams.

Kyoto.