201. *The Three-component Systems composed of Cobalt Chloride and Water with either Calcium, Strontium, or Thorium Chloride.*

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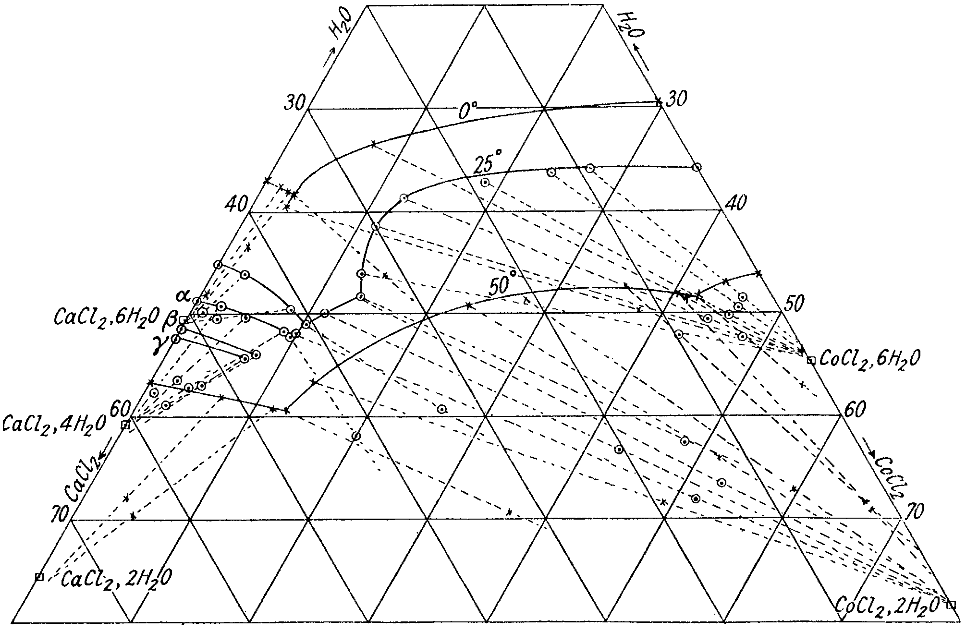
A number of salts when added to solutions of cobalt chloride tend to turn these blue. Solid blue double salts have been isolated from such solutions in only a few cases, however. They have been obtained with magnesium chloride (Bassett and Croucher, J., 1930, 1784), lithium chloride (Bassett and Sanderson, J., 1932, 1855), and with rubidium and cæsium chlorides (Foote, *Amer. J. Sci.*, 1927, **13**, 158).

In the hope of adding to this number, the cobalt chloride systems containing either calcium, strontium, or thorium chloride have been examined, since all of these salts favour the blue condition. The results obtained are recorded in the tables and shown graphically for the calcium system. No double salts have been found, nor is there any indication of any solid-solution formation. The system $CoCl_2$–$CaCl_2$–H_2O has been examined at 25° by Benrath (*Z. anorg. Chem.*, 1927, **163**, 396) whose results do not agree very well with ours. The stable region of $CoCl_2,2H_2O$ was missed and included in that of $CoCl_2,6H_2O$ because no proper examination or analysis of the solid phases was made. We find at 0° only the solid phases $CoCl_2,6H_2O$ and $CaCl_2,6H_2O$, and at 50° the three phases $CoCl_2,6H_2O$, $CoCl_2,2H_2O$, and $CaCl_2,2H_2O$. At 25°, in addition to $CoCl_2,6H_2O$, $CoCl_2,2H_2O$, and $CaCl_2,6H_2O$, which have stable fields of existence, we have been able to trace the solubility curves for the three forms of $CaCl_2,4H_2O$, all metastable at 25°; $CaCl_2,2H_2O$ was also found at this temperature but was too unstable for its solubility to be measured. The solubility curve evidently lay in the position to be expected, approximately parallel to the curves for the tetrahydrate in the region of still lower water content. Inoculation with the appropriate solid was employed in tracing the curves of metastable compounds.



The system $CoCl_2$–$SrCl_2$–H_2O is very simple. It has been examined at 25°, where the two hexahydrates alone occur, and at 80°, where the two dihydrates are the only solid phases. The system was examined at 25° by Benrath (*loc. cit.*) whose results do not differ much from ours.

In the system $CoCl_2$–$ThCl_4$–H_2O at 25° there is a large region of $CoCl_2,6H_2O$ and a small one of $ThCl_4,8H_2O$. The solubility of the latter salt was determined also at 0°, and so was the position of the point of intersection of the solubility curves of the two chlorides, the two solid phases being identified by means of the petrological microscope. No evidence was found for the existence of other solid phases at 0°. Various hydrates of thorium chloride have been reported in the literature but they have not been examined systematically in the light of the phase rule. Cleve (*Bihang. Svensk. Akad. Handl.*, 1874, **2**, 6, 10; *Bull. Soc. chim.*, 1874, **21**, 116) showed that $ThCl_4,8H_2O$ is formed at the ordinary temperature by evaporation of aqueous solutions. We find that the crystals are orthorhombic and positive with an optic axial angle of about 10°.

We have been able to characterise the three forms of $CaCl_2,4H_2O$ more fully than was done by Bassett *et alios* (J., 1933, 151). The α-form is triclinic and negative with an optic axial angle of about 30°. It forms crystals having a "granular" appearance. The β-form is orthorhombic and negative with an optic axial angle of about 5°. The crystals are often rectangular and are somewhat elongated in the direction of slow vibration. The γ-form is more difficult to define owing to its habit of crystallising in large, six-sided plates. These show straight extinction and elongation in the direction of slow vibration, and their general shape and angles are similar to those of one aspect of the much smaller crystals of the β-form. The interference figure shown by the large plates of the γ-chloride is a diffuse cross moving rapidly out of the field as the crystal is rotated. It is visible for less than 10° rotation of the stage. The interference figure shown by the similar small plates of the β-tetrahydrate is a single brush, invisible in the 45° position. It is probable that the crystals of the γ-form are orthorhombic but they certainly differ from the orthorhombic β-form.

During the crystallographic examinations it was found that the β-form was produced almost invariably if plates of the γ-form were crushed with a glass rod in the equilibrium solution. Previously the formation of the β-form had appeared to be somewhat fortuitous.

EXPERIMENTAL.

Iron- and nickel-free cobalt chloride was used. The thorium chloride was anhydrous material converted into octahydrate by crystallisation from water. Thorium and chlorine were shown to be present in the correct ratio.

$CoCl_2$–$CaCl_2$–H_2O.

Solution.		Moist solid.			Solution.		Moist solid.		
$CoCl_2$, %.	$CaCl_2$, %.	$CoCl_2$, %.	$CaCl_2$, %.	Solid phase.	$CoCl_2$, %.	$CaCl_2$, %.	$CoCl_2$, %.	$CaCl_2$, %.	Solid phase.
At 0°.									
29·50	—	—	—	a	2·36	35·82	1·59	41·83	c
7·22	26·42	41·07	7·37	a	1·64	36·25	0·49	47·82	c
2·82	36·77	37·69	11·94	a	—	37·00	—	—	c
2·85	35·48	14·53	31·46	a, c					
At 25°.									
35·87	—	—	—	a	8·34	41·13	2·49	47·91	c
26·88	9·08	45·99	2·39	a	2·77	43·37	0·86	48·96	c
23·66	12·61	45·92	3·33	a	—	45·05	—	—	c
18·50	18·66	45·62	4·50	a	m 9·51	42·53	20·03	41·84	b, d
12·44	26·10	44·05	6·35	a	m 8·76	42·91	3·56	53·60	d
11·39	29·92	47·79	4·62	a	m 4·92	45·27	2·14	54·29	d
12·52	33·46	42·17	9·84	a	m 2·14	46·94	0·78	56·79	d
13·51	34·83	48·07	14·25	a, b	mB —	48·85	—	—	d
13·64	34·90	53·15	13·42	b	m 7·56	46·27	2·33	56·55	e
11·43	38·54	42·94	20·32	b	mB —	51·30	—	—	e
m 9·75	41·99	51·83	16·22	b	m 6·92	47·24	4·42	52·52	f
10·36	40·63	25·71	33·47	b, c	mB —	52·13	—	—	f
At 50°.									
46·00	—	—	—	a	23·24	25·98	51·63	12·42	b
43·50	3·34	53·54	0·26	a	13·72	42·85	49·23	19·40	b
41·92	6·31	55·30	1·92	a, b	12·79	46·63	36·60	32·74	b, g
40·22	7·87	67·10	1·94	b	11·55	47·74	5·00	64·60	g
35·41	11·88	66·08	2·21	b	6·75	51·43	3·64	64·34	g
27·67	20·87	59·53	7·70	b	—	56·70	—	—	g

m = Metastable; B = Bassett *et al.* (J., 1933, 151); a = $CoCl_2,6H_2O$; b = $CoCl_2,2H_2O$; c = $CaCl_2,6H_2O$; d = α-$CaCl_2,4H_2O$; e = β-$CaCl_2,4H_2O$; f = γ-$CaCl_2,4H_2O$; g = $CaCl_2,2H_2O$.

$CoCl_2$–$SrCl_2$–H_2O.

At 25°.

Solution.		Moist solid.		
$CoCl_2$, %.	$SrCl_2$, %.	$CoCl_2$, %.	$SrCl_2$, %.	Solid phase.
35·87	—	—	—	a
32·57	4·28	50·86	0·22	a
29·21	9·00	53·05	0·16	a
26·90	12·19	30·13	24·65	a, b
26·57	12·31	35·94	14·97	a, b
24·55	13·69	8·20	44·12	b
24·17	14·50	3·54	53·13	b
10·83	24·93	1·46	55·63	b
—	35·07	—	—	b

At 50°.

Solution.		Moist solid.		
$CoCl_2$, %.	$SrCl_2$, %.	$CoCl_2$, %.	$SrCl_2$, %.	Solid phase.
49·50	—	—	—	c
42·16	10·71	69·93	1·98	c
41·02	12·25	75·00	0·94	c
31·98	22·16	37·78	32·32	c, d
33·77	22·30	61·18	9·31	c, d
24·45	29·24	7·65	67·50	d
18·05	34·12	7·83	63·06	d
—	47·50	—	—	d

a = $CoCl_2,6H_2O$; b = $SrCl_2,6H_2O$; c = $CoCl_2,2H_2O$; d = $SrCl_2,2H_2O$.

$CoCl_2$–$ThCl_4$–H_2O.

At 0°.

	Solution.		Moist solid.		
	$CoCl_2$, %.	$ThCl_4$, %.	$CoCl_2$, %.	$ThCl_4$, %.	Solid phase.
	0·55	55·20	24·40	33·16	a, b
A	—	55·75	—	—	b
B	—	55·61	—	—	b

At 25°.

	Solution.		Moist solid.		
	$CoCl_2$, %.	$ThCl_4$, %.	$CoCl_2$, %.	$ThCl_4$, %.	Solid phase.
	35·87	—	—	—	a
	22·47	18·50	43·31	6·84	a
	17·34	26·26	44·63	7·25	a
	7·85	42·46	46·62	7·36	a
	4·21	54·25	22·93	38·04	a, b
	3·34	55·17	0·04	67·80	b
C	1·97	56·25	0·33	68·11	b
	—	58·00	—	—	b

A, by Th estimation; B, by Cl estimation; C by estimation of Cl and Co, the latter after separation of Th; a = $CoCl_2,6H_2O$; b = $ThCl_4,8H_2O$.

The cobalt–calcium and cobalt–strontium mixtures were analysed by determining cobalt as Co_3O_4, after separation with α-nitroso-β-naphthol, and total chloride. Direct determination of calcium and strontium was less satisfactory, as it involved previous separation of cobalt as sulphide. Determination of strontium as sulphate in presence of cobalt gave high results owing to contamination with cobalt sulphate.

Thorium and total chloride were determined in the analyses of the cobalt–thorium mixtures, as it was found that α-nitroso-β-naphthol failed to separate the two metals. The solution taken for analysis was diluted to 150 c.c. and precipitated boiling with ammonia in presence of ammonium chloride. After being washed once with hot water, the precipitate was redissolved in hydrochloric acid and reprecipitated. These operations were repeated, sometimes six times, until a perfectly white precipitate free from cobalt was obtained. The thoria should be ignited over the blowpipe and weighed without undue delay, as it is hygroscopic.

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