On the Equilibrium of the System : Ferric Chloride, Aniline Hydrochloride, Hydrogen Chloride and Water at 25·0°.

By

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R. M. McKenzie[1] obtained some double halides of iron and some aromatic bases, of which those of aniline hydrochloride were the following ;

$FeCl_3 . 2C_6H_5NH_3Cl$, $FeCl_3 . 2C_6H_5NH_3Cl.H_2O$,

$FeCl_3 . 6C_6H_5NH_3Cl$, and $FeCl_3 . 6C_6H_5NH_3Cl.2H_2O$.

All his attempts to make quantitative determinations of the water of crystallisation in these salts were unsuccessful and the formulas of the double salts, both anhydrous and hydrated, were calculated from the quantitative determinations of the chlorine and iron.

This work suggested that it might be of some interest to study the system consisting of ferric chloride, aniline hydrochloride, hydrogen chloride and water from the standpoint of the phase theory. The experimental work was first undertaken by G. Shima and then continued by R. Yoshida. The following are the results so far obtained.

MATERIALS.

Aniline hydrochloride. Pure aniline from E. Merck was distilled and then redistilled under reduced pressure. The aniline thus prepared was mixed with an equivalent quantity of redistilled hydrochloric acid

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1 Amer. Chem. J., **50**, 309 (1913).

in a porcelain beaker externally cooled and the aniline hydrochloride, which crystallised out, was preserved in a desiccator over sulphuric acid.

Ferric chloride. The purest preparation of E. Merck was used without further purification.

Hydrochloric acid. A twenty per cent solution was prepared by distillation from the acid of Jap. Pharm.

Water. Ordinary distilled water was used.

PROCEDURE.

Proper quantities of ferric chloride and aniline hydrochloride together with some hydrochloric acid were put in an Erlenmeyer flask of about 30 cc. capacity. It was stoppered with a paraffined cork, which was tightly covered with a sheet of oiled paper, and was made to rotate in a thermostat at 25•0° for a few days. Then the liquid phase and residue, more or less wetted with the mother liquor, were subjected separately to analysis.

When the concentration of ferric chloride is high, aniline is oxidised unless the hydrochloric acid is concentrated, and when the hydrochloric acid is concentrated the solubility of the ferric chloride is very great. Under such circumstances the cases where the ferric chloride is very concentrated, could not be studied.

METHODS OF ANALYSIS.

Aniline. It was separated from a weighed sample by decomposition with caustic potash and steam distillation. It was then titrated with a standard solution of bromine with indigo-carmine as indicator.

Iron. To the ferric chloride solution obtained from a weighed sample by driving off the aniline with caustic potash, some potssaium iodide was added and the free iodine thus formed was titrated by sodium thiosulphate with starch as indicator, (G. S.). Or the residue from the distillation of aniline was separated quantitatively by filtration and washing into a solution and solid residue. The solid residue was dissolved in hydrochloric acid and the ferric chloride thus formed was reduced to ferrous salt by stannous chloride. The excess of stannous chloride was oxidised by mercuric chloride and with addition of manganous sulphate, phosphoric acid, and sulphuric acid, the ferrous iron was titrated with potassium permanganate, (R. Y.).

Chlorine. The filtrate of the residue from the distillation of aniline was acidified with nitric acid. A known quantity of 1/10 n. silver nitrate was added and its excess was titrated back with a 1/10 n. solution of ammonium thiocyanate with iron alum as indicator.

Water. It was estimated by difference.

RESULTS.

The results are given in the following two tables. In these tables the compositions of the solutions and residues are represented in weight percentages.

TABLE 1.

(Experiments by G. Shima.)

No.	Solution.				Residue.			
	Aniline hydro-chloride.	Ferric chloride.	Hydro-gen chloride.	Water.	Aniline hydro-chloride.	Ferric chloride	Hydro-gen chloride.	Water.
1	11·29	0·20	21·20	67·41	69·22	2·45	8·83	19·50
2	12·46	0·49	19·57	67·48	49·94	4·78	12·68	32·60
3	10·77	0·11	21·64	67·48	80·94	2·77	11·78	4·51
4	8·94	1·35	19·41	70·30	36·79	6·91	15·41	40·89
5	7·11	0·69	22·48	69·72	26·24	4·76	17 37	51·63
6	5·85	1·10	23·87	69·18	34·52	7·25	17·35	40·88
7	5·05	1·86	22·03	71 06	23·54	5·42	18·10	52·94
8	4·61	3·01	22·28	70·10	22·33	5·95	18·65	53·07
9	3·99	3·35	23·04	69·62	18·12	5·79	20·49	55·60
10	4·05	3·58	22·35	70·02	28·18	7·47	18·04	46·31
11	5·59	6·37	19 17	68 87	40·51	11·39	13·26	34·84
12	3·44	6·31	22·36	67·89	20·58	8·24	22·21	48·97

TABLE 2.

(Experiments by R. Yoshida.)

No.	Solution.				Residue.			
	Aniline hydro-chloride.	Ferric chloride.	Hydro-gen chloride.	Water.	Aniline hydro-chloride.	Ferric chloride.	Hydro-gen chloride.	Water.
1	22·78	0·00	11·08	66·14	95·08	0·00	1·25	3·67
2	20·24	1·29	11·78	66·69	74·71	2·60	3·45	19·24
3	18·09	1·03	13·02	67·86	64·28	5·51	5·00	25·21
4	19·59	1 31	12·08	67·02	89·04	3·00	1·23	6·73
5	17·17	2·82	11·88	68·13	59·81	12·69	4·03	23·47
6	13·81	5·18	11·32	69·69	61·52	14·03	3·04	21·41
7	10·92	8·51	10·82	69·75	57·31	14·42	3·98	24·29
8	8·85	8·83	12·66	70·11	51·11	13·92	4·76	30·21
9	7·06	12 12	11·44	69·38	62·50	16·24	2·56	18·70
10	7·09	14·30	10·21	68 40	34·06	15·87	6·25	43 82
11	5·29	16·06	11·69	66·96	35·90	16·93	6·45	40·72
12	4·49	18·16	11·91	65·44	63·63	17·44	2·94	15·99
13	3·96	19·95	11·49	64·60	50·84	19·13	4·13	25·90
14	3·57	21·50	12·89	62·04	53·14	24·91	4·04	17·91
15	3·45	22·84	11·22	62·49	21·75	21·94	8·83	47·48
16	3·47	23·82	10·21	62·50	17·93	23·23	8·20	50·64
17	2·58	23·36	12·96	61·10	47·87	36·62	2·71	12·80
18	2·10	25·59	12·48	59·83	46·77	35·56	3·11	14·56
19	2·07	26·20	12·53	59·20	55·33	35·75	2·22	6·70
20	1·71	28·61	11·71	57·97	49·90	36·72	2·33	11·05
21	1·35	33·10	10·98	54·57	42·83	37·00	3·35	16·82
22	1·57	35·17	7·22	56·04	43·92	38·06	1·67	16·35
23	1·34	36·24	7·52	54·90	45·80	38·07	2·64	13·49

From the data given in Table 2, if we take the cases in which the percentage of hydrochloric acid is approximately constant and represent the composition excluding the hydrochloric acid, by the formula :

$$100mH_2O,\ x\ C_6H_5NH_3Cl,\ (100\text{-}x)\ FeCl_3$$

we obtain Table 3.

TABLE 3.

No.	Solution.		Residue.	
	x	m	x	m
1	100·00	20·88	100·00	0·28
2	95·16	22 54	97·29	1·80
5	88·39	25·22	85·53	2·41
6	76·96	27·93	84·59	2·12
9	42·17	29·82	82·83	1·78
11	29·20	26·57	72·63	5·92
12	23·62	24·79	82·04	1·48
13	19·90	23·35	76·89	2·82
14	17·19	21·53	72·75	1·76
17	12·13	20·68	62·07	1·19
18	9·32	19·08	62·21	1·39
20	6·98	16·97	62·97	1·00
21	4·86	14·12	59 17	1·67

From the data in Table 3, Fig. 1 was plotted.

Next, we take a regular tetrahedron as the coordinates to represent the equilibrium of the system under consideration and project orthogonally the points in the space to the face of $C_6H_5NH_3Cl$, $FeCl_3$ and H_2O, then in the triangular diagram, we have as the three coordinates the following values :[1]

$$(C_6H_5NH_3Cl)+1/3(HCl),$$

$$(FeCl_3)+1/3(HCl),$$

$$(H_2O)+1/3(HCl),$$

where the chemical formula in brackets denotes the molar percentage of that substance.

From Tables 1 and 2, Tables 4 and 5 were calculated respectively for the new coordinates of the orthogonal projection.

TABLE 4.

No.	Solution.			Residue.		
	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O
1	18·36	7·26	74·48	72 16	5·40	22·44
2	18·99	7·01	74·00	54·17	9·01	36·82
3	17·99	7·32	74·69	84·87	6·69	8·44
4	15·41	7·82	76·77	41·93	12·05	46·02
5	14·60	8·19	77·21	32·03	10·55	57 42
6	13·80	9·06	77·14	40·30	13·04	46 66
7	12·40	9·20	78·40	29·57	11·46	58·97
8	12·04	10·44	77·52	26·55	12·16	59·29
9	11·67	11·03	77·30	24·96	12·62	62·42
10	11·50	11·03	77·47	34·19	13·48	52·33
11	11·98	12·76	75·26	44·93	15·81	39·26
12	10·89	13·77	75·34	27·98	15·64	56·38

1 F. A. H. Schreinemakers, Zs. physik. Chem., **55**, 563 (1909).

Fig. 1

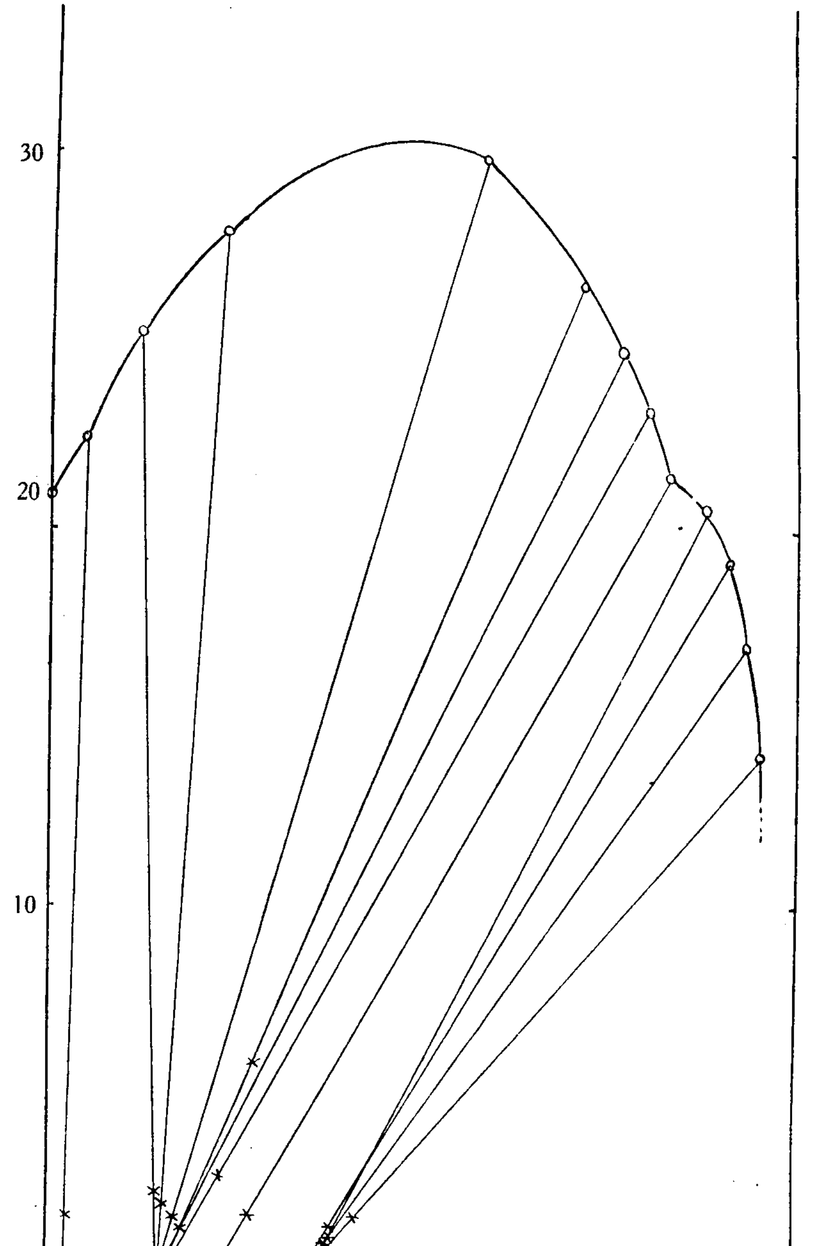

TABLE 5.

No.	Solution.			Resipus,		
	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O	$C_6H_5NH_3Cl$	$FeCl_3$	H_2O
1	26·47	3·69	69·84	95·59	0·42	4·08
2	24·17	5·22	70·61	75·86	3·75	20·39
3	22·43	5·37	72·20	65·95	7·18	26·87
4	23·62	5·34	71·04	89·45	3·41	7·14
5	21·13	6·78	72·09	61·15	14·03	24·82
6	17·58	8·95	73·47	62·53	15·04	22·43
7	14·53	12·12	73·35	58·64	15·75	25·61
8	13·07	12·52	75·00	51·79	15·37	32·84
9	10·87	15 93	73·10	63·35	17·09	29·56
10	10·49	17·70	71·81	36·14	17·95	45·91
11	9·19	19·96	70·85	38·05	19·08	42·87
12	8·46	22·13	69·41	64·61	18·42	26·97
13	7·79	23·78	68·43	52·22	20·51	27·27
14	7·87	25·80	66·33	54·49	26·26	19·25
15	7·19	26·58	66·23	24·69	24·88	50·43
16	6·87	24·22	65·91	20·66	25·96	53·38
17	6·90	27·68	65·42	48·77	37·52	13·71
18	6·26	29·75	63·99	47·81	36·60	15·59
19	6·25	30·38	63·37	56·07	36·49	7·44
20	5·61	32·51	61·88	50·68	30·50	11·82
21	5·01	36·76	58·23	48·95	38·12	17·93
22	3·98	37·58	58·44	44·48	34·62	16·90
23	3·85	38·75	57·40	46·68	36·95	14·37

From the data given in Tables 4 and 5, Fig. 2 was obtained.

From Figs. 1 and 2, it may easily be seen that under the conditions of our experiments there exist tow kinds of bouble salts, namely :

$FeCl_3.6C_6H_5NH_3Cl$ and $FeCl_3.2C_6H_5NH_3Cl$.

The former is in the form of yellowish crystals and the latter, bluish green needle-shaped crystals. These have also been, obtained by McKenzie, but the other two hydrated salts found by him could not be formed under the conditions of our experiments.

SUMMARY.

The equilibrium of the system consisting of ferric chloride, aniline hydrochloride, hydrogen chloride and water at 25·0° was studied and the existence of the two double salts, $FeCl_3.6C_6H_5NH_3Cl$ and $FeCl_32C_6H_5$ NH_3Cl, and the conditions under which they can exist have been ascertained.

Fig. 2.