On the Equilibria in the System:
Mercuric Chloride, Ammonium Chloride,
Potassium Chloride and Water at 25°C.

By

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Mercuric chloride and potassium chloride form from their aqueous solutions at 25° the following three double salts[1]:

$$HgCl_2KCl.H_2O, \quad HgCl_2.2KCl.H_2O \text{ and } 2HgCl_2KCl.2H_2O,$$

and mercuric chloride and ammonium chloride form at 30° the following four double salts[2]:

$$HgCl_2.NH_4Cl.H_2O, \quad HgCl_2.2NH_4Cl.H_2O, \quad 3HgCl_2.2NH_4Cl.H_2O,$$
$$\text{and } 9HgCl_2.2NH_4Cl.$$

On the other hand, potassium chloride and ammonium chloride form from their aqueous solutions two series of solid solutions with a gap. At 25° the gap is 27—95 molar percentages of ammonium chloride according to Uyeda[1] and about 17—97 according to Fock[4].

Stimulated by these facts, we have undertaken the study of the system consisting of mercuric chloride, ammonium chloride, potassium chloride and water at 25°, and the results are presented in this article.

Materials.

The salts were of Jp. Pharm. Mercuric chloride and potassium chloride were thrice recrystallised from neutral aqueous solutions, while

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1 H. W. Foote and Levy, Amer. Chem. J., **35**, 238 (1906).
2 P. M. Meerburg, Zs. anorg. Chem., **59**, 136 (1908).
8 K. Uyeda, Int. Cong. Apl. Chem., **22**, 237 (1912) ; Mem. Coll. Sci. Eng. Kyoto. Imp. Univ., **5**. 148 (1912).
4 A. Fock, Zs. Krystall., **28**, 337 (1897).

ammonium chloride was thrice recrystallised from an aqueous solution with some free ammonia. Ordinary distilled water was used.

Analytical Methods.

The analysis was carried out by ordinary methods. *Mercury* was determinend as mercuric sulphide. *Ammonia* was distilled into a known quantity of a standard sulphuric acid and the excess of the acid titrated back with a standard caustic soda with sodium alizarinsulphonate as indicator. The *total chlorine* was determined by Volhard's method, improved by Rothmund and Burgstaller. *Potassium* and *water* were estimated by calculation.

Experimental Procedure and Calculation of the Results.

The materials were mixed in certain calculated proportions and the mixture in a vessel was made to rotate in a thermostat at $25 \cdot 0°$ until equilibrium was attained.

When KCl is added to a system having $HgCl_2.2NH_4Cl.H_2O$ and NH_4Cl as the solid phases, the double salts, $HgCl_2.2NH_4Cl.H_2O$ and $HgCl_22KCl.H_2O$, form solid solutions and the single salts, KCl and NH_4Cl, also form solid solutions. In this case, the method used by Hayami[1] in this loboratory was adopted with some modification. A special tube of H–form, of a capacity of about 40 c.c., was used and in its horizontal part a hollow cork over which was stretched a piece of cotton cloth, instead of the latter only as Hayami did. This considerably reduced the time necessary to attain equilibrium. When NH_4Cl, or a solid solution of KCl in NH_4Cl, was one of the solid phases, it was nearly perfectly separated from the other, as it floated on the surface. But when a solid solution of NH_4Cl in KCl was formed, the separation of the two kinds of solid solutions became difficult.

In other cases, an Erlenmeyer flask of a capacity of about 30 c.c. was used. When two kinds of crystals were macroscopically observed and were separable by the dfference in densities, they were separeted mechanically as much as possible for analysis.

When the double salt, $9HgCl_2.2NH_4Cl$, is to be a solid phase, a state of supersaturation was retained and it required a long time to attain stable equilibrium, as Meerburg remarked[2]. Thus in this case a

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[1] Th:se Memoirs **4**, 363 (1920).
[2] *Loc. cit.*

small quantity of the crystals of $9HgCl_2.2NH_4Cl$ previously prepared was added and the rotation in the thermostat was further continued for two or three weeks.

When two kinds of solid phases, for example, $xNH_4Cl.(1-x)$ KCl and $HgCl_2y(NH_4Cl)_2.(1-y)(KCl)_2.H_2O$, are in equilibrium with a liquid solution and separable from each other though incomplete, their compositions were found graphically from the composition of the solution and that of each solid phase, mixed with a small quantity of the other and also with some mother liquor, in the following way.

Let the compositions of the solution and impure solid phases be represented by the general formula :

$$100mH_2O.XHgCl_2.Y(NH_4Cl)_2(100-X-Y)(KCl)_2.$$

We designate the two kinds of impure solid phases as A and B and take a special case for illustration :

	X	Y	m
Liquid solution	26·29	27·92	10·37
Solid phase A	3·00	5·00	0·18
Solid phase B	48·71	5·38	0·55

Fig. 1.
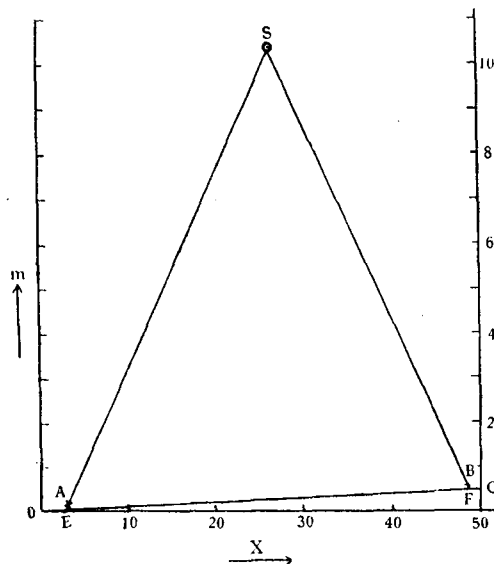
We take rectangular coordinates, taking m as the ordinates and X as the abscisses (Fig. 1). The point S represents the liquid solution and A and B the solid solutions. The point O represents an anhydrous solid phase, $x(NH_4)_2Cl_2.(1-x)K_2Cl_2$, with no mercuric chloride and C the other pure solid solution, $HgCl_2.y(NH_4)_2Cl_2(1-y)K_2Cl_2.H_2O$. Then the solid solutions containing no mother liquor must lie on the straight line OC and also on the straight lines, SA and SB, respectively. Thus the points of intersection, E and F, must correspond to the two solid solutions in question.

Fig. 2.

Then to find the positions of these points on the diagram of triangular coordinates, taking $HgCl_2$, $(NH_4)_2Cl_2$ and K_2Cl_2 as the components, plot the points, S, A and B, from the data given, and on the lines, SA and SB, plot the points, E and F (Fig. 2). Prolong the line EF to meet the lines representing the pure solid solutions respectively. The points of intersection will be the points required.

Results.

1. *The solid phases* :— $x(NH_4)_2Cl_2.(1-x)K_2Cl_2$ (I)

     and $HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.H_2O$ (II).

The results of the experiments are given in Table 1, in which the compositions of the liquid solutions and those of each of the solid solutions, somewhat mixed with the other and also with some mother liquor, are given in gram percentages.

Table 1.

No.	Liquid solution.				Solid solution (I).				Solid solution (II).			
	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O
1	47·80	24·61	0·00	27·59	—	—	—	—	—	—	—	—
2	42·87	23·11	1·84	32·18	2·89	95·20	0·36	1·55	65·73	19·93	9·38	4·96
3	39·93	21·62	4·73	34·71	2·71	95·17	0·28	1·84	65·54	17·96	11·55	4·95
4	32·96	20·74	6·88	39·42	1·43	95·54	0·64	2·39	63·26	12·63	17·78	6·33
5	31·87	20·08	7·99	40·06	4·35	91·30	1·70	2·55	63·26	12·44	18·89	5·41
6	30·37	19·44	8·45	41·74	1·25	94·92	1·56	2·24	63·32	10·88	19·78	6·02
7	28·80	19·37	9·85	41·98	2·28	79·32	16·60	1·80	62·08	10·36	21·34	6·22
8	28·88	19·32	9·68	42·12	2·59	22·72	71·93	2·76	62·69	9·58	22·22	5·51
9	27·31	17·49	11·42	43·78	3·34	13·00	81·50	2·16	60·77	7·84	26·52	4·87
10	24·49	14·40	13·05	48·09	2·92	9·60	81·10	6·38	61·16	4·52	28·43	5·89
11	23·57	12·09	15·83	48·51	2·49	6·79	88·65	2·07	61·32	3·62	30·65	4·41
12	20·04	8·38	19·17	52·41	5·29	3·48	89·18	2·15	61·17	2·66	31·62	4·55
13	18·04	5·40	21·71	54·85	2·25	2·06	93·80	1·89	60·57	1·36	33·47	4·60
14	16·52	3·04	23·57	56·87	2·34	1·55	93·26	2·85	59·38	0·74	35·12	4·76
15	14·76	0·00	26·45	58·79	—	—	—	—	—	—	—	—

From these data the compositions were calculated to be represented by the formula : $100mH_2O.XHgCl_2.Y(NH_4)_2Cl_2.(100-X-Y)K_2Cl_2$, and those of the pure solid phases were estimated graphically by the method above described. The results of the calculation and estimation are given in Table 2.

Table 2.

No.	Liquid solution.			Solid solution (I).					Solid solution (II).				
				Impure.			Pure.		Impure.			Pure.	
	X	Y	m	X	Y	m	X	Y	X	Y	m	X	Y
1	43·35	56·65	3·77	—	—	—	0·0	100·0	—	—	—	—	—
2	40·88	55·93	4·62	1·18	98·55	0·09	,,	99·9	49·28	37·91	0·56	50·0	37·8
3	38·60	53·05	5·06	1·10	98·69	0·11	,,	99·9	49·61	34·48	0·56	,,	34·2
4	33·59	53·65	6·05	0·58	98·94	0·15	,,	99·0	49·56	25·09	0·74	,,	24·2
5	32·73	52·34	6·20	1·82	96·88	0·16	,,	99·1	48·96	24·42	0·63	,,	22·3
6	31·95	51·87	6·62	0·51	98·33	0·14	,,	98·9	49·88	21·74	0·71	,,	21·0
7	30·04	51·26	6·60	0·98	96·10	0·12	,,	97·0	48·79	20 66	0·74	,,	18·9
8	30·24	51·31	6·65	1·35	30·15	0·22	,,	30·0	49·18	19·07	0·65	,,	18·1
9	29·52	48·00	7·30	1·81	17·86*	0·18	,,	17·2	46·95	15·74	0·57	,,	15·0
10	28·88	43·10	8·54	1·67	13·93	0·55	,,	12·0	49·16	9·22	0·71	,,	8·9
11	28·37	36·94	8·80	1·36	9·52	0·17	,,	9·0	48·55	7·74	0·53	,,	7·1
12	26·29	27·92	10·37	3·00	5·00	0·18	,,	4·7	48·71	5·38	0 55	,,	5·4
13	25·30	19·24	11·60	1·26	2·93	0·16	,,	2·6	48·47	2·76	0·55	,,	2·6
14	24·60	11·50	12·76	1·33	2·23	0·24	,,	2·5	47·43	1·49	0·58	,,	1·1
15	23·45	0·00	14·08	—	—	—	,,	—	—	—	—	,,	0·0

These results are graphically represented in Fig. 3, putting *m* out of consideration. As to the mutual solubility of KCl and NH₄Cl in solid solutions, the mean of the values of Fock and Uyeda was adopted and the portions, AQ and BR, represent those solid solutions. The line DE represents the solid solutions (II), in which the miscibility is complete. The curves, FP and PG, represent the liquid solutions and the point P represents the liquid solution in equilibrium with the three solid solutions.

2. *The solid phases* :— $HgCl_2.x(NH_4)_2Cl_2.(1-x)2K_2Cl_2.H_2O$
              and $2HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.2H_2O.$

In this case, both the solid solutions have no gap. They could not be separated from each other and the residues were analysed only for the ascertaining of their nature. The results are given in Table 3.
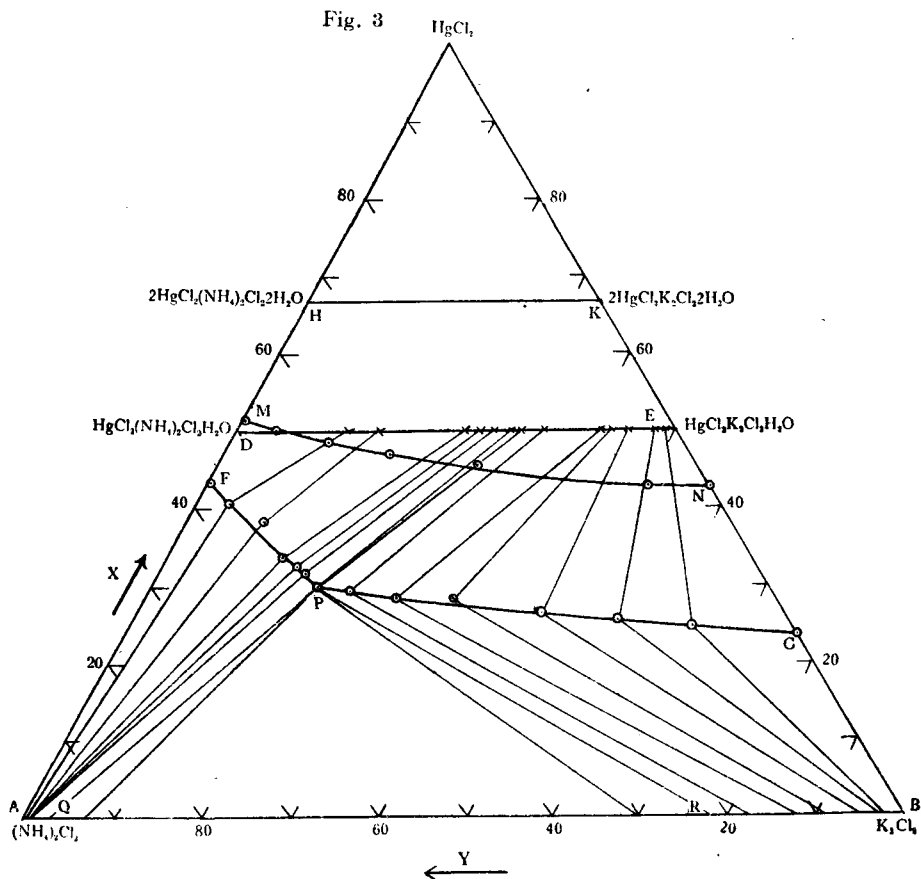
Table 3.

No.	Liquid solution.				Solid phases (mixed).			
	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O
1	56·31	21·01	0·00	22·68	—	—	—	—
2	51·01	18·54	2·57	27·88	66·37	20·63	6·92	6·08
3	46·50	15·30	5·83	32·37	72·95	9·77	12·63	4·65
4	41·54	11·90	9·05	37·51	69·52	5·75	18·31	6·42
5	37·07	8·64	12·28	42·01	61·84	4·15	19·17	14·84
6	29·02	1·94	18·88	50·16	60·58	0·70	29·00	9·72
7	27·34	0·00	20·45	52·21	—	—	—	—

From Table 3, Table 4 was calculated and the results are graphically represented in Fig. 3. The straight lines, DE and HK, represent the two kinds of solid solutions and the curve MN represents tho liquid solutions.

Table 4.

No.	Liquid solution.			Solid phases (mixed).		
	X	Y	m	X	Y	m
1	51·37	48·63	3·12	{50·00 {66·67	50·00 33·33	0·50 0·33
2	49·65	45·79	4·09	50·54	39·59	0·70
3	48·65	40·47	5·06	60·41	20·53	0·58
4	47·10	34·32	6·41	59·19	12·42	0·82
5	45·56	26·95	7·78	57·65	9·81	2·08
6	42·48	7·20	11·07	52·60	1·54	1·29
7	42·34	0·00	12·18	{50·00 {66·67	0·00 0·00	0·50 0·33

Fig. 3

3. *The solid phases* :— $HgCl_2$ and $9HgCl_2 (NH_4)_2Cl_2$.

The double salt, $9HgCl_2.(NH_4)_2Cl_2$ does not form any solid solution. The corresponding potassium salt does not exist. The results are given in Tables 5 and 6.

Table 5.

No.	Liquid solution.				Solid phases (mixed).			
	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O
1	15·63	1·60	0·00	82·77	—	—	—	--
2	16·11	1·56	0·18	82·15	93·64	1·14	0·00	5·02
3	16·64	1·47	0·47	81·42	90·26	2·53	0·02	7·19
4	17·00	1·44	0·61	80·95	87·84	2·70	0·03	9·43
5	18·16	1·40	0·94	79·50	94·08	1·45	0·08	4·37
6	19·24	1·23	1·44	78·09	88·54	3·19	0·15	8·12
7	21·56	1·16	2·03	75·25	75·05	2·50	0·38	22·09
8	25·54	0·94	2·85	72·67	96·35	0·84	0·12	2·69
9	26·20	0·80	3·64	69·36	93·65	2·53	0·52	3·30
10	26·73	0·76	3·86	68·65	85·46	2·13	3·04	9·37

Table 6.

No.	Liquid solution.			Solid phases (mixed).		
	X	Y	m	X	Y	m
1	79·43	20·57	63·38	{ 100 { 90	0 10	0 0
2	79·02	19·44	60·73	96·26	3·77	0·98
3	78·42	17·58	57·87	93·32	6·64	1·12
4	78·11	16·82	56·07	92·70	7·24	1·50
5	77·56	15·14	51·19	96·09	3·76	0·68
6	77·03	12·50	47·12	91·35	8·36	1·26
7	76·46	10·40	40·22	91·43	7·72	3·96
8	75·64	7·68	35·12	97·61	2·17	0·41
9	75·19	5·80	30·00	92·70	6·36	0·49
10	74·88	5·45	28·99	88·65	5·60	1·46

The results are represented in Fig. 4. The solubility is represented by the curve EF, the points, C aud D, representing the solid phases of the definite compounds respectively. The solution at the point F (No. 10) is in equilibrium with another solid phase besides the two, namely a solid solution of the series, $4HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.4H_2O$.

4. *The solid phases* :— $HgCl_2$ (I) and
$$4HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.4H_2O. \text{ (II)}.$$

The results are given in Tables 7 and 8 and graphically represented in Fig. 4. The liquid solutions are represented by the curve FH and the solid solutions by the straight line KL, where the position of K was not directly determined. The extension of HF to G represents a metastable equilibrium and is denoted by a broken line.

Table 7.

No.	Liquid solution.				Solid phase (II).				Solid phase (I).			
	$HgCl_2$	$(NH_4)_2$ Cl_2	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2$ Cl_2	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2$ Cl_2	K_2Cl_2	H_2O
1	25·12	0·00	4·66	70·22	–	—	—	—	—	—	—	—
2	25·75	0·47	4·05	69·73	78·78	0·49	6·73	14·00	—	—	—	—
3	25·68	0·56	3·97	69·79	79·42	0·80	8·37	11·41	98·77	0·01	0·03	1·19
4	27·85	1·31	3·47	67·37	81·70	1·54	5·07	11·69	99·19	0·12	0·39	0·30
5	29·23	1·85	3·15	65·77	75·69	2·32	6·60	15·39	98·45	0·16	0·31	1·08

Table 8.

No.	Liquid solution.			Solid phase (II).				Solid phase (I).		
				Impure.			Pure.	Impure.		
	X	Y	m	X	Y	m	Y	X	Y	m
1	74·74	—	31·49	80·00	—	0·80	0·0	—	—	—
2	75·02	3·50	30·61	85·39	1·33	2·29	1·7	—	—	—
3	74·84	4·11	30·65	82·13	2·11	1·78	2·4	99·11	0·03	0·02
4	74·29	8·84	27·08	86·14	4·13	1·86	6·0	99·00	0·30	0·05
5	73·69	11·84	24·99	80·86	6·29	2·48	6·3	99·04	0·40	0·16

5, *The solid phases* :— $9HgCl_2.(NH_4)_2Cl_2$ and
$$4HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.4H_2O.$$

The two solid phases were separated from each other and analysed. The data for equilibrium are given in Tables 9 and 10. The solubility curve is represented by FP in Fig. 4. The solid solutions coexisting with the liquid solutions are represented by the line KJ, of which the terminal points were not directly determined.

Table 9.

No.	Liquid solution.				Solid solution.			
	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O
1	28·55	1·94	3·14	66·38	78·06	2·57	6·23	13·14
2	29·98	2·57	3·01	64·44	79·54	3·04	5·48	11·94
3	30·83	2·87	2·83	63·47	80·44	3·38	4·39	11·79

Table 10.

No.	Liquid solution.			Solid solution.			
				Impure.			Pure.
	X	Y	m	X	Y	m	Y
1	72·90	12·56	25·54	81·38	6·80	2·06	5·6
2	71·40	15·53	23·13	81·80	7·94	1·85	6·5
3	71·25	16·82	22·24	83·01	8·74	1·83	7·3

6.   *The solid phases :—* $4HgCl_2.x(NH_4)_2Cl_2.(1-x)K_2Cl_2.4H_2O$ (I)

and $3HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.H_2O$, (II).

In this case, the two kinds of solid phases were found impossible to separate from each other and the residues were analysed only to ascertain their nature. The results are given in Tables 11 and 12 and in Fig. 4.

Table 11.

No.	Liquid solution.				Solid solutions (mixed).			
	HgCl₂	(NH₄)₂Cl₂	K₂Cl₂	H₂O	HgCl₂	(NH₄)₂Cl₂	K₂Cl₂	H₂O
1	31·74	3·07	3·14	62·05	76·99	3·55	6·31	13·15
2	29·96	2·52	3·60	63·92	80·63	3·76	9·17	6·44
3	28·24	1·81	4·42	65·53	74·71	2·53	9·41	13·35
4	27·36	1·21	5·20	66·23	74·47	1·74	9·99	13·80

Table 12.

No.	Liquid solution.			Solid solutions (mixed).		
	X	Y	m	X	Y	m
1	70·15	17·20	20·67	78·97	9·25	2·03
2	69·82	14·89	22·45	75·46	8·92	0·91
3	69·07	11·25	24·16	76·93	6·55	2·05
4	68·58	7·69	25·02	76·70	4·55	2·14

The solid phase (I) is represented by a portion of the line LJ and the solid phase (II) by a portion of the line MN. The potassium salt corresponding to $3HgCl_2.(NH_4)_2Cl_2.H_2O$ does not exist, but we find it in solid solutions with the ammonium salt. The terminal point N of the solid solutions on the side of the potassium salt could not be determined, exactly. The curve PS represents the liquid solutions, and at P and S it has another solid phase, $9HgCl_2.(NH_4)_2Cl_2$ or $2HgCl_2.(NH_4, K)_2Cl_2.2H.O$, respectively.

7.   *The solid phases :—* $3HgCl_2x(NH_4)_2Cl_2.(1-x)K_2Cl_2.H_2O$ (I)

and $2HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.2H_2O$ (II).

In this case also the two kinds of solid phases conld not be separated from each other. The results are given in Tables 13 and 14 and in Fig. 4.

Table 13.

No.	Liquid solution.				Solid solution (mixed).			
	HgCl₂	(NH₄)₂Cl₂	K₂Cl₂	H₂O	HgCl₂	(NH₄)₂Cl₂	K₂Cl₂	H₂O
1	53·06	13·00	0·00	33·94	79·16	12·84	0·00	8·00
2	53·84	12·96	0·52	32·68	82·43	11·67	0·69	5·21
3	51·88	12·47	0·56	35·09	83·17	10·26	2·51	4·06
4	47·96	11·00	1·72	39·32	77·51	9·82	6·74	5·93
5	42·92	9·09	2·63	45·36	80·70	7·27	7·37	4·66
6	36·17	6·48	3·75	53·60	74·41	5·49	9·73	10·37
7	33·95	5·51	4·13	56·41	76·08	4·83	10·19	8·90
8	32·63	4·87	4·47	58·03	70·20	5·29	11·63	12·88
9	30·94	4·05	4·66	60·35	77·88	4·06	9·71	8·35
10	28·23	2·52	5·31	63·94	78·40	2·92	11·97	6·71
11	26·60	1·27	5·85	66·28	72·07	1·50	14·34	12·09
12	26·57	0·90	5·96	66·57	74·86	1·47	12·62	11·05
13	26·48	0·67	6·02	66·83	76·31	1·11	13·58	9·00

Table 14.

No.	Liquid solutions.			Solid solutions (mixed).		
	X	Y	m	X	Y	m
1	61·65	38·35	5·94	{75·00 66·67	25·C0 33·33	0·25 0·67
2	61·40	37·52	5·62	72·76	26·13	0·69
3	61·35	37·44	6·26	73·11	22·88	0·54
4	60·70	35·33	7·50	67·58	21·72	0·78
5	60·64	32·59	9·66	71·69	16·39	0·62
6	60·87	27·54	13·59	70·17	13·13	1·47
7	61·21	25·22	15·33	71.17	11·48	1·25
8	61·44	23·24	16·47	67·00	12·80	1·85
9	61·82	20·53	18·32	73·57	9·73	1·19
10	63·72	14·45	21·75	72·86	6·88	0·94
11	65·90	7·71	24·75	70·67	3·72	1·79
12	66·95	5·73	25·33	73·70	3·69	1·64
13	67·64	4·35	25·72	73·48	2·70	1·31

The double salt, $3HgCl_2.(NH_4)_2Cl_2.H_2O$, dissolves the corresponding potassium salt only very slightly and the double salt, $3HgCl_2.K_2Cl_2.H_2O$, does not exist at all. The solid solutions of the two double salts are, however, formed to a wide extent in the middle part of the

diagram. The gap on the side of the ammonium salt is estimated to be about 0·8—10 in molar percentages. The point Q (No. 2) which lies apparently on the curve RS is an intersection of the two solublity curves, RQ and SQ, and is in equilibrium with the two mutually saturated solid solutions of the type (I) besides the solid solution (II).

The solubility curve SQ meets the curve PS at S. The solution at S (No. 13) is also in equilibrium with another solid solution, $4HgCl_2.z(NH_4)_2Cl_2(1-z)K_2Cl_2.4H_2O$.

8. *The solid solutions* :— $4HgCl_2.x(NH_4)_2Cl_2.(1-x)K_2Cl_2.4H_2O$
and $2HgCl_2.y(NH_4)_2Cl_2.(1-y)K_2Cl_2.2H_2O$.

In this case also the two kinds of solid solutions could not be separated from each other. The results are given in Tables 15 and 16 and in Fig. 4.

Table 15.

No.	Liquid solution.				Solid solutions (mixed).			
	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O
1	25·38	0·00	6·67	67·95	69·50	0·00	15·46	15·04
2	26·09	0·37	6·22	67·32	72·27	0·49	12·07	15·17

Table 16.

No.	Liquid solution.			Solid solutions (mixed).		
	X	Y	m	X	Y	m
1	67·64	0·00	27·29	71·17	0·00	2·32
2	68·08	2·42	26·44	75·68	1·31	2·37

The solubility curve TS meets the other two curves, PS and QS, at their point of intersection S, and the solution denoted by S is in equilibrium with the three solid solutions.

9. *The solid phases* :— $9HgCl_2.(NH_4)_2Cl_2$
and $3HgCl_2.x(NH_4)_2Cl_2.(1-x)K_2Cl_2.H_2O$.

In this case, one of the solid phases is a definte compound and the composition of the solid solutions could be determined. The results are given in Tables 17 and 18 and in Fig. 4.

Table 17.

No.	Liquid solution.				Solid solution.			
	$HgCl_2$	$(NH_4)_2Cl_2$	KC_2l_2	H_2O	$HgCl_2$	$(NH_4)_2Cl_2$	K_2Cl_2	H_2O
1	47·31	8·53	0·00	44·16	—	—	—	—
2	47·17	8·17	0·38	44·28	84·81	9·64	2·01	3·54
3	47·57	8·14	0·37	43·92	84·63	9·56	0·41	5·40
4	44·09	7·26	0·95	47·70	88·30	6·01	2·25	3·44
5	41·77	6·55	1·22	50·46	89·20	5·20	1·20	4·40
6	35·13	4·53	1·98	58·36	84·07	5·19	4·29	6·45
7	33·49	3·88	2·51	60·10	84·00	4·27	3·46	8·27
8	32·51	3·40	2·81	61·28	84·28	3·90	3·81	8·01

Table 18.

No.	Liquid solution.			Solid solution.			
				Impure.			Pure.
	X	Y	m	X	Y	m	Y
1	68·60	31·40	9·65	—	—	—	25·00
2	68·77	30·21	9·73	75·10	21·65	0·47	21·50
3	69·03	29·99	9·61	77·18	22·12	0·74	24·00
4	68·72	28·57	11·21	82·03	14·16	0·48	17·50
5	68·90	27·43	12·55	85·31	12·61	0·63	17·00
6	69·93	22·90	17·52	80·03	12·54	0·93	13·00
7	69·90	20·54	18·91	83·06	10·71	1·23	10·50
8	70·26	18·66	19·96	81·78	10·11	1·00	—

As to the solid solutions, $3HgCl_2.(NH_4,K)_2Cl_2.H_2O$, we have already described them. The curves, WZ and ZP, represent the liquid solutions. The point Z (No. 2) represents the liquid solution which has as the residues the compound $9HgCl_2.(NH_4)_2Cl_2$ and the two mutually saturated solid solutions, $3HgCl_2.(NH_4,K)_2Cl_2.H_2O$, on the ammonium salt side. The solution represented by the point P (No. 8) is the end of the solubility curve and has $4HgCl_2.(NH_4,K)_2Cl_2.4H_2O$ as one of the solid phases,

Fig. 4.
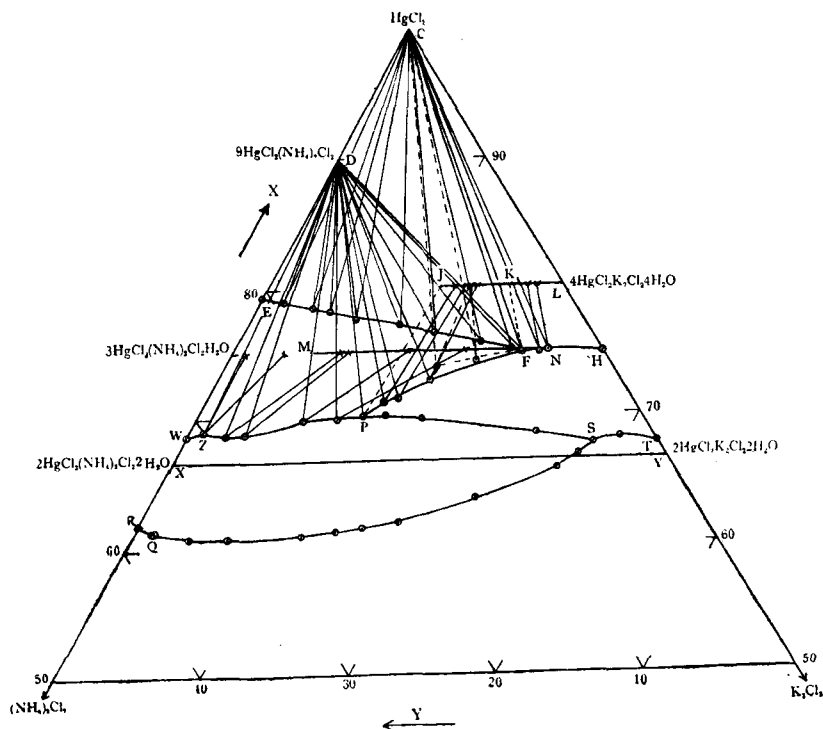
SUMMARY.

The equilibria in the system consisting of mercuric chloride, ammonium chloride, potassium chloride and water have been studied at 25.0°C.

The existence of the double salts between mercuric chloride and one of the alkali chlorides described in literature has been confirmed.

The solubility of the double salts and their solid solutions has been determined and the equilibrium relations have been represented graphically.

A graphical method has been described to find the composition of the solid solutions when two kinds of solid solutions are present mixed, and are somewhat incompletely separable from each other and from the mother liquor.

The donble salts and solid solutions, confirmed or found, are tabulated as follows :

$HgCl_2.KCl.H_2O$	$HgCl_2.NH_4Cl.H_2O$	$HgCl_2.(K,NH_4)Cl.H_2O$	(complete)
$HgCl_2.2KCl.2H_2O$	$HgCl_2.2NH_4Cl.H_2O$	$HgCl_2.2(K,NH_4)Cl.H_2O$	(complete)
$2HgCl_2.KCl.2H_2O$	——	$2HgCl_2.(K,NH_4)Cl.2H_2O$	(a gap)
——	$3HgCl_2.2NH_4Cl.H_2O$	$3HgCl_2.2(K,NH_4)Cl.H_2O$	(gaps)
——	$9HgCl_2.2NH_4Cl$	——	
——	——	$(K,NH_4)Cl$	(a gap)