The Reciprocal Salt-pair $(NH_4)_2SO_4 + 2KCl \rightleftharpoons K_2SO_4 + 2NH_4Cl$ in Water and in Ammonia–Water at 25°

BY ARTHUR E. HILL AND CHARLES M. LOUCKS[1]

In a recent publication by Partridge and Gabriel[2] a method for the preparation of potash from Polyhalite is developed, making use of the reaction between ammonium sulfate and potassium chloride to precipitate potassium sulfate from an aqueous solution saturated with ammonia, in which liquid the potassium sulfate is very insoluble. A complete study of this system has not been carried out previously at any temperature. The present report gives a study of the reciprocal salt-pair $(NH_4)_2SO_4 + 2KCl \rightleftharpoons K_2SO_4 + 2NH_4Cl$ at 25° in water and also in water saturated with ammonia at atmospheric pressure. The four three-component systems concerned in the above reaction all have been studied before. We have repeated the experiments in water, as a check, at all the isothermally invariant points, and added the corresponding points in solutions saturated with ammonia.

In the experimental work, the salts used were c. p. analyzed preparations which we crystallized and analyzed to check their purity. Suitable quantities of the salts were weighed into glass-stoppered solubility tubes, to which weighed quantities of water were added. In the three-component systems in which solid solution occurs, a special procedure was carried through, in order to ensure equilibrium in the solid state and to determine the length of time required for the establishment of equilibrium; in these cases all complexes were made up in duplicate, with the variation that in one tube salt A was dissolved completely in water before salt B was added while in the second the order was reversed, thus ensuring that the final state both of liquid and of solid solutions was approached from two directions. The tubes were rotated in a water thermostat at 25 ± 0.03°; it was found that for these salts, added as material passed through a 40-mesh sieve, equilibrium was attained in three days or less. Samples of liquid phase were withdrawn by means of a filtering pipet for analysis and weighed; in some cases the samples were diluted further and aliquot portions used. The analytical determinations made were four in number. (1) Total solids were determined by evaporation to constant weight, giving also the amount of water. This involves no special precautions except where ammonium chloride is part of the residue; in these cases the evaporation was carried out in a vacuum oven at 75 −80° and a vacuum of 25 inches (63.5 cm.); in the few hours necessary to bring the residue to dryness the loss of ammonium chloride was found to be not greater than a few hundredths of one per cent. and therefore negligible. (2) Chlorides were determined by the method of Volhard, the precipitated silver chloride being filtered off before back titration with thiocyanate. (3) Ammonium ion was determined by rendering the solution alkaline, distilling the free ammonia into 0.3 N hydrochloric acid and titrating back with 0.15 N potassium hydroxide, with methyl red as indicator. (4) Solutions containing only potassium chloride and ammonium chloride were analyzed by a special method, the water being driven off by evaporation at 75–80°, and the ammonium chloride then being volatilized by heating in an electric oven to 400°.

The composition of solid phases was determined sometimes by algebraic extrapolation of tie lines, as will be discussed later, and sometimes by direct analysis of the solid, which was filtered and centrifuged, the small amount of residual water being determined by drying and the small correction for adherent solution then applied to the analysis.

The data in Table I are in reasonably close agreement with the results of previous investigators. Lines 1–3 give for the system KCl–K₂SO₄–H₂O the solubility of the two separate salts and the composition of the invariant solution saturated with both. Lines 3–8 outline the system K₂SO₄–(NH₄)₂SO₄–H₂O; here the solid phase is a continuously varying solution, the composition of which, in equilibrium with various liquid solutions, is shown in the last column. The figure in each case is the mean of the values reached by approach from two directions, as explained above; the maximum deviation for any pair of results was 1.54% and the average deviation 1.07%, so that one may believe the figures to be correct to within less than 1%. Lines 8–10, for the system (NH₄)₂SO₄–NH₄Cl–H₂O, give the solubility of the two salts and the composition of the invariant solution. Lines 10–12 are for the system NH₄Cl–KCl–H₂O; the invariant solution (line 11) is saturated with two limiting solid solutions for which the composition is given; these results were reached by approaching equilibrium from two directions, are in close agreement with themselves and do not differ greatly from the results of previous workers. The letters A to G represent points shown in Fig. 1.

The four-component data are given in Table II and represented in Fig. 1. It will be seen that

(1) The material of this paper is from the thesis of Mr. Loucks, presented in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1937.

(2) Partridge and Gabriel, *Ind. Eng. Chem.*, **27**, 801 (1935).

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TABLE I

THE 3-COMPONENT SYSTEMS, IN WATER AT 25°

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		Wt., %				Equiv. per 1000 moles H₂O				Solid phase
		(NH₄)₂SO₄	KCl	K₂SO₄	NH₄Cl	(NH₄)₂SO₄	KCl	K₂SO₄	NH₄Cl	
1	D	0	26.42	0	0	0	86.7	0	0	KCl[3]
2	G	0	25.90	1.05	0	0	85.6	3.00	0	KCl + K₂SO₄
3	C	0	0	10.80	0	0	0	25.01	0	K₂SO₄[3,4]
4		10.36	0	9.59	0	35.46	0	24.79	0	(0.953K₂SO₄ + 0.047(NH₄)₂SO₄)
5		15.40	0	8.72	0	55.29	0	23.74	0	(0.925K₂SO₄ + 0.075(NH₄)₂SO₄)
6		28.31	0	6.12	0	117.5	0	19.34	0	(0.773K₂SO₄ + 0.227(NH₄)₂SO₄)
7		39.20	0	2.86	0	184.4	0	10.16	0	(0.195K₂SO₄ + 0.805(NH₄)₂SO₄)
8	B	43.42	0	0	0	209.1	0	0	0	(NH₄)₂SO₄[4,5]
9	F	26.12	0	0	16.35	123.7	0	0	95.6	(NH₄)₂SO₄ + NH₄Cl
10	A	0	0	0	28.32	0	0	0	133.0	NH₄Cl[5,6]
11	E	0	11.02	0	21.97		39.57	0	110.2	(0.166NH₄Cl + 0.834KCl) + (0.975NH₄Cl + 0.025 KCl)
12		0	26.42	0	0	0	86.7	0		KCl[5]

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TABLE II

(NH₄)₂SO₄ + 2KCl ⇌ K₂SO₄ + 2NH₄Cl IN WATER AT 25°

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	Satd. soln.			Solid phases present, solid solutions
Equiv. salt per 1000 moles H₂O				
(NH₄)₂SO₄	KCl	K₂SO₄	NH₄Cl	
109.8	..	8.68	100.5	I and II
99.4	..	9.03	102.9	I and II
85.8	..	12.63	107.0	I and II
74.7	..	14.28	110.0	I and II
59.5	..	16.5	113.7	I and II
48.9	..	18.4	117.2	I and II
17.4	..	24.5	128.0	I and II
1.55	..	28.1	132.1	I and II
...	10.5	23.0	127.7	I and II
...	24.2	16.6	119.2	I and II
...	31.0	9.43	113.5	II and III
...	28.1	13.4	117.4	II and III
Pt. O ...	26.7	15.3	118.0	I, II and III
...	29.2	14.5	115.7	I and III
...	39.8	10.5	92.4	I and III
...	55.2	7.34	66.1	I and III
...	57.6	6.23	52.0	I and III
...	65.5	5.19	35.8	I and III
...	75.3	4.32	18.1	I and III

there are but three fields, representing three separate solid phases. The name solid solution I is used for the solid phase varying continuously in composition from pure ammonium sulfate to pure potassium sulfate. Solid solution II, occupying a smaller part of the diagram, consists of

(3) System KCl–K₂SO₄: see Meyerhoffer and Saunders, *Z. physik. Chem.*, **28**, 453 (1899); Blasdale, *Ind. Eng. Chem.*, **10**, 344 (1918).

(4) System K₂SO₄–(NH₄)₂SO₄: see Mitscherlich, *Pogg. Ann.*, **18**, 168 (1830); Rudorf, *Ber.*, **6**, 482 (1873); Fock, *Z. Kryst.*, **28**, 337 (1897); Weston, *J. Chem. Soc.*, **121**, 1223 (1922); Vegard, *Z. Physik*, **5**, 17 (1921); Bovalini and Fabris, *Gazz. chim. ital.*, **65**, 617 (1935); Jänecke, *Z. angew. Chem.*, **42**, 1116 (1929).

(5) System (NH₄)₂SO₄–NH₄Cl: see Schreinemakers, *Z. physik. Chem.*, **69**, 557 (1909); Rivett, *J. Chem. Soc.*, **121**, 379 (1922); Rudorf.⁴

(6) System NH₄Cl–KCl: see Knopp, "Molekular Constitution und Wachstum der Kristalle," Leipzig, 1867; Chevreul, *Compt. rend.*, **85**, 493 (1877); Kirchmeyer, *Z. physik. Chem.*, **21**, 53 (1896); Biltz and Marcus, *Z. anorg. Chem.*, **71**, 166 (1911); Ugeda, 8th Int. Cong. App. Chem., Vol. XXII, 1912, p. 235; Fock,⁴ Vegard.⁴

ammonium chloride dissolving small amounts of potassium chloride, and solid solution III consists of potassium chloride dissolving ammonium chloride up to moderate amounts. The lines OF, OG and OE represent liquid solutions saturated each with two solid phases; the point O is the isothermally invariant liquid saturated with three solid phases.
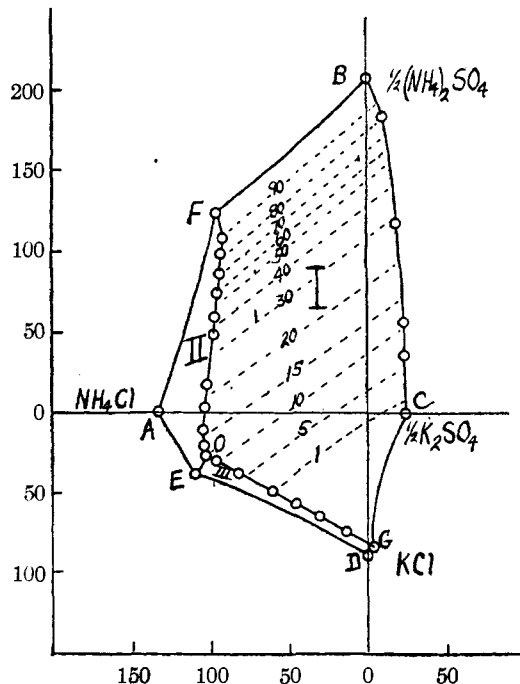

Fig. 1.—Four-component system, (NH₄)₂SO₄ + 2KCl ⇌ K₂SO₄ + 2NH₄Cl in water at 25°.

For the purpose of any industrial preparation of potassium sulfate by this reaction, it is necessary to investigate field I in order to ascertain the percentage of ammonium sulfate which would be present as contamination in the solid phase when

precipitated from liquid solution of varying composition. This was done by making up complexes which would give solutions in that field and determining the composition of both liquid and solid phases after equilibrium had been obtained. The data are given in Table III.

TABLE III

THE SOLID SOLUTION (K, NH₄)₂SO₄ IN WATER AT 25°

Liq. soln.; Wt., % salt				Composition of solid phase	
(NH₄)₂SO₄	NH₄Cl	K₂SO₄	KCl	Wt., % (NH₄)₂SO₄ by analysis	extrapolation
30.84	8.26	2.32	..	82.6	..
24.02	15.67	2.06	..	86.5	86.5
24.20	7.39	5.01	..	32.4	..
19.74	14.34	4.53	..	43.7	42.5
9.21	7.13	8.84	..	11.6	10.7
7.93	13.44	8.02	..	16.4	15.2
6.69	19.08	7.39	..	20.6	19.7
..	7.12	7.40	5.33	0.6	1.3
..	12.84	6.91	5.55	5.2	4.0
..	20.25	5.91	5.80	10.5	9.5
..	7.50	2.33	16.93	0.4	0

The composition of the solid phase was determined by analysis (column 5) and also by the method of extrapolation (column 6) discussed by Ricci and Loucks in a previous paper;[7] it will be observed that the two columns differ but slightly. The data of columns 5 and 6 are supplemented by data on the line BC, where we know (from Table I) the variation in composition of the solid phase in equilibrium with aqueous solution; for every percentage of ammonium sulfate in the solid phase two points are therefore known, one on the line BC and one in the interior of field I, making it possible to draw approximate contour lines across the field; these are shown as dotted lines in Fig. 1. By inspection, it appears that from the vicinity of the line BF, where the ammonium sulfate composition is high, the content falls rapidly in the direction of CG, so that there is a considerable proportion of the surface in which the amount of ammonium sulfate present remains under a few per cent.

The entire series of measurements was now repeated, using as solvent an aqueous solution saturated with ammonia at atmospheric pressure. The usual 28% ammonia solution, in suitable solubility tubes, was treated with the necessary salts in weighed amount and allowed to stand at 25° for some time, the stoppers being loosened from time to time to permit escape of the ammonia salted out. The tubes were then rotated in the thermostat from three to seven days. Samples of

(7) Ricci and Loucks, unpublished.

solution for analysis were forced up into a pipet by gentle pressure; the free ammonia was determined by delivering a weighed sample into a flask containing excess standard hydrochloric acid, afterward titrated with standard alkali. Other samples were analyzed for the other components as previously described.

The effect of ammonia upon the solubility of the four salts differs considerably. Potassium sulfate has its solubility depressed from 10.8% in water to 0.15% in 27% ammonia, as is shown in Table IV; ammonium sulfate suffers a relatively much smaller depression, from 43.4% in water to 13.4% in 23% ammonia, as is also shown in Table IV. For potassium chloride and ammonium chloride we have determined the solubilities in saturated ammonia solutions only, as appears later in Table V; the former drops from 26.4% to 12.34% in 23% ammonia, while the latter undergoes a rise in solubility from 28.3% to 29.8% in 19% ammonia, which becomes a marked rise (35.6%) when referred to water as solvent, in Table V.

TABLE IV

K₂SO₄ AND (NH₄)₂SO₄ IN AQUEOUS AMMONIA AT 25°

Wt., % NH₃	Wt., % K₂SO₄	Wt., % NH₃	Wt., % (NH₄)₂SO
0	10.80	0	43.41
13.90	1.286	12.84	26.80
18.20	0.639	18.33	19.31
22.35	.421	21.39	15.68
24.83	.220	22.62	13.97
27.04	.149	23.34	13.42

The plot of these figures gives an approximate straight line for ammonium sulfate, while the curve for potassium sulfate drops very rapidly with increasing ammonia concentration.

In Table V, the ammonia is given in weight per cent., as analytically determined, and represents solutions approximately saturated with the gas; the figures for the four salts are calculated by subtracting the free ammonia from the total and considering the residue of salts and water as 100%, to afford comparison with the water-basis in Tables I and II. In the case of the system K₂SO₄–(NH₄)₂SO₄, given in lines 3 to 11, the solubility of the potassium sulfate has been reduced to 0.2% at a maximum; the concentrations are so small that they cannot be determined accurately by our regular method of analysis, which gives that salt by difference. A direct determination of the potassium sulfate in several instances gave figures of the same order of magnitude, but again not accurately

TABLE V

THE 3-COMPONENT SYSTEMS IN AQUEOUS AMMONIA AT 25°

	(NH₄)₂SO₄ Wt., %	KCl	K₂SO₄	NH₄Cl	NH₃	(NH₄)₂SO₄ Equiv. per 1000 moles H₂O	KCl	K₂SO₄	NH₄Cl	Solid phase
1	D ...	15.26	...	...	23.65	...	43.47	...	...	KCl
2	G ...	15.30	Trace	...	23.87	...	43.60	Trace	...	KCl + K₂SO₄
3	C ...	...	0.20	...	27.04	...	...	0.42	...	K₂SO₄
4	2.85	...	...		25.60	7.99	...		...	(0.932K₂SO₄ + 0.068(NH₄)₂SO₄)
5	7.56	...	.23	...	24.51	22.32	...	.47	...	(0.776K₂SO₄ + 0.224(NH₄)₂SO₄)
6	11.35	...	...		23.77	35.01	...		...	(0.676K₂SO₄ + 0.324(NH₄)₂SO₄)
7	11.98			...	23.48	37.21	...		...	(0.525K₂SO₄ + 0.475(NH₄)₂SO₄)
8	13.54	...	.20	...	23.48	42.78	...	.42	...	(0.342K₂SO₄ + 0.658(NH₄)₂SO₄)
9	14.97	...	...		23.25	48.08	...		...	(0.186K₂SO₄ + 0.814(NH₄)₂SO₄)
10	17.55	...	.07	...	22.49	58.09	...	.14	...	(0.083K₂SO₄ + 0.917(NH₄)₂SO₄)
11	B 18.4	...	.0	...	23.3	61.1	...	.0	...	(NH₄)₂SO₄
12	F 4.66	...	...	33.72	18.56	19.68	...	..	183.5	(NH₄)₂SO₄ + NH₄Cl
13	A ...		...	35.59	19.16	...	...	..	185.9	NH₄Cl
14	E ...	2.86	...	33.59	18.58	...	10.90	..	177.8	(0.158NH₄Cl + 0.842KCl) + (0.977 NH₄Cl + 0.023KCl)

TABLE VI

(NH₄)₂SO₄ + 2KCl ⇌ K₂SO₄ + 2NH₄Cl IN AQUEOUS AMMONIA AT 25°

	(NH₄)₂SO₄	KCl Wt., per cent.	K₂SO₄	NH₄Cl	NH₃	(NH₄)₂SO₄ Equiv. per 1000 moles H₂O	KCl	K₂SO₄	NH₄Cl	Solid phase
1	1.93	..	0.56	27.95	18.55	10.29	...	2.27	184.4	Solid solns. I and II
2	1.00	..	.82	28.21	18.36	5.26	...	3.28	183.9	Solid solns. I and II
3	Pt. O	1.93	.40	27.49	18.70	...	8.87	1.60	179.5	Solid solns. I, II and III
4	..	4.14	.07	17.98	20.69	...	17.51	0.25	106.0	Solid solns. I and III
5	..	3.18	.17	21.71	19.92	...	13.93	.64	132.8	Solid solns. I and III
6	..	3.05	.16	22.16	20.00	...	13.47	.60	136.5	Solid solns. I and III
7	..	2.31	.31	25.53	19.10	...	10.58	1.21	162.8	Solid solns. I and III

enough to distinguish the small changes occurring from line 3 to line 11; we may imagine, however, a fairly regular decrease from 0.2% to zero.

In the case of the other system showing solid solutions, namely, the system NH₄Cl–KCl (lines 12–14), the curve for liquid solubilities is changed greatly from that found in pure water, because of the considerable decrease in solubility of the potassium chloride and increase in solubility of the ammonium chloride. The invariant liquid solution is correspondingly (line 14) of a widely different composition than that found for water as solvent (Table I, line 11). The two invariant solid solutions, however, are found to be of the same composition, within narrow limits of analytical error, whether in pure water as solvent or aqueous ammonia as solvent (Table I, line 11; Table V, line 14).

Table VI gives the data of the four-component system in aqueous ammonia as solvent; here, as previously in Table V, the ammonia is given as true per cent. of the total solution, the salts as referred to the residue after the ammonia has been subtracted. The data are plotted in Fig. 2. It is apparent that solid solution I [K₂SO₄ + (NH₄)₂-

SO₄] appears as solid phase at nearly all concentrations possible for the liquid phase, leaving only narrow limits for the solid solutions II and III. The line OG, representing saturation with respect to solid solutions I and III, can be dis-
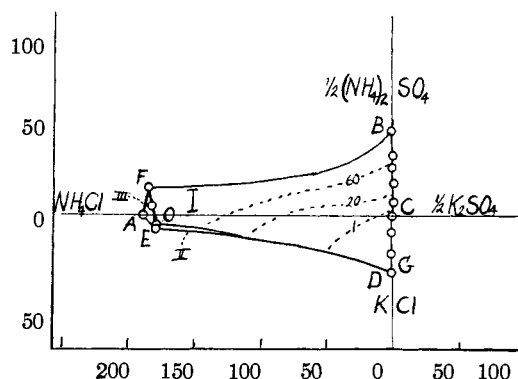

Fig. 2.—Four-component system, (NH₄)₂SO₄ + 2KCl ⇌ K₂SO₄ + 2NH₄Cl in ammonia water at 25°.

tinguished from the three-component solubility curve ED only for a part of its course (lines 3–7), because of the extremely low solubility of potassium sulfate.

The variation in composition of the solid solu-

TABLE VII
THE SOLID SOLUTION (K, NH₄)₂SO₄ IN AQUEOUS AMMONIA AT 25°

| | | Liquid solution | | | | | | | Solid phase, |
(NH₄)₂SO₄	NH₄Cl	Wt., per cent. K₂SO₄	KCl	NH₃	(NH₄)₂SO₄	Equiv. 1000 moles H₂O NH₄Cl	K₂SO₄	KCl	% (NH₄)₂SO₄
8.29	2.75	0.12		23.45	34.45	13.21	0.38		67.9
5.31	8.55	.24		22.77	22.93	45.56	.79		73.7
4.19	13.49	.25		21.79	18.95	75.32	.86		76.2
2.63	21.86	.42		19.75	12.96	132.9	1.57		67.4
2.33	22.47	.47		19.86	11.57	137.8	1.77		63.6
	23.04	.70	0.74	20.06		139.7	2.61	3.20	59.7
2.49	3.20	.46		21.42	9.38	14.88	1.32		16.0
2.03	9.00	.68		20.02	8.11	44.35	2.06		20.5
1.75	14.13	.84		18.96	7.42	73.94	2.70		23.6
	3.08	.07	3.83	21.29		14.44	0.20	12.89	0.5
	5.97	.09	3.70	20.66		28.85	.27	12.86	.8
	13.62	.21	3.43	18.82		71.70	.68	12.95	1.7
	3.10	.06	7.76	17.20		14.51	.17	26.07	0.3
	6.04	.08	7.55	19.64		30.47	.25	27.33	.7

tion I was investigated in equilibrium with the aqueous ammonia solutions: the results are given in Table VII.

A few of the contour lines, from the data of Table VII, are drawn in Fig. 2. It appears that the ammonium sulfate concentration of the solid solution drops off very rapidly in the direction from FB to D, and that solid phases of relatively small content in ammonium sulfate could be obtained from solutions varying considerably in composition.

Summary

The reciprocal salt-pair $(NH_4)_2SO_4 + 2KCl \rightleftharpoons K_2SO_4 + 2NH_4Cl$ has been studied at 25° in water as solvent and in water saturated with ammonia at one atmosphere pressure. The solid phases existing are three solid solutions: (1) ammonium chloride containing potassium chloride up to a maximum of 2.5%, (2) potassium chloride containing ammonium chloride up to a maximum of 16.6% and (3) potassium sulfate–ammonium sulfate in all ratios. The potassium sulfate–ammonium sulfate phase was investigated as to variation of composition with variation in the liquid phase.

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Experimental Tests of Recent Theories Descriptive of the Salting-out Effect[1]

BY PENROSE S. ALBRIGHT[2]

I. Introduction

In the Debye theory[3] of the "salting-out" effect the ions are considered as rigid spheres with the neutral molecules, solvent and solute, behaving as a continuous medium whose interaction with the ions is determined by the macroscopic dielectric constant. As a result of the electrical field existing about the ions the component of higher dielectric constant is pulled preferentially into the field and the one of lower dielectric con-

stant is forced out. Thus, in the ternary system solvent–solute–electrolyte, there is a change of concentration of non-electrolyte solute with changing distance from the ion. In aqueous solution the solvent usually concentrates in the region of the ions because the dielectric constant of water is more frequently higher than those of other neutral molecules. In such cases there is an increase of the solute to water ratio in the portions of the solution removed from the field of the ions and there results a reduction of the solubility of the solute, referred to the total water present. If the dielectric constant of the water is lower than that of the solute, a "salting-in" will result.

The important quantity to be determined in an

(1) More complete details of this work may be found in a thesis presented in August, 1936, to the Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
(2) Present address: Southwestern College, Winfield, Kansas.
(3) Debye, Z. physik. Chem., 130, 56 (1927).