If the above coefficients of diffusion be corrected to 16° (corr. 3 per cent. per degree), we get $k_{CO_2} = 1.378$ and $k_{O_2} = 1.607$, and it is evident that they agree fairly well with the values of Stefan and Hüfner (cited above). Hagenbach's figures (11.37 uncorr.) for the diffusion of oxygen in water must therefore be considered quite incorrect, due to the source of error mentioned above. Further, the ratio between the coefficients of oxygen and carbon dioxide, according to the above experiments, is *1.166*, and this result closely approximates to that calculated for the gases in question from the measurement of the rates of escape of the gases from solution.[1]

Finally, the relation of the results may be considered to be the so-called Exner Rule, according to which the rate of diffusion of a gas is inversely proportional to the square root of its density.

That is, $k_{O_2} : k_{CO_2} = \sqrt{1.5202} : \sqrt{1.1056} = 1.173$.

This result closely agrees with the ratio obtained in the above research.

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THE FORMATION OF DOUBLE SALTS.

[FOURTH PAPER.]

BY H. W. FOOTE AND P. T. WALDEN.

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In two previous articles from this laboratory[2] the double salts which form from water have been compared with those which form from non aqueous solvents at the same temperature. It was shown that when a double salt crystallizes from water with water of crystallization, the latter in general appears to be an essential constituent of the salt, and the substitution of another solvent may affect the type of double salt produced giving an entirely different ratio between the single salts and between these and the solvent of crystallization. On the other hand, double salts which crystallize from various solvents without combining with them appear always to form the same types. In short, double salts with solvent of crystallization are really triple molecular compounds and have no necessary type relation to the true double salt, which is essentially a dual molecular compound.

It is evident that a double salt may form without solvent of crystallization from certain solvents, giving always the same types, and may combine with others, changing the type of salt. In the present investigation, mixtures of cupric chloride with potassium chloride and with ammonium chloride have been studied. Both systems have been thoroughly investigated previously in water solution and only hydrated double salts ob-

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[1] Tor Carlson, *Meddel. fran Vet. Akad. Nobelinstitut.*, Vol. II, No. 5, 1911.

[2] THIS JOURNAL, **32**, 618 (1910); **33**, 459 (1911).

tained at 25°. Using alcohol as solvent in one case and both alcohol and acetone in the other, we have obtained double salts which did not combine with the solvents and they were different in type from the hydrates.

I. Potassium and Cupric Chlorides.

The double salts which form from water have been very thoroughly investigated by Meyerhoffer.[1] He found that up to 57° only one double salt, $2KCl.CuCl_2.2H_2O$, is produced from water while above this temperature the anhydrous 1 : 1 salt can be obtained. Meyerhoffer also noted that the anhydrous salt can be obtained by crystallization from acetic acid containing a little water. We have determined the solubility relations at 25° of potassium and cupric chloride in varying proportions in both absolute alcohol and acetone and in each have obtained the 1 : 1 double salt without solvent of crystallization.

The anhydrous cupric chloride used in this work was prepared by heating the recrystallized dihydrate at 130–140° to constant weight. The method was entirely satisfactory. Absolute alcohol and acetone were obtained by redistilling the best commercial products. In the case of alcohol, sodium was added before distilling and only the middle distillate was used.

In the first experiments, salts and alcohol were mixed in varying proportions and shaken in glass-stoppered bottles in the thermostat at 25°, usually for two days or more. The method was the same which has been used repeatedly for double salt work, but in this case we were unable to obtain consistent results. It became evident after considerable work had been done that complete equilibrium was not being reached. This appeared to be due partly to the fact that the potassium chloride was quite insoluble in the alcohol, which made reaction very slow, and partly to there being small lumps present which were not thoroughly disintegrated even by long shaking and repeated crushing in the bottle. The difficulty was entirely overcome by placing in the bottles a number of short glass rods. The rods were long enough to prevent their becoming wedged crosswise in the bottles but also short enough to allow considerable play so that when the bottles were rotated, the rods kept falling, first at one end of the bottle and then at the other. We think that this device is more serviceable than placing glass or metal beads in the bottle, as the rods have more weight and strike a harder blow. Certainly the arrangement made the difference between success and failure in our own work for we had no further difficulty in reaching equilibrium. We believe the device will be of service whenever equilibrium is to be reached by reaction between difficultly soluble solids in contact with solutions.

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[1] *Z. physik. Chem.*, 3, 336 (1889); 5, 97 (1890).

In analyzing the solutions, copper was usually determined by titrating with sodium thiosulfate after addition of potassium iodide, using starch solution to determine the end point. The amount of potassium chloride in solution was very small and was usually not determined. When necessary to determine it, however, copper was removed by hydrogen sulfide and potassium weighed as chloride. The residues were heated at 130°–140° to determine alcohol or acetone and copper determined by thiosulfate. Potassium chloride was calculated by difference. The residues were exceedingly fine and usually retained a small amount of solvent mechanically. When this was small in amount, and evidently not an essential part of the residue, the results are usually calculated free from solvent, as will be seen.

The following results were obtained, using alcohol:

TABLE I.—SOLUBILITY OF POTASSIUM-CUPRIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. KCl in solution.	Per cent. $CuCl_2$ in residue.	Per cent. KCl in residue.	Per cent. alcohol in residue.	Residue contains
1	1.27	(0.28)[1]	15.88	84.12	...	KCl and $KCl.CuCl_2$
2	1.51	(0.28)[1]	57.43	42.57	...	
3	2.15	...	64.04	35.60	0.36	$KCl.CuCl_2$
4	5.25	...	64.24	35.46	0.30	
5	30.16	...	65.34	32.02	2.64	
	Calculated for $KCl.CuCl_2$		64.32	35.68	...	
6	34.17	(0.21)[1]	67.91	21.35	10.74	$KCl.CuCl_2$ and $CuCl_2.C_2H_5OH$
7	34.45	(0.21)[1]	70.88	12.38	16.74	
8	34.29	(0.21)[1]	72.48	7.29	20.23	
9	33.97	0.00	75.83	0.00	24.17	$CuCl_2.C_2H_5OH$
	Cal. for $CuCl_2.C_2H_5OH$		74.48	...	25.52	

The results in the table show clearly that one salt only forms at 25° from alcohol. The salt was present in pure condition in numbers 3–5 where the composition of the solution varies widely and the residue is practically constant. In numbers 1–2, with constant solubility and variable residue, potassium chloride and double salt were the solid phases. Number 9 shows the solubility of pure cupric chloride at 25°, and also the composition of the solid phase which evidently contains one molecule of alcohol.

The results using acetone as solvent are given in Table II. Equilibrium was obtained without any difficulty using glass rods in the bottle as described before, but on the other hand, a new and quite unexpected complication presented itself. In the first experiments, the bottles were rotated at 25° for several days and after a time the solution darkened and decomposition set in. The reaction was not specially investigated,

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[1] The average of two determinations made in preliminary work. Potassium was not directly determined in the series given above.

but there appears to be a slow action of the cupric chloride on the acetone, producing cuprous chloride which is at first held in solution but may afterwards precipitate, affecting the composition of both solution and residue. The action appears to be negligible for the first twenty-four hours but when once begun seems to run more rapidly. The series of results given below was obtained by rotating the bottles for not more than twenty-four hours. The residues in numbers 1–5 were dried at 130°–140° before analysis to free them from traces of included acetone.

TABLE II.—SOLUBILITY OF POTASSIUM-CUPRIC CHLORIDES IN ACETONE AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. KCl in solution.	Per cent. $CuCl_2$ in residue.	Per cent. KCl in residue.	Per cent. acetone in residue.	Residue contains
1	0.34	(0.38)[1]	6.31	93.69	...	KCl and $KCl.CuCl_2$
2	0.34	(0.38)[1]	59.94	40.06	...	
3	0.48	...	64.39	35.61	...	$KCl.CuCl_2$
4	1.50	...	64.23	35.77	...	
5	2.06	...	65.00	35.00	...	
Calculated for $KCl.CuCl_2$			64.32			
6	2.49	0.27	65.13	32.75	2.12	$KCl.CuCl_2$ and $CuCl_2.C_3H_6O$
7	2.32	...	75.24	11.79	12.97	

The results show the formation of the same anhydrous 1 : 1 salt that was obtained from alcohol. This was to be expected provided the acetone did not enter into the compound. The solubility relations are entirely different from the first case, due to the much smaller solubility of cupric chloride in acetone.

The composition of the limiting solutions between which pure double salt forms is shown by numbers 1–2 and 6–7. The pure double salt was present in numbers 3–5. The acetone found in the residues, numbers 6–7, is only approximately correct as acetone is lost very rapidly indeed by the cupric chloride while being freed from the mother liquor and water is taken up. For the same reason it was difficult to determine the composition of the pure cupric chloride acetonate. The solubility of pure cupric chloride in acetone was found to be 2.49 and 2.32 per cent. in two experiments, but one of the residues gave, on drying, an amount of acetone several per cent. below the calculated value for $CuCl_2.C_3H_6O$, and another, not so thoroughly dried, several per cent. more than the theoretical. There can be no doubt, however, that the above formula for the acetonate is correct, corresponding to the alcoholate.

II. Ammonium and Cupric Chlorides.

A number of hydrated double salts of ammonium and cupric chlorides have been described but the investigation of Meerburg[2] has shown quite conclusively that the compound $2NH_4Cl.CuCl_2.2H_2O$ is the only stable

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[1] Determined in preliminary work.

[2] *Z. anorg. Chem.*, 45, 1 (1905).

double salt that forms from water between —11° and 80°. No anhydrous salt has been described, though Meyerhoffer[1] mentions briefly that he obtained one.

In our work mixtures of the single salts were treated with alcohol just as in the previous case. Glass rods were used in the bottles to assist in reaching equilibrium. In analyzing solutions, only copper was determined (by titration with thiosulfate as before) as the amount of ammonium chloride dissolved was very small, and the solubility relations are sufficiently clear from the data found for cupric chloride alone. The residues were very fine and always included a small amount of alcohol. In the table, the composition of the dry residue is given except in the last two results, where the alcohol formed a compound.

The following results were obtained:

TABLE III.—SOLUBILITY OF AMMONIUM-CUPRIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. $CuCl_2$ in residue.	Per cent. NH_4Cl in residue.	Per cent. alcohol in residue.	Residue contains
1	4.65	10.70	89.30	...	NH_4Cl and $NH_4Cl.CuCl_2$
2	4.74	63.54	36.46	...	
3	6.45	71.45	28.55	...	$NH_4Cl.CuCl_2$
4	12.90	72.33	27.67	...	
Cal. for $NH_4Cl.CuCl_2$		71.53	28.47	...	
5	34.92	72.54	24.56	2.90	$NH_4Cl.CuCl_2$ and $CuCl_2.C_2H_5OH$
6	34.50	74.04	8.09	17.87	

The single 1 : 1 salt is the only one formed. It is entirely different in type from the hydrated double salt but corresponds to the potassium cupric compound, which it also resembles in color.

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EQUILIBRIUM IN THE SYSTEM: LEAD NITRATE AND PYRIDINE.

BY JAMES H. WALTON, JR., AND ROY C. JUDD.

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Pyridine occupies in many ways a unique position among organic solvents. Not only does it dissolve many organic compounds—such as the fats, oils and certain of the carbohydrates—but it also exercises a solvent action on a large variety of inorganic compounds. Moreover, just as water unites with many of these inorganic compounds as water of crystallization, so many of them take up pyridine of crystallization. With pyridine, types of solubility curves have been obtained which are analogous in every way to those resulting from solubility determinations when water was used as a solvent.

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[1] *Z. phys. Chem.*, 3, 340 (1889).