Chlorotrifluoromethane decomposes under similar conditions, producing chiefly carbon tetrafluoride, chlorine and dichlorodifluoromethane. The yields of less volatile substances are very small.

The vapor tensions of a number of the compounds mentioned above have been very carefully measured.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE UNIVERSITY OF NORTH CAROLINA]

The System Ferrous Sulfate–Manganous Sulfate–Water at 0 and 25°

BY A. McLAREN WHITE

This study originated in a class problem involving the crystallization of manganese-free ferrous sulfate from steel mill pickle liquor. Data on the solubility of manganous sulfate in the presence of ferrous sulfate were found to be almost completely lacking. Retgers[1] reported that at 10° two series of solid solutions, one heptahydrate and the other pentahydrate, were formed. Raab[2] found at the temperature of melting ice a single heptahydrate solid solution over the entire concentration range. He also reported solubility measurements, but in the presence of an unspecified amount of sulfuric acid. Preston and Gilchrist[3] made a study of this system at 25°, concluding that two series of solid solutions, one heptahydrate and the other pentahydrate, were formed. They likewise reported solubility data over the entire concentration range. The present work is a revision and extension of their study.

Experimental Work

Baker's C. P. ferrous sulfate and manganous sulfate were placed in varying amounts with distilled water in 8-ounce nursing bottles. The samples at 0° were packed in ice and frequently shaken. Those at 25° were kept in a shaking thermostat accurate to within 0.1°. When the bottles were prepared a small amount of sulfur dioxide was injected to reduce any oxidized iron. This was also found sufficient to prevent further oxidation. Samples at 25° were maintained at this temperature for more than one year, and those at 0° a somewhat shorter time.

Samples for analysis were obtained by weight. The analytical procedure of Majdel,[4] involving precipitation of manganese as $MnO(OH)_2$ from a 0.3 N sulfuric acid solution by means of ammonium persulfate, was followed, and the iron subsequently precipitated as ferric hydroxide. The precipitates were ignited and weighed as Mn_3O_4 and Fe_2O_3, respectively. Sulfates were determined as barium sulfate. Results could be duplicated satisfactorily.

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[1] Retgers, *Z. physik. Chem.*, **16**, 580 (1895).

[2] Raab, *Arch. minéral soc. sci. Varsovie*, **5**, 35 (1929).

[3] Preston and Gilchrist, Jr., unpublished undergraduate thesis, University of North Carolina, 1932.

[4] Majdel, *Z. anal. Chem.*, **81**, 14 (1930).

The System at 0°.—In Table I are recorded data on the solubility of manganous sulfate in the presence of ferrous sulfate at 0°. These indicate that the solid phase in equilibrium with the liquid is a heptahydrate solid solution. The solubility curve, Fig. 1, is in agreement with that of Raab[2] at high manganese concentrations, but at high iron concentrations the present work indicates considerably greater solubility than hitherto reported. Recalculating the solubility of pure ferrous sulfate as given by Raab in terms of weight per cent., a value of 12.41% is obtained. The solubility reported in the "International Critical Tables" is 13.58%, while an extrapolation of the curve of Fig. 1 indicates a solubility of 13.9% for pure ferrous sulfate. The solubility of pure

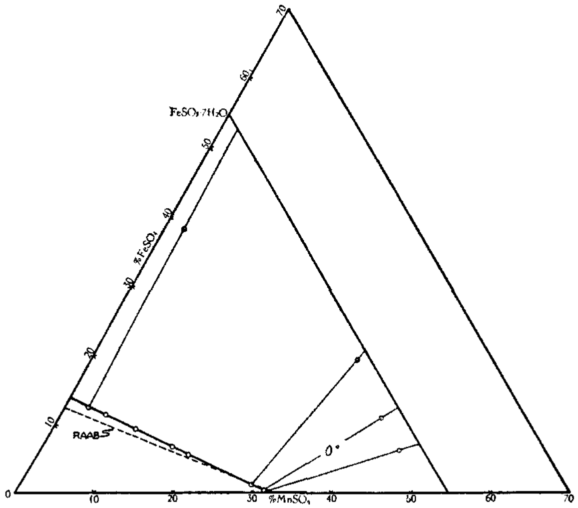

Fig. 1.

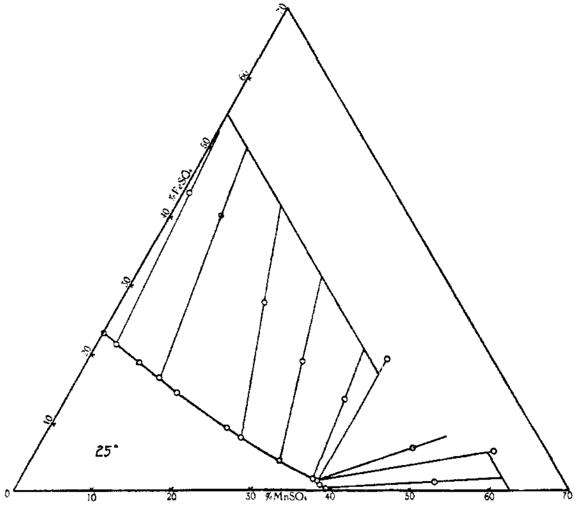

Fig. 2.

manganous sulfate is, according to Raab, 32.37%; according to the "International Critical Tables," 34.76%; and from an extrapolation of the present work, 32.0%.

TABLE I

SOLUBILITY OF MANGANOUS SULFATE IN AQUEOUS SOLUTIONS OF FERROUS SULFATE

Bottle number	Solution, %		Residue, %		Solid phase
	$MnSO_4$	$FeSO_4$	$MnSO_4$	$FeSO_4$	
			Solubility at 0°		
31	3.07	12.55	2.24	38.48	Heptahydrate solid solution
32	5.83	11.44			
34	10.66	9.26			
35	16.52	6.84			
39	19.18	5.69			
29	29.30	1.25	33.73	19.41	
37	31.28	0.34	40.84	10.97	
30	31.84	0.14	45.50	6.16	
			Solubility at 25°		
16	39.39	0.33	52.51	1.46	Pentahydrate solid solution
8	38.29	0.85			
15	37.83	1.33	47.23	6.22	Isothermally invariant point
			37.50	19.43	
			57.72	5.80	
14	36.95	1.82	35.09	13.63	Heptahydrate solid solution
10	31.46	4.34	27.05	19.01	
19	24.96	7.78	18.10	27.45	
9	22.45	9.28			
2	13.57	14.39			
1	10.33	16.62	6.38	40.07	
4	6.82	18.94			
17	2.55	21.41	0.78	43.40	
22	0.09	23.09			

The System at 25°.—Two series of solid solutions, one heptahydrate and the other pentahydrate, are stable at 25°. Both solid solutions are in equilibrium with a solution containing 37.83% $MnSO_4$ and 1.33% $FeSO_4$. At this isothermally invariant point it proved possible to separate and analyze independently the two types of crystals, as shown in Table I. The water content indicated is probably low due to marked efflorescence, particularly of the heptahydrate crystals, but the ratio of iron to manganese is considered correct. The limiting concentration of the heptahydrate solid solution is 37.5% $MnSO_4$, while that of the pentahydrate solid solution is 5.7% $FeSO_4$. The heptahydrate solid solution may evidently be considered as composed of two components, limiting solid solution and pure ferrous sulfate, and the pentahydrate solid solution as made up of limiting solid solution and pure manganous sulfate. Analysis for sulfates indicated no hydrolysis. The solubility of ferrous sulfate, here reported as 23.09%, is an excellent agreement with that of Agde and Barkholt,[5] 22.98%. The solubility of manganous sulfate, reported as 39.39%, is in good agreement with that of 39.42% obtained by interpolation from the "International Critical Tables."

Summary

1. The solubility of manganous sulfate in the presence of ferrous sulfate has been determined over the entire concentration range at 0 and 25°.

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(5) Agde and Barkholt, *Z. angew. Chem.*, **39**, 851 (1926).

2. At 0° a single heptahydrate solid solution is formed. At 25° two series of solid solutions, one heptahydrate and the other pentahydrate, are formed.

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A Revision of the Atomic Weight of Potassium

BY GREGORY PAUL BAXTER AND WILLIAM MARSHALL MACNEVIN

In two papers dealing with the analysis of potassium chloride and potassium bromide, Hönigschmid and Goubeau[1] describe experiments which lead to the atomic weight 39.104 for potassium. Although the result agrees with that found by Richards and Archibald[2] it is considerably higher than that obtained later by Richards and Staehler[3] and Richards and Mueller,[4] who analyzed the chloride and bromide, respectively, and obtained the value 39.096. A puzzling situation is thus created, for the difference between the two values, which amounts to nearly 0.01 unit of atomic weight, is far larger than the apparent experimental error of the comparatively simple analytical operations involved and points to a serious uncertainty either in the purity of the potassium salts or silver, or in the analytical operations.

We have made a long series of analyses of potassium chloride, by comparison with silver, using potassium salts of different origin, and have been utterly unable to find any evidence in favor of the higher value. In fact our results confirm very closely those of Richards and Staehler and Richards and Mueller.

The Preparation of Pure Potassium Chloride

Nine different samples of potassium salt were investigated.

Sample A.—The starting point in this case was commercial potassium chlorate of which the original source could not be ascertained. The chlorate was crystallized three times in Pyrex vessels with centrifugal drainage and then was converted to perchlorate and chloride by gentle heating in a platinum dish. After the chloride had been extracted from the mixture with cold water, the perchlorate was twice crystallized in platinum. Next the perchlorate was converted to chloride by heating in a platinum dish and the chloride was twice precipitated with hydrogen chloride. The chloride was then fused in a platinum dish, dissolved in water, the solution filtered through a platinum sponge crucible and evaporated to crystallization. Sample A_2 was obtained by crystallizing the chloride extracted from the perchlorate, three times from hydrochloric acid and once from water.

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(1) Hönigschmid and Goubeau, *Z. anorg. allgem. Chem.*, **163**, 93 (1927); **177**, 102 (1928).

(2) Richards and Archibald, *Proc. Amer. Acad.*, **34**, 373 (1903).

(3) Richards and Staehler, THIS JOURNAL, **29**, 623 (1907).

(4) Richards and Mueller, *ibid.*, **29**, 639 (1907).