

The system $\text{CuF}_2\text{--HF--H}_2\text{O}$ at 0 °C

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Abstract

The system $\text{CuF}_2\text{--HF--H}_2\text{O}$ has been investigated at 0 °C. The solid phases in equilibrium with the solutions are $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ and CuF_2 .

Introduction

Several years ago a series of phase diagrams involving HF, H_2O and an ionic fluoride were investigated at Texas A&M University. The system $\text{CuF}_2\text{--HF--H}_2\text{O}$ was not reported at the time. This system, at 20 °C, was studied by Kurtenacker et al. [1] in 1933. Since relatively few points were reported, their data are quite incomplete. They reported that $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ is in equilibrium with solutions containing 6.6–34.5 wt.% HF. More recently, Opalovskii and Tyuleneva [2] reported the results of their study of this system at 0 °C. While they reported the solid phases $\text{CuF}_2 \cdot 3\text{H}_2\text{O}$, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, CuF_2 and $\text{CuF}_2 \cdot 3\text{HF}$, Aliev [3], who studied the system at 0, 10 and 25 °C, reported only CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ as solid phases. The conclusions of our study with respect to solid phases are in agreement with those of Aliev.

Experimental

Schreinemaker's [4] method of wet residues was employed in this work.

Samples containing an excess of CuF_2 in $\text{HF--H}_2\text{O}$ solutions of various compositions were placed in ethylene glycol/water baths held at 0 ± 0.03 °C and constantly agitated. The minimum time required for the samples to reach equilibrium was determined by periodically analyzing samples until no further change was noted in the composition of the liquid. Generally, it took 6–10 d to attain equilibrium.

After equilibrium had been reached, portions of the liquid phase and of the wet residue were weighed,

placed in volumetric flasks, dissolved in water and brought to volume. Several ml of hydrochloric acid were needed to dissolve the wet residues. Aliquots were taken for analyses for copper and fluoride.

Hydrofluoric acid (HF, Baker Analyzed, Reagent Grade) and anhydrous hydrogen fluoride (HF, General Chemical, code 72) were used in this work. Cupric fluoride dihydrate, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ was prepared by reacting copper(II) carbonate with an excess of 48% hydrofluoric acid, washing with absolute alcohol and drying at 70 °C. Where a sample was to have a high percentage of HF (low water), white CuF_2 was prepared from the carbonate and anhydrous HF. It was washed many times with the HF but not separated nor dried to avoid picking up moisture. All CuF_2 and its hydrates were prepared on the same day the samples were placed in the bath.

Iodometry [5] was used for the analyses for copper throughout most of this investigation. For low concentrations, the copper was complexed with tetraethylenepentamine. Absorbancy was determined at 644 m μ and compared with a curve prepared from standard solutions.

Total fluoride was determined by a modified Willard and Winter's [6] approach. Aliquots were placed in 60% HClO_4 and steam distilled at 135 °C [7]. Aliquots of the distillate were buffered at pH 3.0 and titrated with a 0.1 N $\text{Th}(\text{NO}_3)_4$ solution which had been standardized against a NaF solution using Alizarin Red S as indicator.

Results and discussion

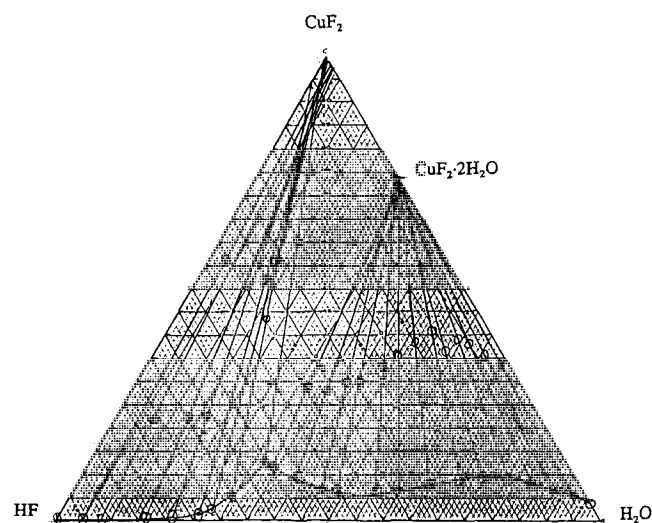
The results of the analyses of the solutions are given on a wt.% basis in Table 1 and presented in the diagram of Fig. 1. Only two solid phases, CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, were found to be in equilibrium with their solutions.

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TABLE 1. Analyses of the solutions and the wet residues

| Solution (wt.%) | | Wet residue (wt.%) | | Composition of solid phase |
|-------------------|-------|--------------------|-------|--|
| CuF_2 | HF | CuF_2 | HF | |
| 3.37 | — | — | — | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 5.46 | 2.51 | 33.71 | 1.69 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 6.90 | 5.48 | 35.37 | 3.78 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 8.30 | 8.83 | 38.07 | 5.05 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 9.05 | 12.89 | 39.21 | 6.79 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 9.16 | 17.13 | 36.58 | 10.69 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 8.75 | 21.42 | 40.68 | 10.85 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 7.84 | 27.49 | 38.23 | 15.09 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 6.77 | 33.98 | 35.57 | 19.23 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 6.26 | 38.46 | 33.28 | 23.33 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 6.11 | 45.60 | 29.90 | 29.11 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 6.71 | 48.03 | 29.81 | 31.89 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 9.23 | 51.42 | 27.98 | 36.73 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 12.00 | 54.13 | 28.72 | 39.81 | $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ |
| 12.80 | 55.56 | 60.31 | 25.24 | CuF_2 |
| 4.94 | 65.56 | 43.33 | 39.85 | CuF_2 |
| 1.96 | 70.71 | 56.09 | 31.68 | CuF_2 |
| 1.21 | 73.41 | 51.93 | 35.63 | CuF_2 |
| 0.61 | 78.48 | 22.46 | 61.19 | CuF_2 |
| 0.38 | 83.20 | 22.25 | 64.66 | CuF_2 |
| 0.07 | 91.64 | 22.01 | 71.14 | CuF_2 |
| 0.06 | 95.12 | 56.85 | 49.46 | CuF_2 |
| 0.01 ^a | 100 | | | |

^aRef. 8.Fig. 1. The system $\text{CuF}_2\text{-HF-H}_2\text{O}$ at 0 °C.

The hydrate is in equilibrium with solutions containing 0–54.4 wt.% HF, while CuF_2 exists from 54.4–100 wt.% HF.

The solubility data are similar to those reported by Kurtenacker *et al.* [1] in their 20 °C study. They reported a maximum solubility of CuF_2 of 12.1 g (100 g)⁻¹ of solution at 21.2 wt.% HF over the range 6.6–34.5 wt.% HF, while we found a maximum solubility of 9.16 g

(100 g)⁻¹ of solution at 17.13 wt.% HF over the same HF concentration range. We found a maximum solubility of 12.80 g (100 g)⁻¹ of solution at 55.56 wt.% HF over the whole range.

The solubility data are also similar to those of Aliev [3] and not very different from those of Opalovskii and Tyuleneva [2]. Aliev found a solubility of 9.98 g (100 g)⁻¹ of solution at 18.54 wt.% and 9.36 g (100 g)⁻¹ of solution at 55.2 wt.% HF, while Opalovskii and Tyuleneva found 9.40 g (100 g)⁻¹ of solution at 19.10 wt.% HF and 5.05 g (100 g)⁻¹ of solution at 60.6 wt.% HF. These maxima in solubilities do not coincide with those in this study. However, solubilities do not change rapidly with HF concentration changes over these regions.

The big problem is in the nature of the equilibrium solid phases. While Aliev [3] reported the existence of CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ as the solid phases, he reported that the transition occurs at 52 wt.% HF. Since there are no points between 52.70 and 55.2 wt.% HF in this study (the former is in the hydrate region and the latter in the non-hydrate region), we consider that little disagreement with our figure of 54.4 wt.% HF exists. However, Opalovskii and Tyuleneva [2] reported the following solid phases and their HF concentration ranges: $\text{CuF}_2 \cdot 3\text{H}_2\text{O}$, less than 12.50 wt.% HF; $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, 12.50–61.47 wt.% HF; CuF_2 , 63–80.6 wt.% HF; $\text{CuF}_2 \cdot 3\text{HF}$, 81.5–100 wt.% HF. The published ternary phase diagram appears to substantiate this claim. However when we replotted their data in order to obtain the same coordinates as those in the plot of our data, we discovered that the plot does not agree with that published and does not substantiate their claim for the solid phase $\text{CuF}_2 \cdot 3\text{H}_2\text{O}$. Support for $\text{CuF}_2 \cdot 3\text{HF}$ is also weak. At high HF concentrations, tie lines approach being parallel with the HF– CuF_2 side of the triangle. Rather small errors in analyses of the wet residues or of the liquid phases would make significant changes in the location of the intersection of the tie lines with the triangle edge. At least one tie line which might have been taken as evidence for the existence of $\text{CuF}_2 \cdot 3\text{HF}$ originates from well within the CuF_2 solid phase region.

Jache and Cady [8], in their study of the solubility of fluorides of metals in anhydrous HF, reported that the wet residue taken from the bottom of the containers after solubility determinations contained 0.28 mol HF per mol CuF_2 . This has generally been interpreted as indicating that the fluoride was unsolvated by HF.

We have also replotted the data of Aliev [3]. Whilst the plot is not as pretty as that published, it is consistent with the solid-state phases reported. There is no evidence for the existence of either the trihydrate or $\text{CuF}_2 \cdot 3\text{HF}$.

Opalovskii and Tyuleneva [2] cite the $\text{AgF-HF-H}_2\text{O}$ system [9] in which several hydrates, hydrogen fluorates and a mixed solvate appear. The behavior of silver(I) fluoride and copper(II) fluoride are quite different. The silver salt, having considerable affinity for HF and for water, is very soluble in both solvents and in mixtures of the two. Silver(II) fluoride shows little solubility in HF [8].

We are led to the conclusion that the solid phases in equilibrium with the solution at 0 °C are CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$.

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