

DIFFERENTIAL THERMOANALYTICAL INVESTIGATION OF Fe(II) SALT SOLUTIONS FROZEN AT DIFFERENT PRESSURES

I. SOLUTIONS FROZEN AT NORMAL PRESSURE

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In the $\text{H}_2\text{O}-\text{FeCl}_2$ and $\text{H}_2\text{O}-\text{Fe}(\text{ClO}_4)_2$ systems frozen under non-equilibrium conditions the nearly eutectic solution is supercooled, and then solidifies in a glassy form. The temperatures of the glass-to-supercooled liquid transition and of the crystallization of the quasi-eutectics, as well as some points of the solidus and liquidus curves were measured by the DTA method. The results are in good agreement with the changes in the Mössbauer spectra of these solutions.

Only incomplete data can be found in the literature on the phase conditions of the $\text{H}_2\text{O}-\text{FeCl}_2$ and especially of the $\text{H}_2\text{O}-\text{Fe}(\text{ClO}_4)_2$ systems [1, 2]. These data do not allow the explanation of some anomalies, e.g. the disappearance of the Mössbauer spectra of rapidly frozen aqueous FeCl_2 and $\text{Fe}(\text{ClO}_4)_2$ solutions in certain temperature ranges [3–8]. In order to elucidate the phenomena, we have performed DTA measurements on these systems; some of the results were reported earlier [9, 10]. In this publication results are given of measurements carried out close to the eutectic concentration.

Experimental

The rapidly frozen samples were prepared in the cell shown in Fig. 1a by immersion into liquid nitrogen. By this method rapid supercooling can be achieved (at an average cooling rate of $3-4^\circ/\text{sec}$). The prepared sample was placed into the boring of the brass block held in liquid nitrogen (see Fig. 1b). After removal of the N_2 bath, the block was warmed with room-temperature air at an average rate of $1^\circ/\text{min}$. The temperature at the outer wall of the cell was measured with a copper-constantan thermocouple, as was the temperature difference between the interior of the sample and the outer wall of the cell. The thermocouple junctions were placed at the same height. This "one-cell" method, the theoretical relations of which are known [11], is more convenient than the previously used "two-cell" method [9] because it is more sensitive. (With the two-cell method, the difference

between the temperatures of the sample and the reference material [water] was measured. The two metal cells were fitted into two symmetrical borings one under the other in the axis of a cylindrical brass block. The measurements with this apparatus were carried out similarly to those made with the one-cell apparatus,

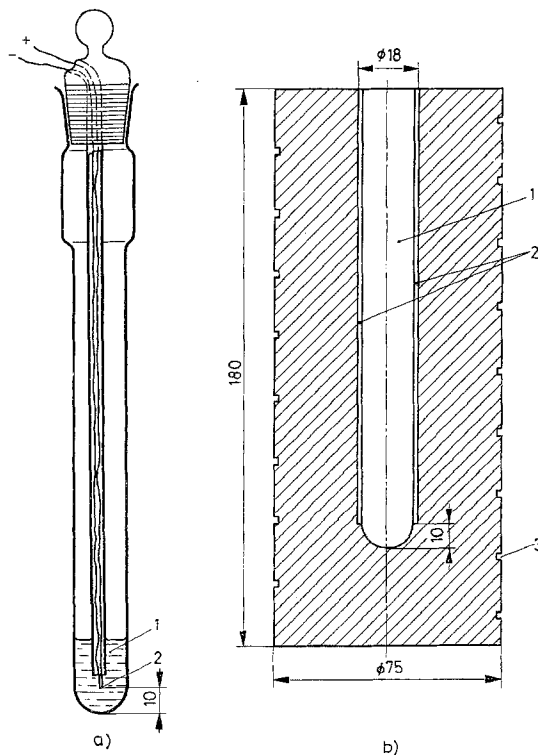


Fig. 1. a: Measuring cell (glass ampoule), 1 — sample; 2 — thermocouple junction. b: Brass block, 1 — boring for glass ampoule; 2 — notches for thermocouple wires; 3 — slot for heating wire

but when the samples were cooled, smaller supercooling rates could be achieved. During warming, the heat-transfer conditions are more complicated. The two-cell apparatus was used when the phase diagram of the $\text{H}_2\text{O}-\text{FeCl}_2$ system was determined and when the effect of the warming rate was measured.) The thermo-voltages were measured vs. time with two compensographs with sensitivities adjustable between ± 3.5 and $\pm 178.5 \mu\text{V}/\text{cm}$ (Laboratorni Pstroje N. P. Praha, Type EZ-3).

Results

The DTA curves of 2 and 7 mole % $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solutions are shown in Fig. 2, and the DTA curves of 6, 7.3 and 10 mole % $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ solutions in Fig. 3. The curve in Fig. 2A is similar to that published in our previous paper [10] for