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

I. SOLUTIONS FROZEN AT NORMAL PRESSURE

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In the $H_2O-FeCl_2$ and $H_2O-Fe(ClO_4)_2$ 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 $H_2O-FeCl_2$ and especially of the $H_2O-Fe(ClO_4)_2$ 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 $Fe(ClO_4)_2$ 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 $3-4°/sec$). 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 $1°/min$. 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,
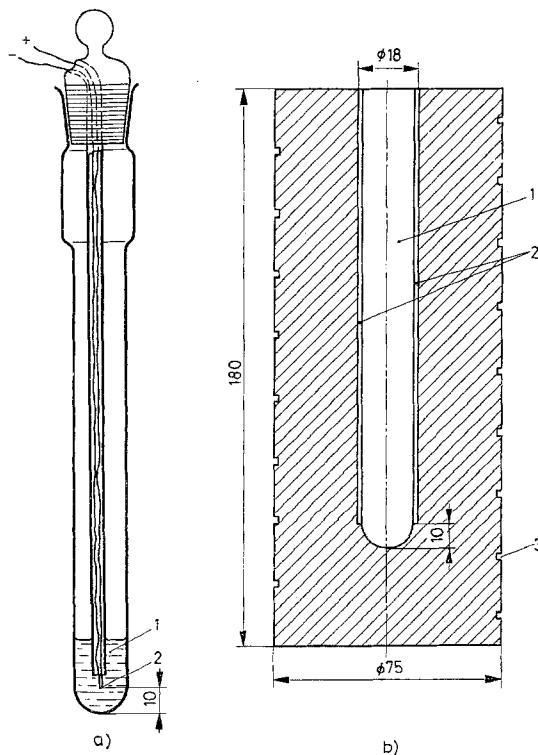

Fig. 1. a: Measuring cell (glass ampoule), 1 — sample; 2 — thermocouple junction. b: Brass block, 1 — boring for glass ampoule; 2 — notches for thermocouple wires; 3 — slot for heating wire

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 $H_2O-FeCl_2$ 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 ± 178.5 $\mu V/cm$ (Laboratorni Pristroje N. P. Praha, Type EZ-3).

Results

The DTA curves of 2 and 7 mole% $FeCl_2 \cdot 4H_2O$ solutions are shown in Fig. 2, and the DTA curves of 6, 7.3 and 10 mole% $Fe(ClO_4)_2 \cdot 6H_2O$ solutions in Fig. 3. The curve in Fig. 2A is similar to that published in our previous paper [10] for

1 mole% $Fe(ClO_4)_2 \cdot 6H_2O$ solution (the numbers and signs of the peaks are the same); the curve shows two melting peaks and one crystallization peak. When the experiments described in the above-mentioned paper were repeated with $FeCl_2$
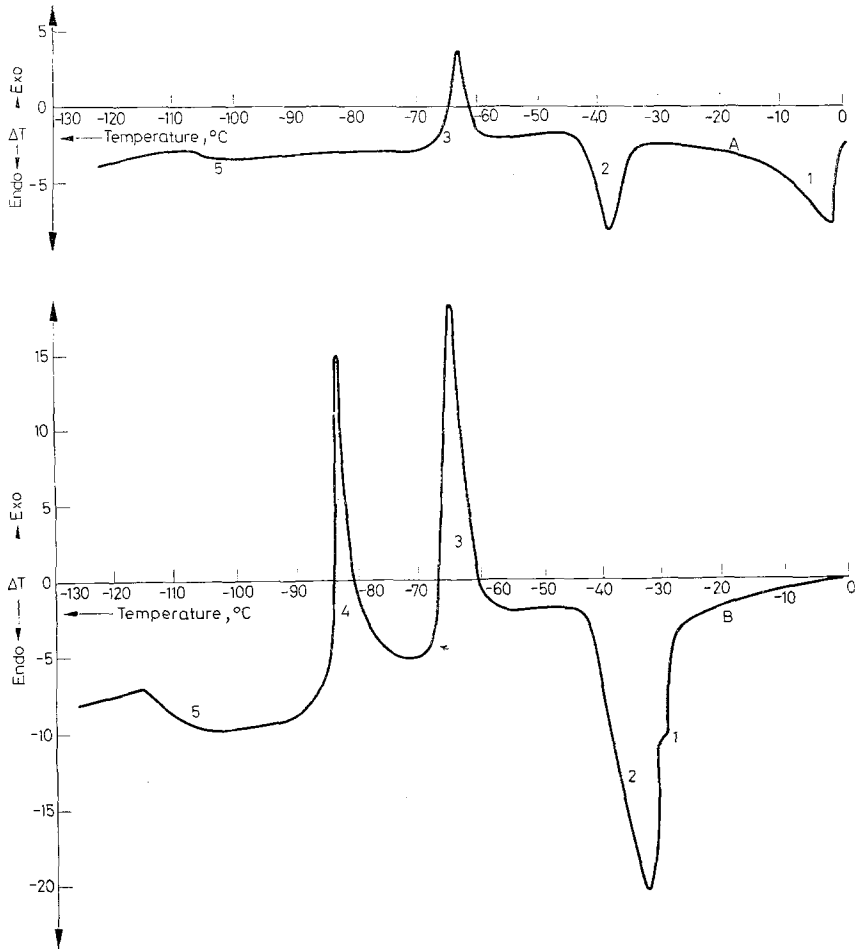

Fig. 2. DTA curves measured on $FeCl_2 \cdot 4H_2O$ solutions frozen in liquid nitrogen. Rate of warming about 1°/min. A — 2.0 mole%; B — 7.0 mole%. Effects: 1 — melting of primarily formed ice or dissolution of the salt; 2 — melting of eutectic phase; 3 — crystallization of supercooled liquid of quasi-eutectic composition; 4 — crystallization of ice in excess of the eutectic composition; 5 — glass-to-supercooled liquid transition

solutions, results of the same character were obtained, so here we disregard describing them in detail. The similarity of the two systems exists not only at low and medium concentrations (0.4 − 4 mole%) but also at concentrations close to the eu-
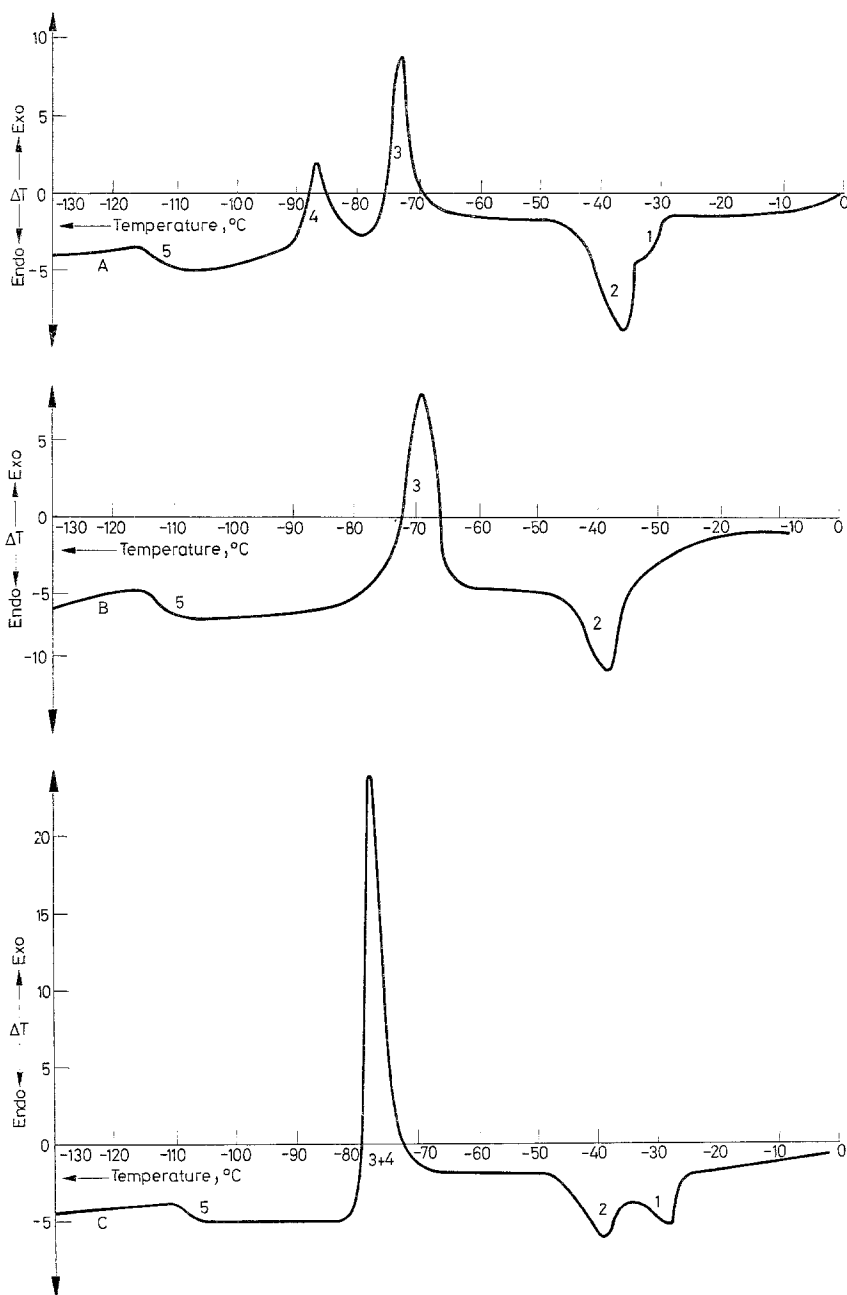
Fig. 3. DTA curves measured on $Fe(ClO_4)_2 \cdot 6H_2O$ solutions frozen in liquid nitrogen. Rate of warming about 1°/min. A — 6.0 mole%; B — 7.3 mole%; C — 10.0 mole%. (Effects are the same as in the case of $FeCl_2$)

tectic composition (6 — 8 mole %) see Figs 2B — 3A. A maximum of five effects can be observed in the figures (see explanation to Figs 2 and 3). On the curves published earlier [9, 10] only effects 1, 2 and 3 could be seen since in the investigated con-
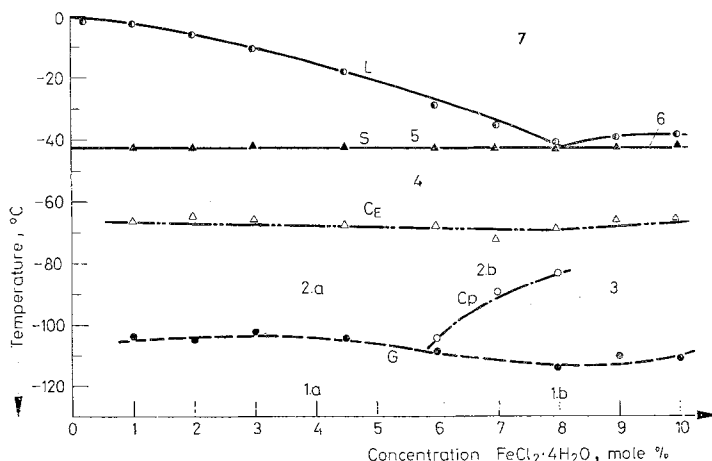

Fig. 4. Phase diagram for $H_2O - FeCl_2 \cdot 4H_2O$ system. L — liquidus line; S — solidus line; C_E — crystallization of quasi-eutectics; C_p — crystallization of pure component; G — glass-to-supercooled liquid transition. (Numbers are explained in the text)
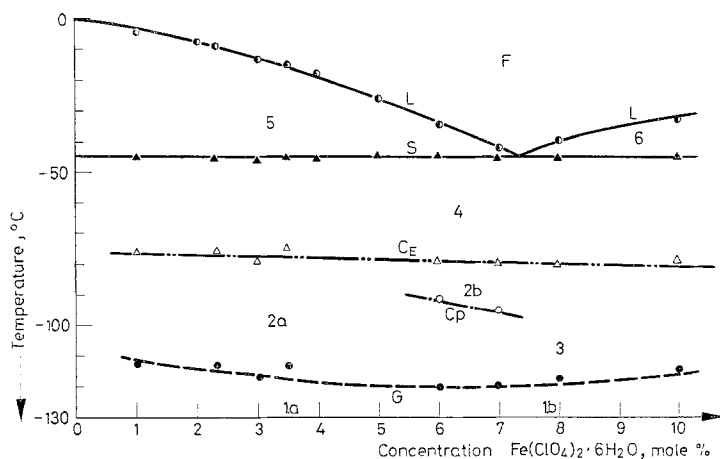

Fig. 5. Phase diagram for $H_2O - Fe(ClO_4)_2 \cdot 6H_2O$ system. (Symbols are the same as in Fig. 4)

centration and temperature range there are no effects. The exothermic peak 4 appears between —105 and —85° at concentrations of 5 — 8 mole %, while the base-line shift 5 (characteristic of a glassy transition, and indicating a change in the specific heat) appears between —120 and —105° at concentrations higher than 2 mole %. On the basis of all our data measured, phase-diagrams were established

for both systems. The data for the $H_2O - FeCl_2$ system were measured by the two-cell, and those for the $H_2O - Fe(ClO_4)_2$ system by the one-cell method (Figs 4 and 5). Although measurements were carried out down to 0.2 mole%, the results measured in the range 0.2 − 1 mole% are not shown, as the effects could not be observed accurately because of the noise, or could not be observed at all. From the effect of concentration on the parameters of the Mössbauer spectra and on the exothermic and endothermic peaks, however, it is probable that similar phase transitions take place in the concentration range below 1 mole%.

Corresponding to the five effects, five lines can be seen on the phase diagrams. The areas on the diagram are as follows: 1. Below line G a) between 0.2 and 6 mole%: glassy eutectics + crystalline ice, b) between 6 and 10 mole%: glassy substance; 2. a) area $G - C_E$ for 0.2 − 6 mole% and b) area $C_P - C_E$ for 6 − 10 mole-%: supercooled liquid with eutectic composition + crystalline ice; 3. area $G - C_P$ 6 − 10 mole%: supercooled liquid of high viscosity; 4. crystalline eutectics + + crystalline pure component; 5. molten eutectics + crystalline salt; 7. homogeneous liquid.

The states shown on the phase diagram can also be observed visually when the solution frozen in a glass ampoule is warmed. On rapid cooling primary crystallization of ice can be seen at 0 − 5 mole% while at 5 − 10 mole% the whole sample gives a translucent, cracked, green glass. On warming, only the melting of ice can be seen at low concentrations. On the warming of a 6 mole% "glass", the following sequence of phenomena can be observed: 1. formation of viscous liquid; 2. formation of growing ice-crystals; 3. with crystallization of the eutectics the whole sample becomes crystalline; 4. melting of the sample.

The eutectic data measured by us are presented in Table 1.

Table 1

Eutectic data measured for the $H_2O - FeCl_2 \cdot 4H_2O$ and
$H_2O - Fe(ClO_4)_2 \cdot 6H_2O$ systems

System	Eutectic temperature °C	Eutectic composition mole%
$H_2O - FeCl_2 \cdot 4H_2O$	−42.5 ± 0.5	8.2 ± 0.5
$H_2O - Fe(ClO_4)_2 \cdot 6H_2O$	−45.0 ± 0.5	7.3 ± 0.5

On the basis of the phase diagram, the course of the curves in Figs 2 and 3 can be explained as follows.

For a solution of eutectic concentration there is no indication of the presence of ice or water (see Fig. 3B). The entire water content is in the eutectics, and thus only effects 2, 3 and 5 appear. Near the eutectic concentration (6 − 8 mole%) the primary crystallization of ice takes place only partly or not at all, which is the consequence of the temperature dependence of crystallization rate [12]. In the supercooling liquid phase, the amount of water is greater than needed for the eu-

tectic composition, and this surplus crystallizes after the melting of the glass when it attains the necessary mobility (exothermic peak 4 in Figs 2B and 3A). The directions and meanings of the other peaks agree with the earlier results published for more dilute (1 and 3 mole %) solutions, and with the picture shown in Fig. 3A. At concentrations higher than the eutectic (e.g. 10 mole %) it might be expected that crystallization of the pure component would also give a separate peak, because the whole sample becomes glassy on freezing. However, the pure component crystallizes together with the eutectics (see Fig. 3C). Effects 3 and 4 give a single exothermic peak at the position of effect 3, with a greater intensity than one would expect for effect 3 alone. Crystallization of the pure component (salt) is indicated by the endothermic peak 1 of its melting. This phenomenon can be explained by the fact that in the case of "extreme eutectics" the region of quasi-eutectic co-crystallization is shifted towards concentrations higher than that of the eutectic [12].

It is the tendency of quasi-eutectics to supercooling that can be assumed to cause the phenomena observed in the course of the DTA studies of rapidly frozen solutions of Fe(II) salts. In these systems, the parameters of the Mössbauer effect vary significantly with temperature; the spectrum can even disappear around $-90°$ in accordance with the results mentioned above. To explain these changes the cubic-to-hexagonal transition of ice has been presumed [5−7]. In order to understand the formation of cubic ice we have carried out further DTA measurements. These studies will be reported in the second part of our publication [13].

Conclusions

Phase-diagrams were established for $H_2O - FeCl_2 \cdot 4H_2O$ and $H_2O - Fe(ClO_4)_2 \cdot 6H_2O$ systems in a concentration range of 0.2 to 10 mole %. The measured eutectic data are given Table 1.

As mentioned in our previous publication, the eutectic parameters of the $H_2O - Fe(ClO_4)_2$ system are in good agreement with the data extrapolated from solubility data [2].

For frozen samples of the $H_2O - FeCl_2$ system, the average of the eutectic temperatures measured by the two-cell and one-cell methods is $-42.5 \pm 0.5°$. This value differs significantly from that measured by Schimmel $(-36.5°)$ by the equilibrium method [1].

We interpret this difference as follows: when the rapidly frozen sample is warmed, some unknown $FeCl_2 \cdot XH_2O$ (where X is probably larger than six) separates between $-75°$ and $-60°$, but no $FeCl_2 \cdot 6H_2O$ (which is normally stable below 13°). The eutectic temperature measured by Schimmel et al. is believed to be that of the unknown allotrope. Our hypothesis is supported by the measurements which show that the quadrupole splitting of the Mössbauer spectra of frozen $FeCl_2$ solutions exhibits significant changes at about $-60°$ on gradual warming [6].

The quadrupole splitting of the changed spectrum is similar to that of solid $FeCl_2 \cdot 6H_2O$ measured at a similar temperature. On slow warming, the ferrous chloride hydrate which had first crystallized from the supercooled mass recrystallizes to form $FeCl_2 \cdot 6H_2O$; this accounts for the rapid decrease of the probability of the MB effect observed in addition to the disappearance of the effect between $-40°$ and $-35°$ (the eutectic temperature corresponding to the hexahydrate).

From a knowledge of the phase diagram of the $H_2O - Fe(ClO_4)_2$ system, it is more exact to use for the temperature of the "glass-to-viscous liquid" transition the expression "around $-115°$" than the earlier established [10] "around or below $-95°$". As the above expression also suggests, the transition is not sharp: at first, the viscosity of the liquid is high, and it decreases only around $-95°$ to an extent causing the disappearance of the Mössbauer absorption.

Recent Mössbauer studies on rapidly frozen dilute methanolic $^{57}FeCl_2$ solutions gave similar results [14]. In the preparation of the sample, a solid, glass-like material was obtained which melted on warming; the melting was followed by a change in the specific heat and a decrease in the Mössbauer effect of the "doped" ions. A similar mechanism was also suggested for the processes taking place in aqueous systems. However, there is a significant difference between the two kinds of systems: pure methanol forms a glass under such conditions, whereas water does not. In our case, only the nearly eutectic mixture can be supercooled to give a glass. It was not mentioned in the publication whether eutectic phenomena were observed or not.

To summarize our results, it can be stated that the DTA studies of structures prepared by rapid freezing of aqueous $FeCl_2$ and $Fe(ClO_4)_2$ solutions are phenomena similar to those described earlier for entirely different organic and aqueous systems. The general description of these phenomena can be found in the book by Kofler [12]. These eutectic structures formed under nonequilibrium conditions can be suitably called "quasi-eutectics" [12].

Frozen $H_2O - HCl$ and $H_2O - HCl - SnCl_4$ solutions have been systematically studied (DTA, conductivity and Mössbauer effect measurements by Ruby et al. [15, 16]), and similar results have been obtained. By measuring the temperature in the Mössbauer cell with high sensitivity, they were the first to detect the melting and crystallization processes simultaneously with the recording of the Mössbauer spectrum.

With a technique similar to the one-cell method used in our DTA studies, the Mössbauer technique and the DTA measurement were recently successfully combined. The DTA method indicates phase-transitions with a much higher sensitivity than does the measurement of temperature. In the combined method both kinds of measurements were carried out simultaneously on the same sample. The results thus measured on frozen aqueous ferrous perchlorate solutions under normal pressure are in the process of publication [17].

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References

1. F. LINDSTRAND, Z. anorg. Chem., 230 (1936) 187.
2. F. SCHIMMEL, Z. anorg. Chem., 176 (1928) 285.
3. I. DÉZSI, L. KESZTHELYI, L. PÓCS and L. KORECZ, Phys. Lett., 14 (1965) 14.
4. I. DÉZSI, L. KESZTHELYI, B. MOLNÁR and L. PÓCS, Phys. Lett., 18 (1965) 28.
5. A. J. NOZIK and M. KAPLAN, J. Chem. Phys., 47 (1967) 2960.
6. A. J. NOZIK and M. KAPLAN, Chem. Phys. Lett., 1 (1967) 391
7. J. V. DiLORENZO and M. KAPLAN, Chem. Phys. Lett., 2 (1968) 509.
8. I. DÉZSI, L. KESZTHELYI, B. MOLNÁR and L. PÓCS, in: Hyperfine Structure and Nuclear Radiations, ed. by E. Matthias and D. Shirley, North Holland, Amsterdam, 1968, p. 566.
9. I. DÉZSI, L. KESZTHELYI, G. NAGY and D. L. NAGY, in: Proc. of the Conference on the Application of the Mössbauer Effect, Tihany, Hungary, 1969. Akadémiai Kiadó, Budapest, 1971 pp. 607—611.
10. G. NAGY and I. DÉZSI, J. Thermal Anal., 2 (1970) 159.
11. S. STRELLA, J. Appl. Pol. Sci., 7 (1963) 569.
12. L. KOFLER and A. KOFLER, Thermo-Mikro-Methoden. Verlag Chemie, Weinheim, 1954, p. 239.
13. G. NAGY, L. KACSÓH, J. NYESTE and I. DÉZSI, J. Thermal Anal. (in press)
14. A. SIMOPOULOS, H. WICKMAN, A. KOSTIKAS and D. PETRIDES, Chem. Phys. Lett., 7 (1970) 615.
15. I. PELAH and S. L. RUBY, J. Chem. Phys., 51 (1969) 383.
16. S. L. RUBY and I. PELAH, preprint
17. J. A. CAMERON, L. KESZTHELYI, G. NAGY and L. KACSÓH, to be published

RÉSUMÉ — Après congélation des systèmes $H_2O-FeCl_2$ et $H_2O-Fe(ClO_4)_2$ dans des conditions de non-équilibre, la solution approximativement eutectique formée est surfondue et se solidifie à l'état vitreux. On a déterminé par ATD la température de la transition de l'état vitreux au liquide surfondu et celle de la cristallisation de la solution presque eutectique ainsi que quelques points du solidus et du liquidus. Les résultats sont en bon accord avec les changements observés sur les spectres Mössbauer de ces solutions.

ZUSAMMENFASSUNG — Ein unter Nicht-Gleichgewichtsverhältnissen gefrorenes System aus $H_2O-FeCl_2$ bzw. $H_2O-Fe(ClO_4)_2$ wurde unterkühlt. Die beinahe eutektische Lösung verfestigt sich zu einer glasartigen Form. Die Temperaturen der Übergänge vom Glas in unterkühlte Flüssigkeit und der Kristallisation der quasi-eutektischen Gemische sowie gewisse Punkte der Solidus- und Liquidus-Kurven wurden differentialthermoanalytisch gemessen. Die Ergebnisse waren in guter Übereinstimmung mit den in den Mössbauer-Spektren beobachteten Änderungen dieser Lösungen.

Резюме — После замерзания систем $H_2O-FeCl_2$ и $H_2O-Fe(ClO_4)_2$, происходящего при неравновесных условиях, образующийся почти эвтектический раствор является переохлажденным и затвердевает в стекловидной форме. Температура перехода стекла в переохлажденную жидкость и температура кристаллизации квазиэвтектиков измерены методом ДТА. Полученные результаты хорошо согласуются с изменениями в мёссбауэрском спектре этих растворов.