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

II. SOLUTIONS FROZEN AT HIGH PRESSURES

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Phase transitions of pure water and aqueous Fe(II) perchlorate solutions, frozen between 1 and 5 kbar were detected by the DTA method at atmospheric pressure. Only the crystal structure of the primarily formed ice varies with the pressure, while water molecules remaining in the near eutectic solution – which solidifies into a glassy state – show no sensitivity towards pressure.

The aim of our experiments was to produce cubic ice under controlled conditions in frozen aqueous solutions of Fe(II) perchlorate. There are two ways of obtaining unstable cubic ice from pure water: 1. steam is condensed on a surface of suitable temperature [1–3]; 2. high-pressure ice is cooled to 77°K, the pressure is released and the metastable sample is warmed up [4–6]. For aqueous systems of two components, only the second method can be applied. For comparison, the DTA curves of pure water-ice samples prepared according to the second method were also measured. The cubic-to-hexagonal transition of ice is accompanied by a small heat effect [7, 8], and this is difficult to detect by a thermal method. With regard to a solution frozen under high pressure, the following questions arise: What kind of physical structure is formed on freezing? Do all water molecules participate in the high-pressure to Ic transition?

Experimental

The apparatus shown in Fig. 1 was used to prepare the high-pressure samples. The apparatus was placed into a hydraulic press and subjected to the required pressure. After this, liquid N_2 was poured into the jacket. Once stationary heat-transport was established, the pressure was released and the sample was pressed into the lower vessel. From here the sample was transferred – together with the nitrogen – into the DTA cell. The DTA measurements were carried out as described in the first part of our paper [9].

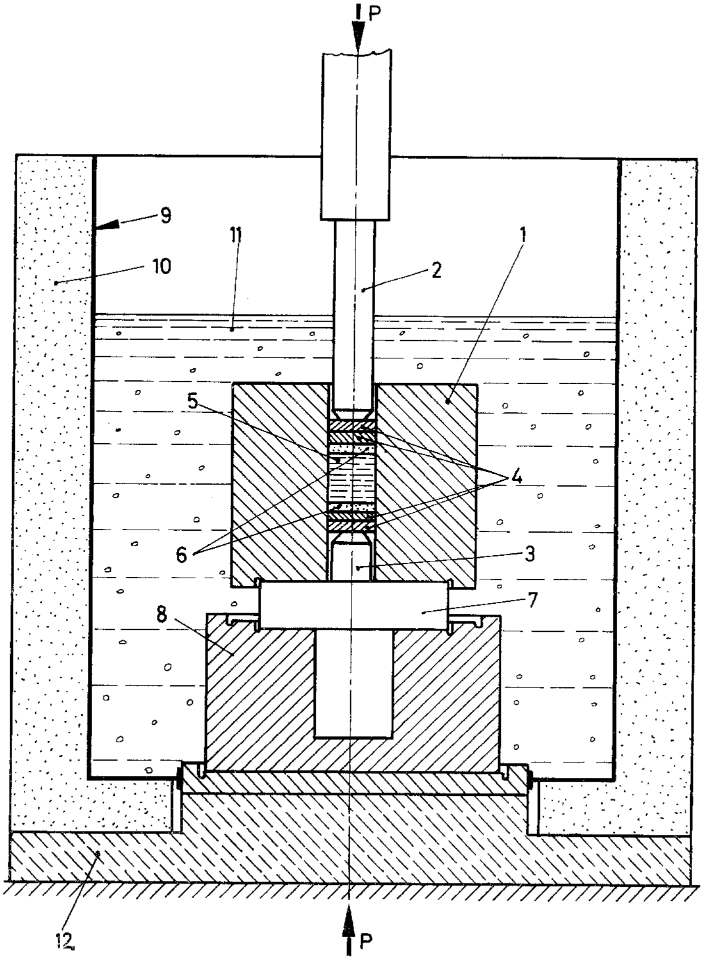

Fig. 1. Apparatus for producing pressurized ices and solutions frozen by liquid nitrogen. 1 — pressure-tight cylinder, 2 — pressing piston, 3 — contra-piston, 4 — double copper gaskets, 5 — rubber gaskets, 6 — sample (2 ml liquid), 7 — fill piece, 8 — vessel for ice pressed out, 9 — brass box, 10 — Styrocell foam, 11 — liquid nitrogen, 12 — bakelite disc

Results

Series 1: Pure water. The samples were prepared at different pressures between 1 and 5 kbar. The results are shown in Fig. 2.

One endothermic (Fig. 2A) or one exothermic (*a*) plus one endothermic (*b*) peak can be seen (Fig. 2B and 2C). The relative heights of the peaks change with the increase of pressure. At 1 kbar only the endothermic effect appears, at about —80°C. At 2.7 kbar one exothermic peak and one endothermic peak, of about equal heights, can be observed, at about −110 and −90°C, respectively. At

5 kbar the exothermic effect predominates. Both effects probably have their origin in the transition of the high pressure to the cubic form. The cubic-to-hexagonal transition is accompanied by a small exothermic effect; the signal of effect could not be distinguished from noise.

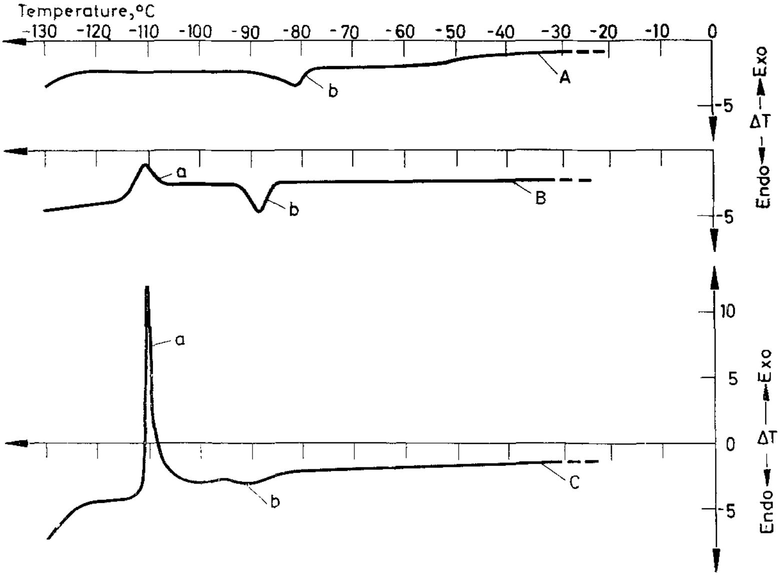

Fig. 2. DTA curves measured on pressurized water frozen by liquid nitrogen at different pressures. Curve A — 1.0 kbar; curve B — 2.7 kbar; curve C — 5.0 kbar. Effects: *a* and *b* are explained in the text

On the basis of the temperature vs. pressure phase diagram of ice [10], the following is a possible explanation for the change of the peak intensity. Under the applied experimental conditions, between 0.5 and 1.8 kbar ice Ih, and then ice IX is formed; on warming, the IX-to-Ic transition gives the endothermic peak. Between 2 and 3.4 kbar ice III is formed which transforms to ice IX at low temperature; nevertheless formation of ice II is also possible. During warming, the exothermic peak may result from the III–Ic and II–Ic transitions, while the IX–Ic transition gives the endothermic peak.

Between 3.5 and 5.1 kbar ice V forms, a small part of which transforms to ice IX in the same way as ice III. Thus a large exothermic and a small endothermic signal can be observed in this case.

The Ic–Ih transition takes place between −130° and −60°, depending on the experimental conditions [8, 10]. It can be expected that in this system the phase transition takes place between −90° and −60°. (There are no data in the literature about the existence of cubic ice above −60°.)

Although the cubic-to-hexagonal transition could not be detected directly, the existence of cubic ice was demonstrated in consequence of the good detectable transition effects of the high pressure to the cubic form.

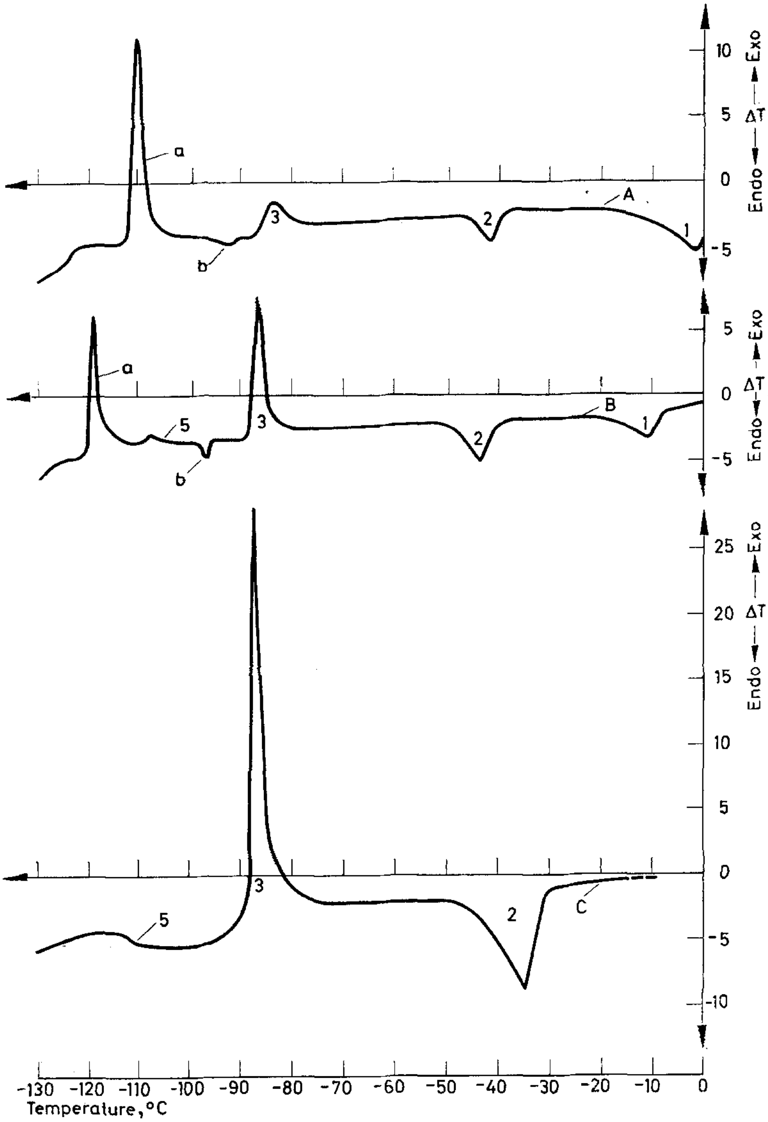

Fig. 3. DTA curves measured on pressurized solutions frozen at 3.5 kbar. Curve A — 1.0 mole%; curve B — 3.0 mole%; curve C — 7.3 mole% $Fe(ClO_4)_2 \cdot 6H_2O$. Effects: *a* and *b* are explained in the text; 1 — melting of primarily formed ice or dissolution of the salt; 2 — melting of quasi-eutectic phase; 3 — crystallization of supercooled liquid of quasi-eutectic composition; 4 — crystallization of ice in excess of the eutectic composition (invisible; see in the text); 5 — glass-to-supercooled liquid transition

Series 2: Solutions. On the basis of the results obtained with *Series 1*, a pressure of 3.5 kbar was chosen to study the effect of concentration. (At about −120°, the major part of the ice is already in phase Ic.) Curves of 1, 3 and 7.3 mole% $Fe(ClO_4)_2 \cdot 6H_2O$ solutions frozen at 3.5 kbar are shown in Fig. 3, while Fig. 4 gives the DTA curve of a 0.2 mole% solution frozen at 3.0 kbar.

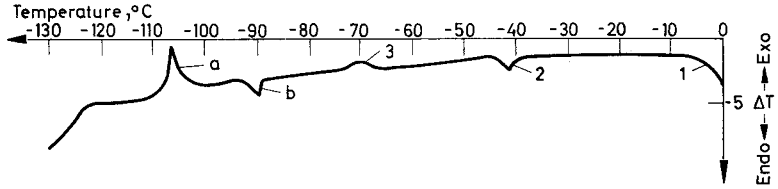

Fig. 4. DTA curve for 0.2 mole% $Fe(ClO_4)_2 \cdot 6H_2O$ frozen at 3.0 kbar. For explanation of designations see Fig. 3

The curves indicate that solutions frozen under high pressures show similar physical structures to those frozen under atmospheric pressure. The primarily formed ice, however, crystallizes in a form which depends on pressure. The resulting ice form is the same as that obtained by freezing water under the given pressure. The remaining nearly eutectic solution supercools, and then congeals in a glassy form. When warmed, high-pressure ice transforms to ice Ic (peaks *a* and *b*) while the glassy phase remains unchanged. As soon as the temperature of the "glass-to-supercooled liquid" transition is reached, the glass liquefies (effect 5), and then the nearly eutectic mixture crystallizes (effect 3). Further transitions take place in the same manner as if the sample had been frozen under normal pressure (effects 2 and 1), and thus the peaks characteristic of both high-pressure ice and the solution of given concentration can be found on the curves (see the first part of our paper [9]). At 6 mole%, effect 4 of the normal-pressure samples could not be observed, that is, primary ice formation (in the high-pressure form) takes place at this concentration, as in the pressure-tight cylinder the freezing rate is smaller than in the glass ampulla.

Conclusions

By carrying out freezing under high pressures, different forms of ice, e.g. cubic ice, can be prepared from the primarily crystallized ice. This ice-phase theoretically contains no Fe^{2+} ions but it is probable that – because of the non-equilibrium freezing conditions – a negligible quantity of the ions is trapped in the ice-lattice. In the environment of the predominant majority of the $[Fe(OH_2)_6]^{2+}$

ions, that is in the supercooled liquid phase, the water molecules show no sensitivity towards pressure in the studied range (up to 5 kbar). High-pressure ice could not be formed in the quasi-eutectics, and thus cubic ice did not form either. Hence, the anomalies of the Mössbauer effect cannot be related with the cubic-to-hexagonal transition of ice.

Recently we succeeded in combining the "one-cell" DTA method used by us with the Mössbauer technique. The two kinds of measurements were carried out simultaneously on the same sample. Results obtained for aqueous Fe(II) perchlorate solutions frozen under high pressure have been published recently [11].

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Résumé — Mise en évidence par ATD à la pression atmosphérique des transitions de phase de l'eau pure et de solutions aqueuses de perchlorate de fer(II) préalablement congelées sous une pression allant de 1 à 5 kbar. Seule la structure cristalline de la phase qui se dépose la première dépend de la pression. Par contre, les molécules qui restent dans la solution presque eutectique — qui se solidifie à l'état vitreux — ne sont pas sensibles à la pression.

Zusammenfassung — Phasenübergänge von reinem Wasser und zwischen 1 und 5 kbar gefrorenen wäßrigen Eisen(II)perchlorat Lösungen wurden durch DTA bei atmosphärischem Druck nachgewiesen. Nur die Kristallstruktur des primär segregierenden Eises wird durch den Druck beeinflußt. Die in der beinahe eutektischen Lösung zurückbleibenden Wassermoleküle, die in einem glasartigen Zustand erstarren, scheinen nicht druckempfindlich zu sein.

Резюме — Методом ДТА при атмосферном давлении зарегистрированы переходы фазы чистой воды и водного раствора перхлората железа, замороженных между 1 и 5 кбар. С давлением изменяется только кристаллическая структура первичного отделяющегося льда, молекулы же воды, остающейся в придлизимельно эвтектическом растворе, затвердевающем в стекловидное состояние, не чувствительны к давлению.