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Abstract

Full Text

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MELTING DIAGRAM OF THE SYSTEM Cl_2O_7—SO_3—H_2O IN THE REGION OF HIGH CONCENTRATIONS OF PERCHLORIC AND SULFURIC ACIDS

(Presented by Academician I. I. Chernyaev, 11 V 1963)

Anhydrous perchloric acid exists under ordinary conditions only in the form of the equilibrium
$3HClO_4 \rightleftarrows HClO_4 \cdot H_2O + Cl_2O_7$, shifted considerably to the left-hand side (^{1}). An objective reflection of this is the absence of a crystallization line of perchloric acid on the melting diagram Cl_2O_7—H_2O. The stable compound—perchloric acid monohydrate $HClO_4 \cdot H_2O$

Fig. 1. Liquidus diagram of the system SO_3—Cl_2O_7—H_2O in the region of intermediate concentrations

crystallizes up to a concentration of 53 mol.% Cl_2O_7, corresponding to the eutectic of the monohydrate and chlorine anhydride, and above 55 mol.% Cl_2O_7 a region of stratification already begins (^{2,3}).

In connection with the elucidation of the conditions for the existence of perchloric acid as an individual compound, considerable interest attaches to the study of the melting diagram of the ternary system Cl_2O_7—SO_3—H_2O in the part adjacent to the composition of perchloric acid, i.e., in the concentration region where $Cl_2O_7 : H_2O = 1 : 1$. Taking into account the dehydrating action of sulfuric anhydride, it was possible to expect to obtain in the ternary system

field of crystallization of perchloric acid. The construction of the ternary fusibility diagram is based on the study of the binary system Cl_2O_7—H_2O by Van Wijk (^{2}) and A. A. Zinov' ev and V. Ya. Rosolovskii (^{3}), and of the binary system SO_3—H_2O by Pickering (^{4}) and Buiar (^{5}). The liquidus surface of the system Cl_2O_7—SO_3—H_2O (Fig. 1) was constructed mainly from data obtained by the visual-polythermal method and, in some regions, by studying heating

Fig. 2. Fusibility diagram of the section H_2SO_4—$HClO_4$

Figure 2: Fig. 2. Fusibility diagram of the section H_2SO_4—$HClO_4$

Fig. 3. Fusibility diagram of the system H_2SO_4—$HClO_4 \cdot H_2O$

Figure 3: Fig. 3. Fusibility diagram of the system H_2SO_4—$HClO_4 \cdot H_2O$

and cooling curves with the use of an N. S. Kurnakov pyrometer.

The composition of all mixtures was determined by chemical analysis. Considerable difficulties were overcome in establishing equilibrium in the low-temperature region, around −100° and below, and in taking samples for analysis of active and highly hygroscopic substances.

The fusibility diagram of the central part of the system Cl_2O_7—SO_3—H_2O is characterized by the existence of five fields corresponding to the primary crystallization of solid phases: $\alpha = HClO_4 \cdot H_2O$ $(e_3P_4P_2)$, $\beta = HClO_4 \cdot H_2O$ $(P_3P_2P_1Ee_4)$, H_2SO_4 $(e_2P_2P_1p_3)$, $H_2SO_4 \cdot H_2O$ $(pP_3P_2e_2)$, and a newly found ternary phase (p_3P_1E), the small field of primary crystallization of which is elongated in the direction of the secant H_2O—$Cl_2O_7 : SO_3 = 1 : 1$.

Fig. 2. Fusibility diagram of the section H_2SO_4—$HClO_4$

The section $HClO_4$—H_2SO_4, in accordance with the absence of a dystectic point and even of a crystallization line of the compound $HClO_4$ in the system Cl_2O_7—H_2O (^{3}), is not binary in the region rich in H_2ClO_4. However, as the concentration of SO_3 increases, it assumes the character of a binary system (Fig. 2). The constancy of the temperature of joint separation of two phases and the nature of the curvature of the middle branch of the liquidus indicate crystallization of a new ternary compound, to which, from the combined data of the study of the section $HClO_4$—H_2SO_4 and the liquidus of the ternary system, we assign the composition $SO_3 \cdot Cl_2O_7 \cdot 2H_2O$, or $H_2SO_4 \cdot 2HClO_4$. This compound is unstable and decomposes at −92°C with separation of sulfuric-acid crystals and a liquid phase.

Fig. 3. Fusibility diagram of the system H_2SO_4—$HClO_4 \cdot H_2O$

A large part of the concentration triangle of the fusibility diagram is occupied by the crystallization fields of the α- and β-modifications of perchloric acid monohydrate, which have clearly expressed folds of the anticlinal type corresponding to the section H_2SO_4—$HClO_4 \cdot H_2O$.

Perchloric acid monohydrate gives with sulfuric acid a binary system of the eutectic type (Fig. 3). All this confirms the considerable stability of perchloric acid monohydrate in comparison with other crystallizing-

···present in this system: other hydrated forms of perchloric acid, sulfuric acid, and its derivatives.

Fairly clearly defined fields with folds of a nonsingular type correspond to the primary crystallization of sulfuric acid and its monohydrate.

The smallest field, located between the fields of crystallization of perchloric acid monohydrate and sulfuric acid, corresponds to crystallization of the phase of the ternary compound $H_2SO_4 \cdot 2HClO_4$. The nature of the field and the polytherm of crystallization of H_2SO_4–$HClO_4$ (Fig. 2) confirm the instability of this compound.

Of the three invariant points found in the studied part of the fusibility diagram, two are peritectic. Point P_1 (14.19% Cl_2O_7, 31.54% SO_3, $t = -42°$) corresponds to the reaction: $H_2SO_4 + HClO_4 \cdot H_2O + l \rightleftarrows H_2SO_4 \cdot 2HClO_4$; point P_2 (7.50 mol. % Cl_2O_7, 34.99 mol. % SO_3, $t = -40.0°$) corresponds to the equilibrium $H_2SO_4 \cdot H_2O + l \rightleftarrows H_2SO_4 + HClO_4 \cdot H_2O$. In the ternary eutectic E, with liquid-phase composition 36.3% Cl_2O_7 and 13.7% SO_3, and at a temperature of $-116°$, perchloric acid monohydrate, chlorine anhydride, and the phase of the ternary compound $Cl_2O_7 \cdot SO_3 \cdot 2H_2O$ crystallize.

Thus, fields of primary separation and lines of monovariant equilibrium corresponding to crystallization of perchloric acid have not been found on the fusibility diagram. Perchloric acid participates in the equilibrium only in the form of a component of the ternary compound, which has its own field of primary crystallization on the liquidus diagram of the ternary system.

This ternary compound $Cl_2O_7 \cdot SO_3 \cdot 2H_2O$, or $H_2SO_4 \cdot 2HClO_4$, may be regarded as sulfonium perchlorate $[H_4SO_4]^{2+}[ClO_4^{2-}]_2$ or $[SO_2][ClO_4]_2 \cdot 2H_2O$, where sulfuric acid acts as a base with respect to the stronger perchloric acid.

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CITED LITERATURE

[1] A. A. Zinov' ev, ZhNKh, **3**, 1205 (1958).
[2] H. I. Van Wyk, Zs. anorg. Chem., **48**, 1 (1906).
[3] A. A. Zinov' ev, V. Ya. Rosolovskii, ZhNKh, **3**, 2382 (1958).
[4] S. U. Pickering, Ber., **25**, 1099, 1314 (1892).
[5] G. Willard, Bull. Soc. Chim., No. 6, 802 (1954).

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