57. A.M.Golub and Yu.V.Kosmatyi, Zhur.Neorg.Khim., 4, 1347 (1959) [Russ.J.Inorg.Chem., 606 (1959)].
58. A.M.Golub and V.V.Skopenko, Zhur.Neorg.Khim., 7, 1012 (1962) [Russ.J.Inorg.Chem., 520 (1962)].
59. A.M.Golub and V.V.Skopenko, Dokl.Akad.Nauk SSSR, 141, 851 (1961).
60. A.M.Golub and V.V.Skopenko, Zhur.Neorg.Khim., 7, 1265 (1962) [Russ.J.Inorg.Chem., 653 (1962)].
61. A.V.Ablov and N.M.Samus', Dokl.Akad.Nauk SSSR, 133, 1327 (1960).
62. J.W.Clarke, Ber., 11, 1325 (1878).
63. W.Peters, Z.anorg.Chem., 77, 182 (1912).
64. A.Minozzi, Atti Ist.Veneto, 69, 456 (1909, 1910); "Gmelins Handbuch der anorganischen Chemie", 8th Edn., Syst.No.68, "Platin", Verlag Chemie, Berlin, 1940, p.212.
65. E.Billow, Z.Krist., 50, 494 (1912).
66. A.M.Golub, Nauk.Zap.Kiivs'k.Derzh.Univ., Sbirnik Khim. Fak., No.8, 13 (1957).
67. A.M.Golub, Zhur.Neorg.Khim., 1, 2517 (1956).
68. A.M.Golub and V.V.Skopenko, Zhur.Neorg.Khim., 6, 140 (1961) [Russ.J.Inorg.Chem., 69 (1961)].
69. V.V.Skopenko, Visn.Kiivs'k.Univ., Seriya Astron., Fiz., Khim., 4, No.1, 81 (1961).
70. O.E.Andreichenko, Ukrain.Khim.Zhur., 30, 1255 (1964).
71. V.V.Skopenko and A.I.Brusilovets, Ukrain.Khim.Zhur., 30, 24 (1964).
72. A.Rosenheim and R.Cohn, Z.anorg.Chem., 27, 280 (1901).
73. V.V.Skopenko, Thesis, Kiev, 1962.
74. D.H.Hume, D.D.Ford, and G.S.Cave, J.Amer.Chem.Soc., 73, 5323 (1951).
75. A.M.Golub, L.I.Romanenko, and V.M.Samoilenko, Ukrain. Khim.Zhur., 25, 50 (1959).
76. A.M.Golub, Ukrain.Khim.Zhur., 19, 210 (1953).
77. M.Lehne, Bull.Soc.chim.France, 76 (1951).
78. S.Fronaeus, Acta Chem.Scand., 7, 21 (1953).
79. L.M.Kul'berg and A.K.Gorlinskii, Zhur.Obshch.Khim., 9, 1707 (1939).
80. M.Oudinet and F.Gallais, Compt.rend., 236, 373 (1953).
81. G.S.Zhdanov and Z.V.Zvonkova, Uspekhi Khim., 22, 3 (1953).
82. E.K.Yukhno and M.A.Porai-Koshits, Kristallografiya, 2, 239 (1957).
83. G.S.Zhdanov and Z.V.Zvonkova, Izv.Sektora Platiny Drug. Blagorod.Metal., Inst.Obshch.Neorg.Khim.Akad.Nauk SSSR, No.26, 235 (1951).
84. W.Kondratjew and O.Setkina, Phys.Z.Sowjetunion, 9, 279 (1936).
85. P.Spacu, Bull.Soc.chim.France, [5], 3, 2074 (1936).
86. H.W.Morgan, J.Inorg.Nuclear Chem., 16, 367 (1961).
87. F.A.Cotton, D.M.L.Goodgame, M.Goodgame, and T.E.Haas, Inorg.Chem., 1, 565 (1962).
88. C.Pecile, A.Turco, and G.Pizzolotto, Ricerca sci., [ii], IIA, 1, 247 (1961).
89. E.Frasson, A.Turco, and C.Panattoni, Gazzetta, 91, 750 (1961).
90. J.W.Jeffery, Nature, 159, 610 (1947).
91. G.V.Tsintsadze, M.A.Porai-Koshits, and A.S.Antsishkina, Zhur.Strukt.Khim., 5, 148 (1964).
92. Yu.Ya.Kharitonov and G.V.Tsintsadze, Zhur.Neorg.Khim., 10, 35 (1965) [Russ.J.Inorg.Chem., 18 (1965)].
93. Yu.Ya.Kharitonov and V.V.Skopenko, Zhur.Neorg.Khim., 10, 1803 (1965) [Russ.J.Inorg.Chem., 984 (1965)].
94. Yu.Ya.Kharitonov, G.V.Tsintsadze, and M.A.Porai-Koshits, Dokl.Akad.Nauk SSSR, 60, 1351 (1965).
95. Yu.Ya.Kharitonov and G.V.Tsintsadze, Zhur.Neorg.Khim., 10, 1191 (1965) [Russ.J.Inorg.Chem., 645 (1965)].

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STUDY OF THE THERMAL STABILITY OF INORGANIC PEROXO-COMPOUNDS BY THE DIFFERENTIAL THERMAL ANALYSIS METHOD

I. I. Vol'nov

The inorganic peroxo-compounds are special higher forms of oxygen compounds of the elements and every year they acquire new fields of use. The diverse use of the different types of this broad class of compounds is determined not only by their oxygen content, which can be readily released in active form, but also by the singular nature of the bonding to oxygen in their molecules.

The presence of the peroxo-group, the so-called "oxygen bridge" was thought until recently to be sufficient for defining "inorganic peroxo-compounds". A detailed study of the structure and properties of a series of peroxo-compounds, made in the 'thirties of the present century, with the active participation of Soviet scientists, showed that this concept embraces at least nine groups of compounds, which are distinguished by the nature of the bond between the oxygen atoms in the bridge and by the nature of the bond between the oxygen bridge and the atoms of the element forming the peroxo-compounds. Some authors tend to include all the inorganic peroxo-compounds within the framework of complex compounds dividing them into three groups: polyoxides, peroxo-acids, and peroxohydrates. However, the group of polyoxides includes peroxo-compounds with a crystal lattice consisting of metal ions (predominantly of the Ia and IIa subgroups of the Periodic System) and the molecular anions O_2^{2-}, O_2^-, and O_3^- respectively, which differ both in their structure and in the nature and length of the O–O bond. The bonds of the metal atoms with the oxygen bridge in these compounds are of the ionic type, whereas in other peroxo-compounds the peroxo-group as such or in the form H_2O_2 or HO_2 is joined to the atom of the element forming the peroxo-compound by a coordinate, not an ionic bond. It is therefore desirable to keep the division of inorganic peroxo-compounds into simple and complex.

The simple inorganic peroxo-compounds can be subdivided into four groups: (1) the hydrogen peroxides, which are characterised by the presence of the hydrogen peroxide ion HO [presumably HO_2^- (Ed. of Translation)]; (2) the peroxides, characterised by the presence of the peroxide ion O_2^{2-}; (3) the superoxides, characterised by the presence of the superoxide ion O_2^-; (4) the ozonides, characterised by the presence of the ozonide ion O_3^-.

The complex peroxo-compounds can be subdivided into five groups: (1) peroxo-acids and their salts, in which the peroxo-group forms part of the complex anion, mono- and poly-nuclear representatives of this group being known; (2) peroxo-complexes which are neither peroxo-acids nor their derivatives, represented by compounds which include in the inner sphere a peroxo-group (peroxo-complexes), or hydrogen peroxide (perhydro-complexes [Russian nomenclature (Ed. of Translation)]), or the hydrogen peroxo-group (hydrogen peroxo-complexes); (3) peroxide hydrates — addition compounds of peroxides with water of crystallisation; (4) peroxohydrates — molecular compounds of

peroxides or salts analogous to crystal hydrates containing hydrogen peroxide of crystallisation; (5) hydrates of peroxohydrates — molecular compounds of peroxides or salts which contain both water of crystallisation and hydrogen peroxide of crystallisation.

Specific properties of compounds of each of the above groups have been described in a monograph[1] and an article[2].

A characteristic property of the peroxo-compounds, whether simple or complex, is the ability to lose oxygen in an active form during thermal decomposition or under the action of chemical agents.

To determine whether it is possible to use inorganic peroxo-compounds as sources of chemically bound oxygen it is necessary to have accurate information on their behaviour on heating.

Up to 1952, with the exception of Kapustinskii and Bayushkina's data[3] on the dissociation temperature of BaO_2, obtained by use of an apparatus which was a combination of a Kurnakov thermal analysis apparatus and a Beckmann manostat, and data on the thermal decomposition of several minerals under the action of sodium peroxide, obtained by differential thermal analysis[4], the literature does not contain objective information about the thermal stability of the inorganic peroxo-compounds based on the use of the last method. In the Peroxide Compounds Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR since 1952 Makarov, Rode, Mironov, Vol'nov, Dobrynina, Grigor'eva, Firsova, and Chamova have widely used the method of differential recording of heating curves on a Kurnakov recording pyrometer for the thermal characterisation of representatives of the above-mentioned groups of peroxide compounds. It appeared that, depending on the type of peroxo-compound, the nature of the heating curves is different. In recent years the method of differential thermal analysis has been applied to peroxides by several foreign scientists: Margrave, Hoffman, Ghormley, Duval, etc.

It is necessary to note that unlike the manostat-pyrometric method used by Kapustinskii, which, as the author mentioned at the First Conference on Thermography[5] made possible the automation of the investigation of all three variables (t, p, and c), which determine the state of equilibrium of systems which dissociate with evolution of gas (liberation of oxygen, for peroxides), most of the heating curves for peroxo-compounds given in the present paper were recorded at a given external (atmospheric) pressure. Consequently, these curves reflect only the behaviour of the peroxo-compounds on heating under the real conditions of their use as sources of chemically bound oxygen and the value of the decomposition temperature thus obtained cannot be a basis for any rigorous thermodynamic calculations. Nevertheless, since these curves were obtained under comparable conditions, a comparison of them can throw light on the difference in structure of the individual groups of peroxo-compounds.

STUDY OF THE THERMAL STABILITY OF THE PEROXIDES M_2O_2 AND $M^{II}O_2$†

Mironov[6] has widely used the thermographic method in investigating phase transformation diagrams of the H_2O_2–H_2O system. Fig. 1 shows low-temperature heating curves

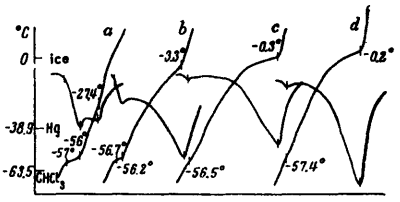


Fig. 1. Low-temperature heating curves of hydrogen peroxide solutions. H_2O_2, %: *a*) 77; *b*) 96.1; *c*) 99.3; *d*) 99.8.

for various compositions in this system, which can serve as a criterion of the purity of hydrogen peroxide. From the last curve of the diagram it is evident that thermography enables the presence of up to 0.2 wt.% water to be detected, which it is difficult to do by the usual chemical methods. Mironov[7] also took heating curves of the glassy substance which is formed when the dissociation products of water vapour in a glow discharge are frozen in a trap cooled with liquid air. The originality of the effects which appear on the curves and their difference from the effects obtained at low-temperature recording of solutions of hydrogen peroxide enabled the author to conclude that the glassy substance contained a compound of the type of higher peroxides of hydrogen. This conclusion was later also confirmed thermographically[8,9].

The heating curves for solutions of hydrogen peroxide of different concentrations in the region of positive temperatures [presumably above 0° (Ed. of Translation)] are characterised by the presence of an endothermic effect of boiling (at 151° for 100% H_2O_2) with a subsequent exothermic effect for the decomposition into water and oxygen, due to the liberation of heat (23.44 kcal mole^{-1} for 100% H_2O_2).

Unlike the decomposition of hydrogen peroxide, the decomposition of alkali and alkaline earth metal peroxides into the oxide and hydrogen is accompanied by absorption of heat, as shown on the heating curves of lithium, sodium, calcium, and strontium peroxides[10–13]. It is not necessary to reproduce all these curves, since the effects characteristic for them also appear on the curves of the peroxide hydrates, which will be given below. It is also necessary to note that the effect at 510° on the heating curve of sodium peroxide[11] (Fig. 2), which was previously ascribed to fusion, really corresponds, according to new

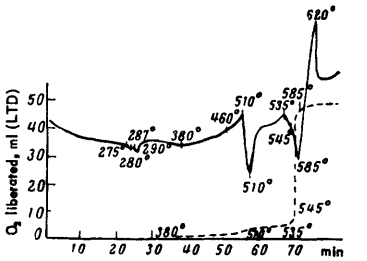


Fig. 2. Differential heating curve of sodium peroxide. Broken line: oxygen liberation curve.

† M denotes metal.

results[14], to the transformation of the hexagonal modification of Na_2O_2 (I) into another modification Na_2O_2 (II), the symmetry of which has not been determined. According to Tallman and Margrave[14], sodium peroxide melts above 596°.

STUDY OF THE THERMAL STABILITY OF PEROXIDE HYDRATES, $M_2O_2.xH_2O$

There is considerable interest in the heating curves of the alkali and alkaline earth metal peroxide hydrates, which enable us to judge whether it is possible to obtain the peroxide in the anhydrous state. Fig. 3 shows the differential heating curves of lithium peroxide monohydrate[15] and sodium peroxide octahydrate[16,17]. On heating, lithium peroxide monohydrate loses water at 100–140° and forms the anhydrous peroxide. An endothermic effect, starting at 325°, corresponds to the decomposition of Li_2O_2 into Li_2O and $\frac{1}{2}O_2$. On heating sodium peroxide octahydrate, it melts at 68°, dissolving in the water of crystallisation, and loses its active oxygen completely, being converted into sodium hydroxide dihydrate. An effect at 131° corresponds to the boiling off of the solution. Consequently, sodium peroxide cannot be obtained like lithium peroxide by dehydrating the hydrate formed in the oxide hydrate–hydrogen peroxide–water system.

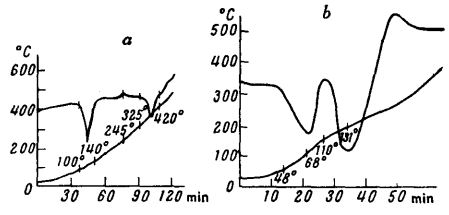


Fig. 3. Heating curves for:
a) lithium peroxide monohydrate $Li_2O_2.H_2O$; *b*) sodium peroxide octahydrate $Na_2O_2.8H_2O$.

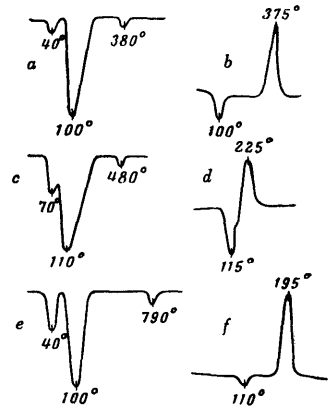


Fig. 4. Differential heating curves for peroxide hydrates of elements of Periodic Group II:
a) $CaO_2.8H_2O$; *b*) $MgO_2.xH_2O$; *c*) $SrO_2.8H_2O$; *d*) $ZnO_2.xH_2O$; *e*) $BaO_2.8H_2O$; *f*) $CdO_2.xH_2O$.

A marked difference is apparent on comparing the differential heating curves of calcium[12], strontium[18], and barium[19] peroxide octahydrates with those of the hydrated forms of magnesium[19], cadmium[19-21], and zinc[22] peroxides of gross composition $MO_2.xH_2O$ (Fig. 4). Those of the calcium, strontium, and barium peroxide octahydrates have three endothermic effects, corresponding respectively to incongruent melting, dehydration, and decomposition of the peroxide into the oxide and oxygen. With increase in the atomic weight of the element forming the peroxide, the stability of the latter increases: thermal decomposition starts at 380° for CaO_2, 480° for SrO_2, and 790° for BaO_2. On the heating curves of the hydrated forms of magnesium, zinc, and cadmium peroxides there is no fusion effect. The curves are characterised by the presence of a single endothermic effect within the limits 100–115°, corresponding to the removal of the mother-liquor, and a single exothermic effect, corresponding to decomposition to the oxide with liberation of oxygen and water. In this, with increase in the atomic weight of the element forming the peroxide the decomposition temperature decreases: MgO_2 375°, ZnO_2 225°‡, CdO_2 195°. Owing to this difference and also because the oxides of these metals show less basic properties than calcium, strontium, and barium oxides, it can be suggested that the hydrated forms of magnesium, zinc, and cadmium peroxides are not hydrates of the true peroxides MO_2, but belong to a group intermediate between the peroxides of this composition and peroxo-acids. The probable structure of these compounds can be written $(HO).M(OOH).xH_2O$. The infrared spectra recently obtained[23] for these compounds also show the absence of water of crystallisation. If, for example, the magnesium peroxide hydrate had the actual formula $MgO_2.xH_2O$, its heating curve should show, after the removal of water, an endothermic effect for decomposition, as on the heating curve of, for example, $CaO_2.8H_2O$. The heats of the reactions $CaO_2 \rightarrow CaO + \frac{1}{2}O_2$ (-5.8 ± 0.5 kcal mole^{-1}) and $MgO_2 \rightarrow MgO + \frac{1}{2}O_2$ (-5.1 ± 1 kcal mole^{-1}) are very close.

STUDY OF THE THERMAL STABILITY OF METAL PEROXIDE–HYDROGEN PEROXIDE ADDITION COMPOUNDS, $M_2O_2.xH_2O_2$, "PEROXOHYDRATES"

Differential heating curves of the alkali and alkaline earth metal peroxide–hydrogen peroxide addition compounds, that is, compounds in which hydrogen peroxide of crystallisation replaces water of crystallisation, are given in Fig. 5.[12,16,18,24-26] They show an exothermic effect of the decomposition of the crystallisation hydrogen peroxide in the range 45–65° with a subsequent endothermic effect of dehydration (with the sodium compound, fusion at 285°) at ~100° and the final endothermic effect of decomposition of the peroxide into the oxide and oxygen. On comparing the heating curves for the hydrated forms of magnesium, zinc, and cadmium peroxides (Fig. 4) with the heating curves of calcium, strontium, and barium peroxide–2-(hydrogen peroxide)s (Fig. 5), then the hypothesis that the first group of compounds contain hydrogen peroxide of crystallisation fails, since the exothermic effect corresponding to their decomposition does not precede the dehydration effect, as is characteristic for peroxide–(hydrogen peroxide) addition compounds.

‡ The report[21] that the decomposition of ZnO_2 at 200° is accompanied by an endothermic effect is evidently incorrect.

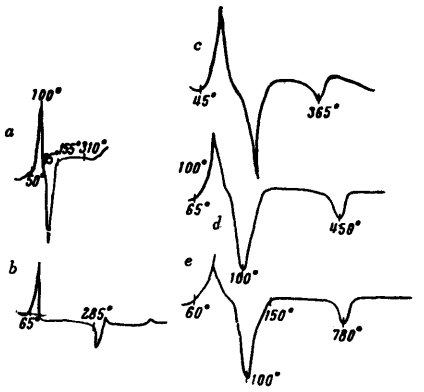


Fig. 5. Differential heating curves of the alkali and alkaline earth metal peroxide–(hydrogen peroxide) addition compounds:
a) $Li_2O_2.2H_2O_2$; *b*) $Na_2O_2.H_2O_2$; *c*) $CaO_2.2H_2O_2$; *d*) $SrO_2.2H_2O_2$; *e*) $BaO_2.2H_2O_2$.

STUDY OF THE THERMAL STABILITY OF THE SUPEROXIDES M^IO_2

Only four representatives are known of this group of peroxide compounds: sodium, potassium, rubidium, and caesium superoxides. We have obtained the calcium, strontium, and barium superoxides[27] only admixed with peroxide and hydroxide of the metal. Rode[11,28] has made a detailed study of the behaviour of sodium superoxide on heating. It was found (Fig. 6) that in dry oxygen sodium superoxide starts to decompose at ~120°, in dry, CO_2-free air at 80–90°. In oxygen at 250° and in dry, CO_2-free air at ~215° it decomposes vigorously and endothermically with formation of sodium peroxide. Rode[29] also confirmed thermographically (Fig. 7) that sodium and potassium superoxides had two low-temperature polymorphic transformations, at -43° and -80° and at -75° and -120° respectively. As for the melting point of potassium superoxide, it must be pointed out that the values of 380°[30] and 440°[31] given in the literature were found over 30 years

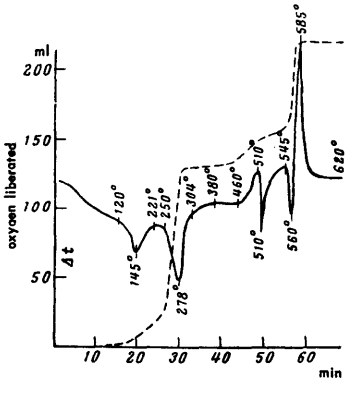


Fig. 6. Differential heating curve of sodium superoxide. Broken line: oxygen liberation curve.

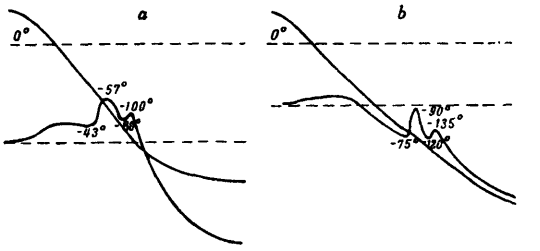


Fig. 7. Low-temperature heating curves for:
a) sodium superoxide NaO_2; *b*) potassium superoxide KO_2.

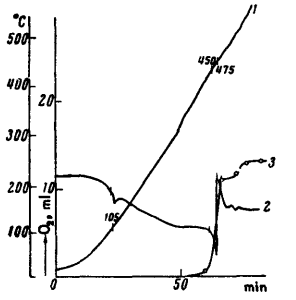


Fig. 8. Heating curves for caesium superoxides:
1) simple record; 2) differential record;
3) oxygen liberation curve.

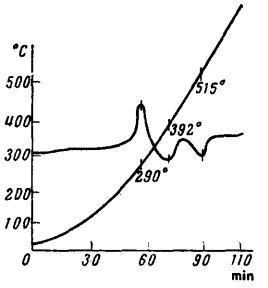


Fig. 9. Heating curve for a peroxide preparation containing calcium superoxide.

ago and were evidently obtained with insufficiently pure material. In the Peroxide Compounds Laboratory of the Institute of General and Inorganic Chemistry a heating curve has been recorded for caesium superoxide prepared in a pure form[45] (Fig. 8); it has an endothermic effect for fusion at 450°. The effect at 475° is due to the reaction of caesium oxide with the glass of the test-tube in which the recording was made. Fig. 9 shows the heating curve obtained by Vol'nov[27] for a preparation containing 16% calcium superoxide as well as calcium peroxide and hydroxide. The interpretation of this curve, together with chemical analysis and magnetic measurements, showed that the exothermic effect at 290° corresponds to the decomposition of

the superoxide and the endothermic effects at 392° and 516° correspond to the decomposition of calcium peroxide and hydroxide to the oxide.

STUDY OF THE THERMAL STABILITY OF THE ALKALI METAL OZONIDES $M^{I}O_3$

Sokovnin and Matveev[32,33] recorded the heating curves of a new class of inorganic peroxo-compounds, discovered by Kazarnovskii, but obtained by their use of a new method: the reaction of the corresponding superoxides with O_3 in a pseudo-liquefied layer created by a current of ozonised oxygen, with subsequent extraction with liquid ammonia. Caesium ozonide with a purity of 92.5% was first obtained by this method[32]. The heating curve of potassium ozonide (Fig. 10), in agreement with the thermodynamic data which show that during the decomposition of the ozonide to the superoxide 5.5 kcal mole^{-1} is released, is characterised by the presence of an exothermic effect for decomposition to KO_2 at 60° ± 2° and the endothermic effect of the decomposition of KO_2 to K_2O_2 at 390°. The oxygen liberation curve shows clearly how the process takes place in two stages[33]. The heating curve of caesium ozonide[32] (Fig. 11) is characterised by the analogous exothermic effect of the decomposition of CsO_3 to CsO_2 at 70–100°. The exothermic effect at 408° corresponds to the fusion and decomposition of the decomposition products of CsO_3. Both effects are confirmed by the nature of the oxygen liberation curve, shown by a broken line in the diagram. A comparison of the heating curves for KO_3 and CsO_3 shows that the limit of thermal stability rises with the atomic number of the elements.

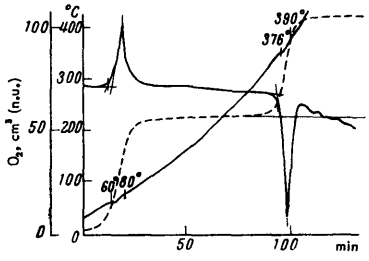


Fig. 10. Heating curve for potassium ozonide. Broken line: oxygen liberation curve.

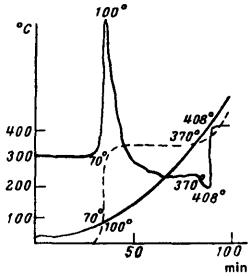


Fig. 11. Heating curve for caesium ozonide. Broken line: oxygen liberation curve.

STUDY OF THE THERMAL STABILITY OF PEROXO--ACIDS AND THEIR SALTS

Peroxo-acids are quite unstable compounds which are difficult to isolate in the free state. Their salts have a greater thermal stability and can be used as initiators in some polymerisations. Grigor'eva and Selezneva[34] succeeded long ago in isolating crystalline hydrates of metaperoxo-acids of niobium and tantalum. The heating curves of these compounds are given in Fig. 12. The endothermic effects at 75–100° for $HNbO_4.H_2O$ and 100–145° for $HTaO_4.H_2O$ correspond to the decomposition of these compounds to the meta-acid with evolution of active oxygen and water[34]. The heating curves of the sodium salts of peroxoorthoniobic and peroxoorthotantalic acids Na_3NbO_8 and Na_3TaO_8 (Fig. 13) are characterised by the presence of an exothermic effect of the liberation of all four atoms of active oxygen at 130°.[34] The sodium salt of peroxoorthovanadic acid is decomposed in a similar manner, but at 115°.[35]

Fig. 14 shows the heating curves of several salts of dinuclear peroxo-acids: potassium peroxodicarbonate $K_2C_2O_6$,[36] potassium peroxodisulphate $K_2S_2O_8$,[37] and sodium peroxopyrotantalate $Na_4Ta_2O_{12}$.[35] The endothermic effect on the heating curve of the potassium peroxodicarbonate at

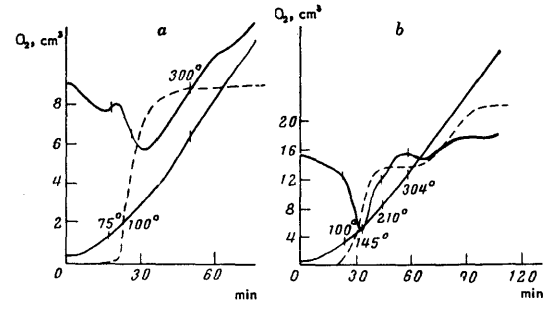


Fig. 12. Heating curve for hydrates of peroxoniobic and peroxotantalic acids:
a) $HNbO_4.H_2O$; *b*) $HTaO_4.H_2O$. Broken line: oxygen liberation curves.

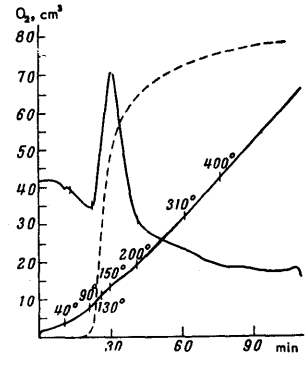


Fig. 13. Heating curves for sodium peroxoorthotellurate Na_3TaO_8. Broken line: oxygen liberation curve.

106° corresponds to its decomposition into carbonate with liberation of oxygen and carbon dioxide. The second effect at 198–200° corresponds to the decomposition of $KHCO_3$ impurity. On the heating curve of potassium peroxodisulphate the exothermic effect at 200° corresponds to the decomposition of this salt into pyrosulphate with liberation of oxygen. The endothermic effect at 350° corresponds to the fusion of pyrosulphate and the effect at 470° to the decomposition of the latter to sulphate with the liberation of sulphur trioxide. Sodium peroxopyrotantalate decomposes exothermically at 120° with liberation of all five atoms of active oxygen add the formation of $Na_4Ta_2O_7$. Potassium peroxopyrovanadate $K_4V_2O_{11}$ decomposes in a similar manner, but at 130–145°.[35]

Comparison of the heating curves shown in Fig. 14 suggests that when the decomposition of peroxo-salts is accompanied only by the liberation of active oxygen, this is shown by an exothermic effect (Figs. 14*b* and 14*c*). When the decomposition is more extensive, for example, by the reaction:

$$K_2C_2O_6 \rightarrow K_2CO_3 + CO_2 + {}^1/_2O_2$$

(Fig. 14*a*), the effect is endothermic.

Peroxide complexes which are not derivatives of peroxo--acids have been very little studied. Only one paper, devoted to the so-called uranium peroxide hydrates, has been published[38]. These compounds, which are peroxo--complexes and which contain a peroxo-group and water in the inner sphere, lose active oxygen stepwise on heating, with the formation of U_3O_8 finally at ~600°.

STUDY OF THE THERMAL STABILITY OF SALTS WITH HYDROGEN PEROXIDE AND WATER OF CRYSTALLISATION

The heating curves of salts containing hydrogen peroxide of crystallisation have an exothermic effect for the decomposition of the peroxide into water and oxygen. In several alkali metal carbonate–hydrogen peroxide addition compounds (Fig. 15) this effect, which was studied by Chamova[39] and by Dobrynina[40], is preceded by the endothermic effect of the fusion of a salt in the crystallisation water. When the salt contains water of crystallisation in addition to hydrogen peroxide of crystallisation (the so-called hydrates of peroxyhydrates), the type of curves, as is evident from the example of $Na_2SiO_3.3H_2O_2.H_2O$,[41] is the same as for anhydrous hydrogen peroxide addition compounds (Fig. 16). But sometimes, as for example, on heating $Na_2CO_3.2H_2O_2.H_2O$ (Fig. 17), an endothermic effect, corresponding to the removal of water of crystallisation, precedes an exothermic effect of the decomposition of the

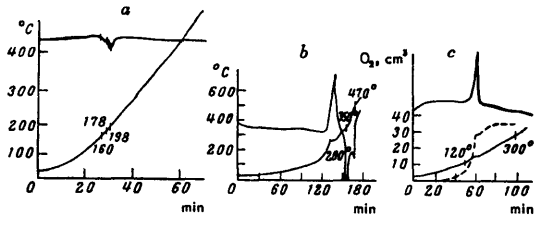


Fig. 14. Heating curves:
a) potassium peroxodicarbonate $K_2S_2O_6$; *b*) potassium peroxodisulphate $K_2S_2O_8$; *c*) sodium peroxopyrotantalate $Na_4Ta_2O_{12}$.

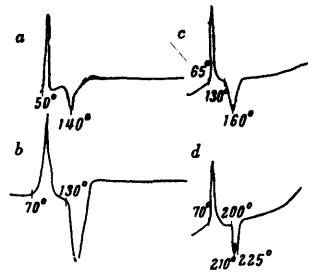


Fig. 15. Differential heating curves for hydrogen peroxide addition compounds of alkali metal carbonates:
a) $Na_2CO_3.2H_2O_2$; *b*) $K_2CO_3.3H_2O_2$;
c) $Rb_2CO_3.3H_2O_2$; *d*) $Cs_2CO_3.3H_2O_2$.

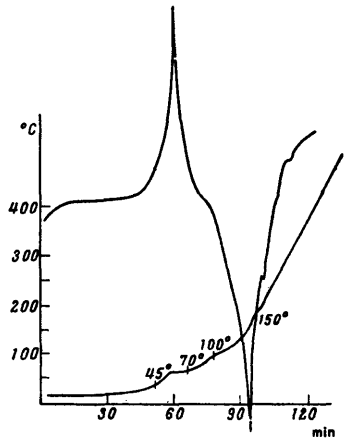


Fig. 16. Heating curve for sodium metasilicate–3-(hydrogen peroxide)–water, $Na_2SiO_3.3H_2O_2.H_2O$.

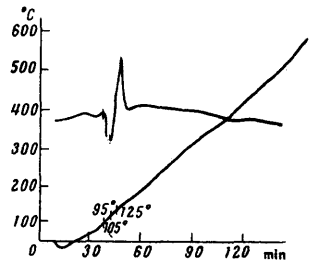


Fig. 17. Heating curve for sodium carbonate–2-(hydrogen peroxide)–water, $Na_2CO_3.2H_2O_2.H_2O$.

hydrogen peroxide of crystallisation. The curve permits the recommendation of temperature conditions for obtaining anhydrous sodium carbonate–hydrogen peroxide, which is widely used as a mild oxidant in the home and in the textile, food, and cosmetic industries. In some other salt–hydrogen peroxide addition compounds, for example, sodium sulphate–hydrogen peroxide[42], the endothermic

effect which corresponds to the incongruent melting of the compound precedes the exothermic effect of decomposition of hydrogen peroxide of crystallisation (Fig. 18).

Some bases — ammonia and urea — are also capable of forming molecular compounds with hydrogen peroxide. Their behaviuur on heating has been studied by Mironov[43], Lebedev[44], and Vol'nov[13]. Release of active oxygen in these compounds is shown on the heating curves by an exothermic effect at 40° and 80° respectively.

The example of several representatives of the groups of inorganic peroxo-compounds has shown that the use of differential thermal analysis in studying their thermal stability permits: (1) the rapid and objective determination of the nature and temperature limits of release of active oxygen: (b) the recommendation of a temperature regime for their production as hydrates, hydrogen peroxide addition compounds, or in the anhydrous state; (c) to recommend a temperature regime for their use in various oxidations; (d) to recommend temperature conditions for their safe storage; (e) to give a preliminary qualitative appraisal of the nature and strength of the bonding of the active oxygen in their molecules.

Depending on the group to which the peroxide compound belong, the heating curves are different:

1. The heating curves of the alkali and alkaline earth metal peroxides have an endothermic effect corresponding to the decomposition $M_2O_2 \rightarrow M_2O + \frac{1}{2}O_2$. With an increase in the atomic weight of the element forming the peroxide, the thermal stability increases. Barium peroxide is the most thermally stable compound of this group; it decomposes into oxide and oxygen at 790°.

2. The heating curves of alkali metal superoxides have successive endothermic effects for decomposition by the sequence $2MO_2 \rightarrow M_2O_2 + O_2 \rightarrow M_2O + \frac{1}{2}O_2$. The thermal stability of these compounds rises in the series Na–Cs.

3. The ozonides are the least stable of the simple (ionic) peroxides. Their heating curves have an exothermic effect for decomposition to superoxides by the reaction $MO_3 \rightarrow MO_2 + \frac{1}{2}O_2$ between 60° and 70°.



Fig. 18. Heating curve for sodium sulphate–3-(hydrogen peroxide), $Na_2SO_4.3H_2O_2$.

4. The heating curves of alkali and alkaline earth metal peroxide hydrates have an endothermic effect for decomposition by the reaction $M_2O_2 \rightarrow M_2O + \frac{1}{2}O_2$, which usually precedes the endothermic effects of incongruent melting and dehydration.

5. Unlike the alkaline earth metal peroxide hydrates, the hydrated forms of magnesium, zinc, and cadmium peroxides have heating curves with an endothermic effect corresponding to the loss of mother-liquor and the exothermic effect of decomposition. This can be explained by ascribing to these compounds the hydrogen peroxide form HO–M–OOH.

6. The heating curves of the salts of peroxo-acids have an exothermic effect at the thermal decomposition by the reaction $M_2E_2O_8 \rightarrow M_2E_2O_7 + \frac{1}{2}O_2$. When they undergo more extensive decomposition at the same time as they lose the active oxygen, there is an endothermic effect on their heating curves. The salts of the peroxo-acids exhibit considerable thermal stability and usually decompose above 130°. The peroxosulphates (~200°) are the most stable thermally.

7. The least stable of the peroxo-complexes are the molecular compounds with hydrogen peroxide — the "peroxohydrates" of peroxides and salts. Their heating curves have the exothermic effect of decomposition at 50–70°.

1. I.I.Vol'nov, "Perekisi, Nadperekisi i Ozonidy Shchelochnykh i Shchelochnozemel'nykh Metallov" (Peroxides, Superoxides, and Ozonides of the Alkali and Alkaline Earth Metals), Izd.Nauka, Moscow, 1964.
2. I.I.Vol'nov, in "Kratkaya Khimicheskaya Entsiklopediya" (Short Chemical Encyclopaedia), Vol.3, Sovetskaya Entsiklopediya, Moscow, pp.931–937.
3. A.F.Kapustinskii and K.S.Bayushkina, Trudy Vses.Nauch.-Issled.Inst.Mineral'.Syr'ya, No.109, 95 (1936).
4. T.A.Rafter, Analyst, 75, 485 (1950).
5. A.F.Kapustinskii, in "Trudy Pervogo Soveshchaniya po Termografii" (Proceedings of the First Conference on Thermography), Izd.Akad.Nauk SSSR, Moscow, 1955, p.182.
6. K.E.Mironov, Izv.Sektora Fiz.-Khim.Anal., Inst.Obshch. Neorg.Khim.Akad.Nauk SSSR, 26, 216 (1955).
7. A.I.Gorbanev, K.E.Mironov, A.B.Tsentsiper, and co-workers, "Izyskanie Vozmozhnosti Polucheniya i Izuchenie Fiziko-Khimicheskikh Svoistv Soedineniya Tipa H_2O_4" (Investigation of the Possibility of Obtaining and Studying the Physicochemical Properties of Compounds of the H_2O_4 Type), Otchet Laboratorii Perekisnykh Soedinenii, Inst.Obshch. Neorg.Khim., Akad.Nauk SSSR, Moscow, 1956.
8. J.A.Ghormley, J.Amer.Chem.Soc., 79, 1862 (1957).
9. I.I.Skorokhodov, L.I.Nekrasov, and N.I.Kobozev, Zhur. Fiz.Khim., 35, 2025 (1961) [Russ.J.Phys.Chem., 994 (1961)].
10. T.V.Rode and T.A.Dobrynina, Dokl.Akad.Nauk SSSR, 91, 125 (1953); Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 618 (1955).
11. T.V.Rode and G.A.Gol'der, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 301 (1956).
12. S.Z.Makarov and N.K.Grigor'eva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 598 (1954).
13. I.I.Vol'nov, Dokl.Akad.Nauk SSSR, 94, 477 (1954).
14. B.L.Tallmann and J.L.Margrave, J.Inorg.Nuclear Chem., 21, 40 (1961).
15. T.A.Dobrynina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 964 (1960).

16. S.Z.Makarov and N.K.Grigor'eva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 209 (1955).
17. A.Kh.Mel'nikov and T.P.Firsova, Zhur.Neorg.Khim., 6, 169 (1961) [Russ.J.Inorg.Chem., 83 (1961)].
18. S.Z.Makarov and T.I.Arnol'd, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 776 (1959).
19. I.I.Vol'nov, Zhur.Neorg.Khim., 3, 539 (1958).
20. C.Hoffman and R.Kopp, J.Amer.Chem.Soc., 81, 3830 (1959).
21. R.C.Ropp and M.A.Aia, Analyt.Chem., 34, 1288 (1962).
22. L.V.Ladeinov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 201 (1959).
23. N.G.Vannerberg, Arkiv Kemi, 14, 107 (1959).
24. S.Z.Makarov and T.A.Dobrynina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 298 (1956).
25. S.Z.Makarov and N.K.Grigor'eva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1164 (1959).
26. I.I.Vol'nov and A.N.Shatunina, Zhur.Neorg.Khim., 4, 1491 (1959) [Russ.J.Inorg.Chem., 671 (1959)].
27. I.I.Vol'nov, V.N.Chamova, V.P.Sergeeva, and E.L.Latysheva, Zhur.Neorg.Khim., 1, 1937 (1956); I.I.Vol'nov, V.N.Chamova, and E.I.Latysheva, *ibid.*, 2, 263 (1957); I.I.Vol'nov, V.N.Chamova, and A.N.Shatunina, *ibid.*, 3, 1097 (1958); I.I.Vol'nov and V.N.Chamova, *ibid.*, 3, 1098 (1958); 5, 522 (1960) [Russ.J.Inorg.Chem., 249 (1960)]; I.I.Vol'nov and E.I.Latysheva, *ibid.*, 2, 259 (1957); I.I.Vol'nov, V.N.Chamova, and V.P.Sergeeva, Zhur.Neorg.Khim., 4, 253 (1959) [Russ.J.Inorg.Chem., 109 (1959)]; I.I.Vol'nov and E.I.Latysheva, Zhur.Neorg.Khim., 2, 1696 (1957); I.I.Vol'nov and A.N.Shatunina, Dokl.Akad.Nauk SSSR, 110, 87 (1956).
28. T.V.Rode and G.A.Gol'der, Dokl.Akad.Nauk SSSR, 110, 1001 (1956).
29. T.V.Rode, Dokl.Akad.Nauk SSSR, 90, 1075 (1953).
30. M.Blumenthal, Roczniki Chem., 12, 127 (1930).
31. R.de Forcrand, Compt.rend., 158, 991 (1914).
32. I.I.Vol'nov and V.V.Matveev, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 1136 (1963).
33. E.I.Sokovnin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 181 (1963).
34. N.K.Grigor'eva and K.I.Selezneva, Izv.Akad.Nauk SSSR, 1138 (1962); S.Z.Makarov, N.K.Grigor'eva, and K.I.Selezneva, in Collected Papers, "Khimiya Perekisnykh Soedinenii" (The Chemistry of Peroxide Compounds), Izd. Akad.Nauk SSSR, Moscow, 1963, p.177.
35. N.K.Grigor'eva and K.N.Dergacheva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 943 (1962).
36. A.Kh.Mel'nikov, T.P.Firsova, and A.N.Molodkina, Zhur. Neorg.Khim., 7, 1237 (1962) [Russ.J.Inorg.Chem., 637 (1962)].
37. I.N.Vol'nov, V.N.Chamova, and E.I.Kolotova, Zhur. Neorg.Khim., 6, 268 (1961) [Russ.J.Inorg.Chem., 137 (1961)].
38. E.Ya.Rode, Z.S.Golovleva, V.G.Kuznetsov, and P.A.Koz'min, Zhur.Neorg.Khim., 6, 2635 (1961) [Russ.J.Inorg. Chem., 1331 (1961)].
39. S.Z.Makarov and V.N.Chamova, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 632 (1952).
40. B.S.Dzyatkevich and T.A.Dobrynina, in Collected Papers "Khimiya Perekisnykh Soedinenii" (The Chemistry of Peroxide Compounds), Izd.Akad.Nauk SSSR, Moscow, 1963, p.113.
41. I.I.Vol'nov and A.N.Shatunina, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 201 (1963).
42. I.I.Vol'nov and E.I.Kolotova, Zhur.Neorg.Khim., 4, 2143 (1959) [Russ.J.Inorg.Chem., 971 (1959)].
43. K.E.Mironov, Candidate's Thesis, Peroxide Compounds Laboratory, Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow, 1953.
44. S.Z.Makarov and B.A.Lebedev, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 785 (1955).
45. I.I.Vol'nov and V.V.Matveev, in Collected Papers, "Issledovaniya v Oblasti Okislov" (Investigations in the Field of Oxides), Izd.Nauka, Moscow–Leningrad, 1965, p.305.

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PHYSICOCHEMICAL INVESTIGATIONS AND METHODS OF PRODUCING COMPLEX FERTILISERS WITH THE USE OF UREA

G. L. Tudorovskaya and F. G. Margolis

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I. INTRODUCTION

Urea is a highly concentrated fertiliser containing 46.6% nitrogen, free of inert materials, and is used either independently or in complex fertilisers which contain phosphorus and potassium as well as nitrogen. Furthermore, urea finds use as foodstuff for farm animals, is widely employed in plastics manufacture, in the pharmaceutical industry, and in medicine.

The increase in the demand by agriculture and industry for urea has brought about a considerable increase in the production in the USSR and abroad[1]. The greatest amount of urea is produced in Japan, where 85–90% of the total output is used as a fertiliser, compared with 60–65% in USA, and 20–40% in Europe.

In 1962 urea formed only 8% of the world production of nitrogenous fertilisers; in 1966 [1963 ?] this had grown to 17.5% calculated on nitrogen[2]. The production of urea for industrial purposes is also growing steadily.

In the USSR until recently the use of urea as a fertiliser was quite limited. In 1958 the total fraction of urea in the balance of nitrogenous fertilisers was 1% (calculated on