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Oxygen Compounds of Iron(VI, V, IV)

I.G.Kokarovtseva, I.N.Belyaev, and L.V.Semenyakova

Published information on the chemistry of oxygen compounds of iron—the ferrates(VI, V, IV)—has been reviewed briefly. The methods of preparation, chemical properties, thermal decomposition in air and in O_2, the kinetics and mechanism of decomposition in solution, methods of analysis, structural, spectroscopic, and magnetic studies, the nature of the covalent bonding, and the uses of the ferrates(VI, V, IV) have been described. The bibliography contains 108 references.

CONTENTS

I. Ferrates(VI) 929
II. Ferrates(IV) 932
III. Ferrates(V) 935

I. FERRATES(VI)

Compounds of sexavalent iron in the form of salts of ferric acid ($MFeO_4$) have been known for a long time [1,2]. About twenty to thirty of these compounds have now been prepared; only the ferrates(VI) of potassium, rubidium, caesium, strontium, and barium have been obtained in the pure crystalline state, and the others are known in solution or have been isolated from solution in the solid state but with a considerable amount of impurity. The difficulties associated with the preparation of pure crystalline ferrates(VI) are due chiefly to their instability.

Preparation. The alkali metal ferrates(VI) can be prepared by the following methods: 1) by heating to red heat a mixture of iron filings and potassium nitrate or a mixture of iron oxide, alkali, and potassium nitrate [1-3]; 2) by oxidising, by heating in a stream of O_2, solid phases consisting of an alkali metal oxide, peroxide, or hydroxide with iron (or its oxide) in the ratio $M_{alk}:Fe = 2:1$; [4-8] 3) by the electrochemical dissolution of an iron anode in alkali solutions [9-12]; 4) by oxidising iron salts or the freshly prepared hydroxide with various oxidising agents (Cl_2, Br_2, NaOCl etc.) in a strongly alkaline medium [13-19]; and 5) by double decomposition [20].

Methods (1) and (2) are the simplest, but the ferrates(VI) obtained by these methods are usually contaminated by traces of the starting materials and side products of the reactions, and these cannot be removed without decomposition of the chief product. Method (3) gives only solutions of the alkali metal ferrates(VI), the concentration of which increases with increase in temperature to 50°, or with increase in the alkalinity of the solution and the current density.

Method (4), which has been used to prepare the pure crystalline ferrates(VI) of K, Rb, and Cs, is of particular interest. These ferrates have a limited solubility in saturated solutions of the corresponding alkalis. This property is used to precipitate them from solution. A product with a purity of 98–100% is obtained by recrystallising the precipitated ferrates(VI) and washing with alcohols [21]. The high solubility of Li_2FeO_4 and Na_2FeO_4 in concentrated alkalis makes it impossible to isolate them from solution in the crystalline state [22]. Solid Li and Na ferrates(VI) can be obtained by method (5), by the double decomposition of $LiClO_4$ or $NaClO_4$ with K_2FeO_4 with subsequent vacuum-drying of the filtrate [20]. The products, however, have a purity of only 15–69%. The ferrates(VI) of Na and more particularly Li decompose much more rapidly than the ferrates(VI) of the other alkali metals during preparation and purification.

As far as the alkaline earth metal ferrates(VI) are concerned, it should be noted that unlike the ferrates(VI) of Ca and Mg, the ferrates(VI) of Sr and Ba are sparingly soluble in water and are precipitated when K_2FeO_4 solution is treated with Sr or Ba nitrates, chlorides, or acetates [10, 16,23,24]. It has been possible to obtain pure crystalline $SrFeO_4$ and $BaFeO_4$† only at 0° in the complete absence of CO_2. In the moist state they decompose fairly rapidly by reacting with CO_2. [17] Solutions of Ca and Mg ferrates(VI) have been obtained by the double decomposition of Ca and Mg sulphates, carbonates, or oxalates with $SrFeO_4$. [23]

The ferrates(VI) of other metals have been obtained by double decomposition from solutions of the metal nitrates and a suspension of $BaFeO_4$ in water [25]. Solid ferrates(VI) of Pb, Cu, Ag, Hg, Al, Zn, Th, Co, Ni, Fe^{II}, and Fe^{III} have been isolated in this way. Most of these compounds decompose on drying or with a slight increase in temperature (30–40°).

Attempts to replace oxygen in ferrate(VI) by fluorine by fluorinating K_2FeO_4 [26] or a $4KO_2 + Fe_2O_3$ mixture [27] were unsuccessful.

Physicochemical properties. The dry crystalline ferrates(VI) of K, Rb, Cs, and Sr are stable in air and can be kept in closed vessels. Barium ferrate(VI) in the moist state with a water content of 4–5% is spontaneously converted into $BaFeO_3$ at room temperature [17,28]. The decomposition corresponds exactly to the equation

$$BaFeO_4 \cdot aq = BaFeO_3 \cdot aq + \frac{1}{2} O_2$$

At a moisture content of 1–2%, $BaFeO_4$ has an almost unlimited stability.

When heated, all ferrates(VI) decompose with the liberation of O_2 and the final formation of tervalent iron compounds. The decomposition of ferrates(VI) in air takes place at different temperatures: 150–400° for K_2FeO_4, 80–600° for $SrFeO_4$, and 105–800° for $BaFeO_4$. [29] The liberation of active oxygen in the thermal decomposition is not accompanied by the immediate reduction of Fe^{VI} to Fe^{III}, but involves the conversion of the ferrates(VI) through intermediate reduction states to

†$SrFeO_4$ is less stable than $BaFeO_4$. The maximal purity of Sr ferrate(VI) obtained did not exceed 95–97%.

ferrates(III).[17,30,31] For example, the decomposition of K_2FeO_4 in a stream of O_2 from 200° to 700° involves the formation of potassium ferrate(V) and ferrate(III) by the reaction:

$$2K_2FeO_4 = K_3FeO_4 + KFeO_2 + O_2$$

Above 700°, after the complete disappearance of K_2FeO_4, decomposition of K_3FeO_4 begins:

$$K_3FeO_4 = KFeO_2 + K_2O + \frac{1}{2}O_2$$

Pure $KFeO_2$ is obtained at 1000°, after the volatilisation of K_2O.

Sr and Ba ferrates(VI) decompose in a stream of O_2 as follows: at low temperatures (~200°) vigorous liberation of active oxygen takes place with the formation of ferrates(III); oxidation of Fe^{III} to Fe^{IV} begins at about 400°, reaching a maximum (~90% Fe^{IV}) at 700–900° with the formation of $SrFeO_3$ and $BaFeO_3$.[32]

The red-violet aqueous solutions of ferrates(VI) are unstable and gradually decompose according to the scheme:

$$2FeO_4^{2-} + 3H_2O = 2FeO(OH) + \frac{3}{2}O_2 + 4OH^-$$

Study of the rate of decomposition by measurement of the change in pH with time in solutions with different K_2FeO_4 concentrations[33] has shown that dilute solutions of ferrates(VI) are more stable than concentrated solutions. For example, after standing for 1 h, 0.02–0.025 M solutions still contained 89% of the FeO_4^{2-} taken initially, whereas 0.05–0.086 M solutions decomposed completely.

The decisive factors influencing the stability of ferrate(VI) solutions are temperature and alkalinity[34]. The rate of decomposition of ferrates(VI) decreases considerably at low temperatures. Thus the rate of decomposition of 0.01 M K_2FeO_4 solution at 25° is five times that at 0°. The influence of alkalinity on the decomposition of ferrate(VI) solutions is complex and depends on the magnitude of the surface area of the $Fe(OH)_3$ formed in the decomposition[35]. The properties of the latter are determined by the concentration of alkali. Thus in 10% and 40% alkali solutions the $Fe(OH)_3$ precipitate is bulky and settles very slowly. In this instance the ferrate(VI) solutions decompose rapidly. In 20% alkali solutions, in which $Fe(OH)_3$ is precipitated in a compact form and rapidly produces a binding film on the walls of the vessel, ferrate(VI) solutions decompose much more slowly.

The addition of salts to ferrate(VI) solutions influences their stabilities in different ways. Potassium periodate[37], metaphosphates, pyrophosphates, and borates[36] produce a sharp increase in their stability. The addition of alkali metal cations to a ferrate(VI) solution, on the other hand, increases the rate of decomposition in the order Li^+, Na^+, K^+, Rb^+, and Cs^+, the increase being greater, the greater the concentration of the added cation[38].

The decomposition may take place in different ways, depending on the initial ferrate(VI) concentration[39]. In dilute solutions the decomposition is homogeneous and corresponds to the kinetic equation $dx/dt = k(a-x)^2/x$. When the active form of iron hydroxide appears, the reaction rate increases and corresponds to fractional-order kinetics. In concentrated solutions (greater than 0.01 M) iron hydroxide is formed immediately on decomposition, and the reaction is heterogeneous almost from the start.

The decomposition of ferrates(VI) in highly concentrated alkali solutions is monomolecular and gives $Fe(OH)_3$ with the intermediate formation of ferrates(IV).[35,40,41] The first stage of the decomposition is characterised by the complete decolorisation of the violet ferrate(VI) solutions and the precipitation of dark-blue or black Na and K ferrates(IV) respectively. The composition of the latter has not been determined. In the second stage the unstable ferrates(IV) decompose, the decomposition being slow in concentrated alkali solutions and immediate on dilution with water.

Recent studies[42] have established that the decomposition of ferrates(VI) in alkali solutions (like the decomposition of permanganates and perrhenates) is catalysed by traces of nickel and cobalt always present in the reagents. It has been proved experimentally that the rate of decomposition of alkali ferrate solutions prepared from highly pure reagents is extremely low. On the addition of nickel or cobalt salts (10^{-6} M) the stability of these solutions decreased sharply. The influence of other salts, or of $Fe(OH)_3$, was slight, however. This specific influence of nickel and cobalt salts proves that the course of the decomposition of ferrates(VI) (like that of permanganates and perrhenates) cannot be explained by any of the mechanisms previously put forward. The reaction mechanism probably involves reduction on the surface of nickel or cobalt micelles and the reduction of their hydroxo-complexes. It is suggested[41] that the use of very pure chemical reagents in the study of oxidation may give qualitatively new results even for simple and familiar reactions.

Ferrates(VI) are powerful oxidising agents, more powerful than permanganates. Even in weakly acidic medium they decompose with the formation of Fe^{III} salts and the liberation of O_2. Mg, Al, P, and S powders react violently with solid K_2FeO_4 on heating. Ammonia is oxidised to nitrite by the action of small quantities of K_2FeO_4, and to nitrate by a large excess. Nitrites are oxidised to nitrates, bivalent manganese to quadrivalent[43], iodates to periodates[44], chromite to chromate[45], arsenite to arsenate[46], etc. Hydrogen peroxide in strongly alkaline medium reduces FeO_4^{2-} to $Fe(OH)_3$. The addition of H_2O_2 in the presence of Trilon B to a suspension of $Fe(OH)_3$ in alkali solution, however, gives ferrate(VI) solution[47,48]. The addition of Trilon B to a prepared alkaline solution of ferrate(VI) increases its rate of decomposition. The reason for the accelerating action of Trilon B on the formation of FeO_4^{2-} by the reaction with H_2O_2 has not been determined.

Organic substances, for example paper, wood, etc., are slowly oxidised by dilute ferrate(VI) solutions; sugar and egg albumin decolorise ferrate(VI) solutions rapidly[30]. Ferrates(VI) are insoluble in alcohols (except Li_2FeO_4 and Na_2FeO_4) and gradually oxidise them to aldehydes.

Ferrates(VI) are isomorphous with chromates and sulphates, and form solid solutions with them[16,49,50]. The infrared (IR) spectra of the isomorphous compounds K_2XO_4 and $BaXO_4$ (X^{VI} = S, Se, Cr, or Fe) are similar, particularly in the high-frequency range. The spectra of the solid solutions of these compounds are also similar[51].

Spectroscopic studies of ferrates(VI) have been shown that the following vibrational frequencies are characteristic of the FeO_4^{2-} ion. The infrared range (220–2000 cm^{-1}) shows an absorption band at about 800 cm^{-1}, with triplet splitting which is distinct for K_2FeO_4 and $BaFeO_4$ but much less distinct for $SrFeO_4$.[29] The visible spectra show a sharp maximum at 505 μm and two minima at 390 μm and 675 μm.[52,53] The high-frequency visible and ultra-violet spectra show a large absorption peak at 19 600 cm^{-1}, asymmetric with a shoulder at 17 800 cm^{-1}, and a small

peak at 12700 cm^{-1}. [54,55] This spectrum is similar to the spectrum of the isoelectronic ion MnO_4^{3-}. The interpretation of the electronic spectra of FeO_4^{2-} and MnO_4^{3-} on the basis of the MO method previously developed for the CrO_4^{2-} and MnO_4^{2-} ions [56] led to the conclusion that the unpaired electrons must occupy a triply degenerate orbital. The earliest measurements of the electron paramagnetic resonance (EPR) of FeO_4^{2-} and MnO_4^{3-} in alkali solutions confirmed this suggestion [57], but later measurements with single crystals of these salts led to the conclusion that the unpaired electrons occupy a doubly degenerate orbital [58].

K and Cs ferrates(VI) are paramagnetic [8]; the effective magnetic moments amount to 2.8–2.9 μ_B, corresponding to two unpaired electrons. The formation of regular tetrahedra is possible only for sp^3- or d^3s-hybridisation. According to Klemm [8], ferrates(VI) show sp^3- and not d^3s-hybridisation. This conclusion was reached by analogy with the FeO_4^{3-} ion, for which magnetic studies showed three unpaired electrons, so that d^3s-hybridisation is impossible. The interpretation of the isomeric shift in the Mössbauer spectrum of K_2FeO_4 shows, however, that the covalent contribution from the oxygen ligands is made to hybridised d^3s-orbitals of the iron [59,60].

Analyses. The familiar methods for the analysis of ferrates(VI) are based on their oxidising properties (arsenite and chromite methods) or on the instability of ferric acid H_2FeO_4 (gas-volumetric method).

The arsenite method is based on the reduction of the ferrate(VI) ion in strongly alkaline arsenite solution [46]:

$$2FeO_4^{2-} + 3AsO_3^{3-} + 11H_2O \rightarrow 2Fe(OH)_3(H_2O)_3 + 3AsO_4^{3-} + 4OH^-$$

The back titration of the excess of arsenite can be carried out with standard solutions of bromate (Methyl Orange indicator, 70–80°), cerate (phenanthroline indicator, in the cold), or permanganate (with the addition of KI). The arsenite method is recommended for the analysis of pure ferrate(VI) specimens which have not undergone decomposition and which do not contain impurities capable of oxidising arsenite.

The chromite method [45] is based on the oxidation of chromite by the ferrate(VI) ion in strongly alkaline solution according to the equation:

$$Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3(H_2O)_3 + CrO_4^{2-} + OH^-$$

The chromate ion is titrated with a standard solution of Fe^{2+} and Na diphenylaminesulphonate indicator. The chromate method is particularly suitable for the analysis of dilute ferrate solutions. It can also be modified for insoluble ferrates(VI), with which reaction takes place only on prolonged heating (95–100°, 1 h). [24]

The gas-volumetric method [17,61] is recommended for ferrates(VI) with different degrees of purity; this method involves the decomposition of the ferrates by dilute acids, for example

$$2K_2FeO_4 + 5H_2SO_4 \rightarrow 5H_2O + 2K_2SO_4 + Fe_2(SO_4)_3 + \frac{3}{2}O_2$$

CO_2 impurity in the oxygen liberated in the analysis of specimens contaminated with carbonates is removed by absorption in KOH solution.

The reduction of ferrates(VI) by iodide ions in acid medium according to the equation $FeO_4^{2-} + 4I^- + 8H^+ \rightarrow Fe^{2+} + 4H_2O + 2I_2$ cannot give quantitative results, because of the expected reduction of Fe^{III} impurities usually present in the specimens. The iodometric method is sometimes used, however, for the determination of active oxygen (equivalent to the iodine liberated) together with the determination of the total iron in the specimen [16,17]. The degree of oxidation of the iron is readily calculated from the observed molar ratio Fe : O_{act}. The reaction of KI with ferrate(VI) solutions takes place smoothly, without spontaneous decomposition, but in the reaction of the insoluble $BaFeO_4$ and $SrFeO_4$ with KI in acid solution, which requires longer treatment and increased temperature, a small quantity of O_2 is volatilised, so that the analysis gives low results [17]. Thus for insoluble ferrates(VI), accurate values for O_{act} are obtained only by the gas-volumetric determination.

Uses of ferrates(VI) and their role in various industrial processes. In recent years there has been an increase in interest not only in the theoretical aspects of ferrates(VI) but also in their applied chemistry, chiefly in relation to their oxidising function.

Vil'nyanskii and Pudovkin [62] concluded that the production of sodium chromate from a mixture of natural chrome ironstone, sodium carbonate, and other additives involves the formation of sodium ferrate(VI), which is soluble in the liquid melt formed by the reaction mass at high temperatures (1150°). The ferrate(VI) acts as a carrier of oxygen from the furnace gas to the surface of the chromite granules. It is suggested that the existence of Na_2FeO_4 at such high temperatures is due to an increase in its thermal stability on dissolution in the molten chromate.

Studies of the passivation of iron in concentrated nitric acid have given interesting results [63]. It has been shown that the passivity of iron is due to the formation of a film of ferric acid H_2FeO_4 or a related compound of iron, and not a layer of iron oxide, as assumed by other workers. The sexavalent iron compound is formed in the anodic region as a consequence of the intense local action of galvanic currents when iron reacts with concentrated HNO_3. The formation of this compound is accompanied by its chemisorption on the iron surface, and it has a higher chemical stability in this state than in the free state (analogous to the stability of the passive chromate films chemisorbed on iron). It is unaffected by a large number of reagents with which it reacts, with rapid decomposition, in the free state. On reaction with solutions of ferrates(VI) (or chromates) iron was covered with a passive film which was the same as that formed in the reaction of the acid with iron. When the passivated iron was immersed in NaOH solution, the red-violet colour typical of the ferrate ion was produced, by the replacement of this ion on the iron surface by the preferentially adsorbed OH^- ion. This solution exhibited oxidising properties typical of ferrate(VI). The metastable ferrate film is decomposed by cathodic reduction, mechanical shock, and heating, and in the presence of halide ions.

The production of a corrosion-resistant layer on metallic surfaces by ferrate(VI) solutions has been used to develop a method for protecting iron and steel castings from corrosion [64]. The method is based on the rapid formation of Fe_2O_3 by the decomposition of the thin film of ferrate(VI) on the metal and ferrate(VI) solution. It involves bringing the metal successively into contact with an alkali solution containing a reducing agent (12.5% NaOH + 0.4% 8-quinolinol) and a solution containing an alkali metal ferrate (1%).

Alkali metal ferrates(VI) have found application for decolorising coloured impurities in the caustic solutions obtained in electrolyte baths [65]. The addition of a small quantity of ferrate(VI) (for example 0.5 g Na_2FeO_4) to a very large quantity of a solution containing coloured

impurities (for example 100 g of blue NaOH solution) leads to decolorisation on gentle heating. The resulting solution, purified from chlorine and iron, satisfies industrial standards.

Na_2FeO_4 has proved useful for the purification of hemicellulose by precipitation from alkali solutions [66]. Compared with other methods for precipitating hemicellulose by means of $CuSO_4$, $Pb(CH_3COO)_2$, or Na_3AlO_3, the new method not only gives better purification of the alkali solution and an improvement in the quality of the viscose, but also gives a hemicellulose precipitate which can be filtered off rapidly and used for the production of other materials. It is recommended that Na_2FeO_4 be produced in the plant by direct electrolysis in the baths in which the precipitation is carried out.

Solid K_2FeO_4 is used as an activator in the production of catalysts used in the Fischer–Tropsch process [67,68]. The catalyst is prepared by mixing Fe_2O_3 (α- or γ-modification) with potassium ferrate(VI) powder (0.2–20 wt.%) in a small quantity of alcohol. Tablets with this composition are heated for 4 h at 540° in an oxidising atmosphere and then for approximately 24 h in a reducing atmosphere at 370–870°.

II. FERRATES(IV)

The first papers on the preparation and study of properties of compounds of quadrivalent iron were published in the nineteen-forties [69], although the possibility of existence of these compounds was noted as early as 1909, by Moeser and Borck [70]. They were the first to prepare Sr and Ba ferrates(IV), for which they used the formulae $SrO.FeO_2$ and $BaO.FeO_2$, by heating dry $Fe(NO_3)_3 + Sr(NO_3)_2$ and $Fe(OH)_3 + Ba(OH)_2$ mixtures in a stream of O_2 at 600° and 400° respectively. As shown later by Scholder [71], the Sr and Ba ferrates obtained in this way are always extensively contaminated by oxides of iron and the alkaline earth metals.

Four types of compound of quadrivalent iron are now known: 1) metaferrates(IV) $MFeO_3$‡ (alkali metals, Ba, Sr, Ag, and Pb); 2) orthoferrates(IV) M_2FeO_4 (alkali metals, Sr, and Ba); 3) pentaoxoferrates(IV) M_3FeO_5 (Ba only); and 4) ferrates(IV) of the type $M_3Fe_2O_7$ (Ba and Sr only).

Preparation. The simplest and most widely encountered method for preparing ferrates(IV) is by the thermal oxidation of a mechanical mixture of two solid phases with an M : Fe ratio corresponding to that in the ferrate(IV). In a study of the oxidation of mixtures of two solid phases, Wahl [72] established that for complex compounds§ in which the central atom is in a high oxidation state, neglecting the temperature and the pressure of the gas, the following stabilisation methods are possible: 1) selection of complex-forming ligands; 2) selection of cation; 3) change in the ratio of the number of cations to the number of central atoms.

It can readily be appreciated that the choice of ligand has a significant influence on the degree of oxidation. When it is necessary to stabilise a low or intermediate oxidation state, ligands with a low electronegativity are chosen; on the other hand, the formation of complexes in which the central atom is in a high oxidation state requires ligands with a high electronegativity, such as fluorine and oxygen. Oxygen is preferred, however; there are then extensive possibilities for the stabilisation of higher oxidation states, since oxygen can carry a negative charge greater than unity, and can form π-bonds.

A not unimportant factor in the production of highly oxidised complexes is the choice of cation. Chemical experiments have shown that the formation of these complexes is most favoured by large cations.

The influence of change in the ratio of the number of cations to the assumed central atom on the degree of oxidation is small. For example, it is observed for the oxidation of an $Fe_2O_3 + K_2O$ mixture: $KFeO_2$ is formed at K : Fe = 1 : 1, K_2FeO_4 at 2 : 1, and K_3FeO_4 at 3 : 1. It is not observed, however, for an $Fe_2O_3 + BaO$ mixture: $BaFeO_3$ is formed at Ba : Fe = 1 : 1, Ba_2FeO_4 at 2 : 1, and Ba_3FeO_5 at 3 : 1. Here, the iron in all the products is quadrivalent.

In the preparation of ferrates(IV), combinations of iron oxides, hydroxide, or nitrate with the oxide, hydroxide, carbonate, nitrate, or other compound of the alkali, alkaline earth, or other metal can be used in the mixture being oxidised. A large number of experiments on the preparation of ferrates(IV) by the oxidation of mixtures of two solid phases under different conditions (400–1000°, stream of dry or moist O_2) showed that the Fe^{IV} concentration in the products does not exceed 90%. [32,71,74–77] An Fe^{IV} concentration of 100% was observed in only one instance, in the preparation of Na_4FeO_4 by the oxidation of a stoichiometric $Fe_2O_3 + Na_2O$ mixture in a stream of dry O_2 at 450°. [75] The study of the kinetics of the oxidation of a mechanical $Fe_2O_3 + 2BaCO_3$ mixture in a stream of O_2 at 700–900° showed that the reaction between the components is incomplete at the temperatures of the experiment, leading to the presence of Ba and Fe oxides in the reaction products [73]. Similar results can evidently be expected in the oxidation of other mechanical mixtures.

Recent experiments [77–80] have shown that it is more appropriate to prepare ferrates(IV) by the oxidation of a single solid phase, that is ferrate(III), previously prepared by sintering the above mixtures in air or in an atmosphere of an inert gas at high temperatures (1100 to 1400°). Subsequent saturation of ferrates(III) with oxygen under high pressure increases the degree of oxidation of iron, raising the Fe^{IV} concentration to even 100% (see Table). In most instances, however, Fe^{III} cannot be oxidised completely to Fe^{IV} even by carrying out the preparation at super-high O_2 pressures.

Because of the incomplete oxidation of Fe^{III} to Fe^{IV}, which is evidently due to the insufficient thermal stability of ferrates(IV), non-stoichiometric compounds containing oxygen vacancies in the crystal lattice are obtained. The loss of each oxygen anion is compensated by the conversion of two Fe^{IV} ions into two Fe^{III} ions. Thus the empirical formulae of the oxygen-deficient compounds are: for the metaferrates(IV) $M(Fe^{IV}_{1-2x}Fe^{III}_{2x})O_{3-x}$, for the orthoferrates(IV) $M_2(Fe^{IV}_{1-2x}Fe^{III}_{2x})O_{4-x}$, and for ferrates(IV) of the type $M_3Fe_2O_7$ $M_3(Fe^{IV}_{2-4x}Fe^{III}_{4x})O_{7-2x}$, where $0 \leq x \leq 0.5$.

Van Hook [82,83] established that the degree of oxidation of iron in ferrates depends to some extent on the area of the surface being oxidised. In the study of the influence of the surface area, three $BaFeO_{2.5}$ specimens—a fine powder with an average particle size of ~ 5 μm, a ceramic

‡M represents a bivalent metal atom or two univalent metal atoms.

§Metallates formed on the oxidation of mixtures of two solid phases.

tablet with a porosity of ~ 25%, and a piece of a single crystal grown in air by cooling from the melting point 1370°—were oxidised under identical conditions until their weight showed no further change with time. It was found that the degree of oxidation of iron was greater in the first specimen than in the second, and greater in the second than in the third. It was noted that although adsorption of oxygen took place, it was clearly a secondary factor, since only small differences in the degree of oxidation were observed for specimens for which the surface areas differed considerably from one another.

Preparation of ferrates(IV) by the thermal oxidation of ferrates(III) by oxygen under pressure.

No.	Starting materials (ceramic)	t, °C	P_{O_2}, atm.	Time, h	Composition of ferrate obtained	Fe^{IV}/Fe_{total} %	References
1	$BaFeO_{2.5}$	325	18500	184	$BaFeO_{2.95}$	90	78
2	$BaFeO_{2.5}$	400	20500	88	$BaFeO_{2.95}$	90	78
3	$SrFeO_{2.5}$	1000	65	24	$SrFeO_{2.98}$	96	79
4	$SrFeO_{2.5}$	760	337	168	$SrFeO_3$	100	80
5	$Sr_3Fe_2O_6$	400	15000	144	$Sr_3Fe_2O_{6.9}$	90	77
6	$CaFeO_{2.5}$	300	200	24	$CaFeO_{2.5}$	0	81

Sr and Ba ferrates(IV) can be obtained by the decomposition, in an oxidising atmosphere, of complex compounds containing iron and the alkaline earth metal, for example $M_3[Fe(OH)_6]_2.xH_2O$ and $M_2[Fe(C_2O_4)_3]_2.xH_2O$ (M = Sr or Ba). Here, the formation of the ferrates involves the reaction between the decomposition products of the complexes and the subsequent oxidation of Fe^{III} to Fe^{IV}. Thus when the hydroxoferrates(III) $M_3[Fe(OH)_6]_2$ are heated in a stream of O_2 at 300–450°, products with the composition $MFeO_3 + \frac{1}{2}M(OH)_2$, containing only quadrivalent iron, are formed [32,71]. Attempts to remove the component $M(OH)_2$ by extraction with anhydrous methanol led to appreciable decomposition of the metaferrates(IV) (to 56% Fe^{IV}).

Sr_2FeO_4, Ba_2FeO_4, and Ba_3FeO_5 with an Fe^{IV} concentration of 100% are formed when $M_3[Fe(OH)_6]_2 + xM(OH)_2$ mixtures ($x = 1$ for M_2FeO_4, $x = 3$ for M_3FeO_5) are heated in a stream of O_2 at 800°. [75]

In the products obtained by heating tris(oxalato)-ferrates(III) $M_3[Fe(C_2O_4)_3]_2$ in a stream of O_2, the Fe^{IV} concentration does not exceed 75%. [84,85]

For the preparation of Sr and Ba metaferrates(IV) from the corresponding ferrates(VI), the most suitable starting materials are Ba and Sr ferrates(VI). As already noted, when $BaFeO_4.aq$ specimens are kept, their colour changes from cherry-red to dense black, accompanied by the quantitative conversion of barium ferrate(VI) into barium metaferrate(IV). The liberation of oxygen is complete in several weeks (sometimes days) even in a sealed glass vessel; when the latter is opened, the oxygen volatilises with a loud crack. An important feature is that the oxidation coefficient does not fall below 0.97 even when the experiment is continued for a long time (240 days). Strontium ferrates(VI) do not undergo this transformation.

The conversion of $BaFeO_4$ into $BaFeO_3$ takes place much more rapidly, in 7–20 min, when freshly prepared $BaFeO_4$ is heated to 90–100° in 50% KOH or NaOH solution [32,38]. In concentrated alkali solutions, $SrFeO_4$ decomposes immediately to $Fe_2O_3.aq$, $Sr(OH)_2$, and O_2, and in hot saturated $Sr(OH)_2$ solution it is converted into Sr metaferrate(IV), extensively contaminated by Fe^{III}. [32] Ba and Sr metaferrates(IV) containing not more than 85 to 92% Fe^{IV} can be obtained by the thermal decomposition of Ba and Sr ferrates(VI) in a stream of O_2 at 700 to 1000°.

Only lithium and silver ferrates(IV) have been prepared by double decomposition. Li_2FeO_3 (94–98% Fe^{IV}) was obtained by the reaction of solid K_2FeO_4 and LiOH (Li : Fe = 8) at 300° and subsequent removal of the excess of LiOH by extraction with absolute methanol at −30°. Ag_2FeO_3 (100% Fe^{IV}) was obtained by adding $AgNO_3$ to K_2FeO_4 solution at 0° (Ag : Fe = 2) and washing the resulting precipitate with ethanol and ether at 0°. [32]

Analyses. The compositions of ferrates(IV, V, VI) are usually determined by analysis for the component elements, and expressed as atomic ratios M : Fe : O$_{act}$. The concentration of active oxygen is determined iodometrically (Fe^{IV}, V, VI $\xrightarrow{I+H^+}$ Fe^{II}) or gas-volumetrically (Fe^{IV}, V, VI $\xrightarrow{H^+}$ Fe^{III}). The gas-volumetric method can be used as an independent method for the determination of the Fe^{IV} concentration [61]. An original method for the determination of Fe^{IV} was proposed by Mori [86]. The ferrate(IV) specimen is dissolved in hydrochloric acid containing an excess of Fe^{2+} ions, which reduce Fe^{IV} to FeIII. The quantities of Fe^{IV} and FeIII in the specimen are determined from the total quantity of Fe^{3+} ions and the quantity of unreacted Fe^{2+} ions in the solution. The analysis is carried out in a stream of CO_2 to avoid the oxidation of Fe^{2+} by atmospheric oxygen.

Some authors have used the Mössbauer spectra for analytical studies; the ratio of the intensities of the characteristic peaks of Fe^{III} and Fe^{IV} was taken as equal to the ratio of the concentrations of the corresponding ions [85,87]. Chemical analysis confirmed that the results were correct.

Chemical properties. All the alkali metal ferrates(IV) form loose black powders without a definite crystal structure, stable at room temperature in the absence of moisture. In aqueous solutions or dilute alkali solutions they disproportionate with the formation of the corresponding ferrates(VI) and $Fe(OH)_3$. An exception is Li_2FeO_3, which decomposes in water to $Fe(OH)_3$ with the liberation of O_2. [32] The alkali metal ferrates(IV) are used as oxidising agents for organic substances and for water purification [88].

All the alkaline earth metal ferrates(IV) form black or dark-grey powders, stable in air, with the exception of Ba_3FeO_5. In moist air, the latter disproportionates in a few minutes with the formation of chiefly $BaFeO_4$, with a colour change from black to cherry-red. In a stream of O_2, all Sr and Ba ferrates(IV) are stable as far as 700–1000°; they are insoluble in water, but gradually (very slowly for $BaFeO_3$) decompose to alkaline earth metal salts, Fe^{III} salts, and O_2. On treatment with hydrochloric acid, Cl_2 and O_2 are liberated simultaneously.

Ba and Sr metaferrates(IV) begin to decompose in air at 320°. The decomposition has the characteristics of reversible thermal dissociation. With increase in temperature the dissociation pressure, equal to the atmospheric pressure of oxygen, is reached by $M(Fe^{IV}_{1-2x}Fe^{III}_{2x})O_{3-x}$ with increasing oxygen deficiency.

Structure and physical properties. The series of ferrates(IV) $SrFeO_3$, Sr_2FeO_4, and $Sr_3Fe_2O_7$ are the structural analogues of the corresponding titanates $SrTiO_3$, Sr_2TiO_4, and $Sr_3Ti_2O_7$.[77] These three structural types of ferrate(IV) are related to one another: the compounds with higher alkaline earth metal contents are derived from the perovskite structure by the introduction of layers of Sr and O ions between single or double perovskite layers.

Studies by a number of authors[85,86,90-92] has shown that the compounds with the composition $M(Fe^{IV}_{1-2x}Fe^{III}_{2x})O_{3-x}$ and $M_3(Fe^{IV}_{2-4x}Fe^{III}_{4x})O_{7-2x}$ are characterised by a constant crystal structure over a fairly wide range of values of x. Thus according to Brisi[91], compounds with the composition $Sr(Fe^{IV}_{1-2x}Fe^{III}_{2x})O_{3-x}$ crystallise in a single phase with the ideal perovskite structure, like $SrTiO_3$. No significant displacement of the lines in the X-ray diffraction patterns of specimens with different degrees of oxidation (40, 50, or 75% Fe^{IV}) was observed, and the values of the lattice parameter remained almost unchanged at 3.853 Å. In this instance the contraction which it might appear should have taken place with decrease in the quantity of oxygen ions and the formation of vacancies in the lattice is almost completely compensated by the increase in the ionic radius of iron on going from the quadrivalent to the tervalent state. The observed fact that the lattice parameter remains constant suggested that any compound $SrFeO_{3-x}$, including the stoichiometric compound, can be assigned a lattice parameter within the range 3.85 Å. On this basis it is possible to calculate the minimal distance between the ions in the cubic lattice:

O—O 2.70Å, Sr—O 2.73Å, Fe—O 1.93Å

The value 0.58 Å was obtained empirically for the Fe^{IV} radius by subtracting from the last of the above quantities the radius of the oxygen ion (1.35 Å). The value of 0.58 Å is only approximate, however. In fact we have close packing of the Sr and O ions, and the Fe ions merely occupy the free space in the centre of the octahedron formed by the oxygen ions.

The lattice parameter of recently prepared stoichiometric $SrFeO_3$ was in fact found to be equal to 3.850 Å. Detailed X-ray diffraction studies[80], however, established, in contrast to Brisi's results[91], that in the compounds $SrFeO_{3-x}$, increase in the oxygen deficit is accompanied by a gradual, albeit slight, increase in the parameter of the cubic cell. As oxygen is lost, tetragonal distortion of the cubic perovskite cell is observed, beginning at the composition $SrFeO_{2.84}$¶. As the composition approaches $SrFeO_{2.5}$, the tetragonal cell gradually changes into the monoclinic perovskite cell[93]. Thus as Fe^{IV} is reduced to Fe^{III} in the $SrFeO_3$–$SrFeO_{2.5}$ system there is a decrease in the symmetry of the perovskite cell, related to the change in the oxidation state of iron.

The first studies of the structure of the metaferrates $BaFeO_{3-x}$[74,94,95] showed that the cubic (a = 3.995 Å), tetragonal (a = 3.981 Å, c = 4.005 Å), and hexagonal (a = 5.69 Å, c = 13.89 Å) phases formed by these compounds have structures analogous to that of the corresponding phases of the familiar ferroelectric $BaTiO_3$.

¶ The tetragonal distortion is very small ($c : a \simeq 1.005$). The specimens are "almost cubic". It was probably for this reason that the distortion of the cell was not observed for Brisi's specimens[91].

This feature aroused particular interest in the compounds $BaFeO_{3-x}$ and stimulated further study of their structure[78,84-86,91,96-98].

Some workers considered that the structures found for the ferrates $BaFeO_{3-x}$ should also be shown by stoichiometric $BaFeO_3$, and some, without determining the compositions of the specimens, assigned their structure directly to $BaFeO_3$. If $BaFeO_3$ specimens with known compositions, prepared by different methods, are arranged in order of increasing Fe^{IV} concentration, the following change in structure can be observed. Highly oxidised specimens generally have a hexagonal structure[78,86,91], which may be preserved as far as the composition $BaFeO_{2.70}$,[86] and with decrease in the concentration of Fe^{IV} in the specimens the unit cell parameter gradually increases. When oxygen is lost, beginning from the composition $BaFeO_{2.88}$ (76% Fe^{IV}), the products have the cubic perovskite structure and its distorted forms—tetragonal, orthorhombic, monoclinic, and triclinic[84-86,96]. The dynamics of their interconversion is such that with decrease in the Fe^{IV} concentration there is a gradual decrease in the symmetry of the perovskite cell. Thus analysis of published data indicates that the structural changes in $BaFeO_{3-x}$ are related to the change in the oxidation state of the iron present.

The fundamental importance of this conclusion lies in the fact that the barium metaferrate phases, with structures analogous to those of the polymorphic modifications of $BaTiO_3$, correspond not to $BaFeO_3$, but to different compounds in the $BaFeO_3$–$BaFeO_{2.5}$ system.

The conclusion that $BaFeO_3$ is not a complete structural analogue of $BaTiO_3$, since the metaferrate(IV) corresponds to a single hexagonal structure, was confirmed by recent X-ray diffraction studies of $M(Fe^{IV}_{1-2x}Fe^{III}_{2x})O_{3-x}$ with Fe^{IV} concentrations from 0 to 100%, for which the starting material was $BaFeO_4$.[99]

It was established experimentally that the thermal stability of the hexagonal phase $BaFeO_{3-x}$ increases with increase in the oxygen pressure. The compound exists as far as 915° in air and as far as 1250° at 10 atm O_2, and at 50 atm O_2 it melts without decomposition at 1412°.[82]

The existence of Fe^{IV} in ferrates(IV) and the appreciably covalent character of the bond between Fe and the oxygen ions coordinated to it were confirmed by the Mössbauer spectra[77,79,87,96,100]. The nature of the covalent bond is similar to that observed in compounds containing Fe^{VI}. The Mössbauer spectra show isomer shifts due to the quadrivalent state of iron. The theoretically calculated isomer shift for the free Fe^{4+} ion[101], equal to -1.30 mm s^{-1}, is more negative than the experimental values observed for the compounds containing Fe^{IV}. Thus the isomer shift had the values -0.17 mm s^{-1} for $SrFeO_3$ and -0.29 mm s^{-1} for $BaFeO_{2.95}$ at 298°K. These more positive values are interpreted as resulting from a considerable covalent contribution to the 3d orbitals of the Fe^{4+} ion from the oxygen ligands. Comparison of the values of the isomer shifts for $BaFeO_{2.95}$ and $SrFeO_3$ showed that the covalent contribution to the Fe–O bond is smaller for $BaFeO_3$ than for $SrFeO_3$. Comparison of the isomer shifts for $Sr_3Fe_2O_{6.9}$ and $SrFeO_3$ showed that the introduction of the layers of Sr and O ions between the double perovskite layers has little influence on the bonding. The spectra of the ferrates with an oxygen deficit show quadrupole splitting, indicating the presence of Fe^{III} in addition to Fe^{IV}.

It is suggested[78] that $BaFeO_3$ has an interesting future, primarily because of its unusual magnetic properties.

When $BaFeO_{2.95}$ is cooled, a sharp change from ferrimagnetism to antiferromagnetism is observed at 164°K. The maximal value of the specific magnetisation $\sigma_g = 13.8$ electromagnetic units at 164°K. The change in the magnetic ordering is accompanied by a sudden change in the temperature dependence of the conductance. The plot of $\lg\rho$ against $1/T$ shows a peak at the temperature of the transition. No departure from hexagonal symmetry was observed below the temperature of the transition.

Stoichiometric $SrFeO_3$ is antiferromagnetic with a Neel temperature of 130°K. It exhibits anomalous electrical properties. Ceramic discs of this material are good conductors ($\rho \simeq 10^{-3}\ \Omega\,cm^{-1}$) with the same temperature coefficient as metallic conductors [80].

$SrFeO_3$ forms unrestricted solid solutions with $SrTiO_3$, [102] with a linear increase in the lattice parameter a as Fe^{IV} is replaced by Ti^{IV}.

Perovskite series of solid solutions $La_{1-x}Sr_xFeO_{3-y}$ were obtained in an atmosphere of oxygen by replacing the tervalent La by the bivalent Sr. [79,103] With increase in the oxygen pressure during preparation, the oxygen deficit in the solid solutions decreases to almost zero. The stoichiometric compositions $La_{1-x}Sr_xFeO_3$ have distorted perovskite structures.

The system of solid solutions $SrFeO_3$–$BiFeO_3$ shows the structural transformation: cubic → tetragonal → cubic, with increase in the degree of replacement of Sr by Bi. [104]

Tauber [105], from a melt with Ba : Bi : Fe = 1 : 2 : 3, obtained dendritic cubic crystals $(Ba_{0.33}Bi_{0.67})(Fe^{III}_{0.67}Fe^{IV}_{0.33})O_3$ with lattice parameters very close to those of cubic $BaFeO_{3-x}$.

$BaFeO_3$ forms solid solutions with $BaTiO_3$. The conclusion [106] that the addition of small quantities of $BaFeO_3$ (3–5%) to the titanate produces a sharp change in its structure from tetragonal to hexagonal cannot be regarded as correct with respect to Fe^{IV}, since the solid solution specimens were prepared by a method which excluded the formation of Fe^{IV} (heating at 1380°). In this instance the observed sharp change in the structure and ferroelectric properties are due to the introduction of Fe^{III} ions into the $BaTiO_3$ lattice.

III. FERRATES(V)

The only known quinquevalent iron compounds are potassium, sodium, and rubidium ferrates(V). K_3FeO_4 was first prepared in 1956, by the oxidation of an $Fe_2O_3 + 6KO_X$ mixture in a stream of O_2 at 400–500°. [7] The K_3FeO_4 obtained in this way always contains small quantities of $KFeO_2$ and KO_X. Potassium ferrate(V) mixed with $KFeO_2$ is also formed by the thermal decomposition of K_2FeO_4 at 700° in a stream of O_2 [17] (see Russian page 1979). Pure K_3FeO_4 is obtained by the reaction of Fe_2O_3, $KFeO_2$, or K_2FeO_4 with anhydrous KOH (Fe : K = 1 : 3) in a stream of O_2 at 600–700°. [107]

The oxidation of mixtures of RbO_X or RbOH with Fe_2O_3 at 600° in a stream of O_2 gives rubidium ferrate(V) with the composition $Rb_3FeO_{4.4-4.7}$, containing peroxide. When heated for a short time at 350° in a stream of N_2, these products are converted into Rb_3FeO_4. [107]

Sodium ferrate(V) could not be obtained by the corresponding reactions. Na_3FeO_3, prepared from Fe_2O_3 and Na_2O_2 in a stream of N_2 at 600°, reacts with O_2 with the formation of Na_3FeO_4, the degree of conversion being proportional to the pressure of oxygen. Thus the product contains 40 mole % Na_3FeO_4 at 20 atm O_2, and 80 mole % Na_3FeO_4 at 120 atm O_2, and the conversion of Na_3FeO_3 into Na_3FeO_4 is probably quantitative at 200 atm O_2. [107]

In dilute H_2SO_4 and HNO_3, ferrates(V) decompose to Fe^{III} with the liberation of O_2, and in the reaction with HCl, Cl_2 and O_2 are liberated simultaneously. In water or dilute alkali solutions, disproportionation takes place:

$$6K_3FeO_4 + 8H_2O = 4K_2FeO_4 + 2Fe(OH)_3 + 10\ KOH$$

The concentration of active oxygen can be determined iodometrically only in very pure ferrates(V); when $MFeO_2$ or MO_X are present, correct results are obtained only in the gas-volumetric method. The quantity of Fe^V in the specimens can be determined by analysis of the products of disproportionation, in which 66.6% of the Fe^V is converted into Fe^{VI}.

K_3FeO_4 begins to decompose in a stream of O_2 above 700° according to the equation $K_3FeO_4 = KFeO_2 + K_2O + \frac{1}{2}O_2$. At 250–500° in a stream of O_2, K_3FeO_4 is slowly converted into $KFeO_2 + 2KO_X$, and in this instance the decomposition products are formed not by the simple decomposition of K_3FeO_4 but by its reaction with molecular oxygen. This was established from comparative experiments in which K_3FeO_4 was heated in a stream of O_2 or N_2. In the latter, potassium ferrate(V) remains unchanged at these temperatures. Analysis of the products of the decomposition of K_3FeO_4 in O_2 at a pressure of 100 atm and temperatures up to 400° indicates that the following reaction takes place: $K_3FeO_4 + 0.75O_2 = KFeO_2 + 2KO_{1.75}$. [107]

Unlike potassium ferrate(V), Na_3FeO_4 in a stream of O_2 at 200–250° gives up active oxygen with the conversion of Fe^V into Fe^{IV}.

The X-ray diffraction patterns of K_3FeO_4 show that it is amorphous towards X-rays. Magnetic measurements gave an effective magnetic moment of 3.6–3.7 μ_B. [7] These values are close to the spin magnetic moment for three unpaired electrons (3.87 μ_B), expected for Fe^V.

Compounds of octavalent iron have not been prepared. The electron affinities calculated by Ionova and Dyatkina [108] for the isoelectronic oxo-anions of the first transition series, of which the last member is the FeO_4 molecule, change in the following order: TiO_4^{4-} 2.4 eV, VO_4^{3-} 3.8 eV, CrO_4^{2-} 5.5 eV, MnO_4^- 7 eV, and FeO_4 10.7 eV. It can be seen that the FeO_4 molecule should have a very high electron affinity, and this explains the difficulty of obtaining iron tetroxide and the perferrate ion.

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Rostov-on-Don State University
Siberian Metallurgical Institute,
Novokuznetsk