some organic substances can be oxidized by direct titration with ceric sulfate.

Though none of the acids listed above can compare in accuracy with oxalic acid (used as sodium oxalate) as primary standards in oxidimetry reactions, a number of them have been suggested as primary standards in acidimetry reactions, notably maleic, fumaric, malic and tartaric in the form of potassium acid tartrate. The authors found potassium acid tartrate to be by far the most satisfactory of these four. It is obtained in very pure form by one recrystallization, and compares favorably in accuracy with potassium acid phthalate, an accepted primary standard in acidimetry.

Summary

1. Formic, acetic, succinic, fumaric and maleic acids are not oxidized by ceric sulfate in hot sulfuric acid solution.

2. Tartaric, malonic, malic, glycolic and citric acids are oxidized under the same conditions, the products being, usually, formic acid and carbon dioxide. Because the formic acid is not oxidized by ceric sulfate, it has been possible to develop accurate analytical procedures for each of this last group of acids, based on their oxidation in hot sulfuric acid solution by excess standard ceric sulfate and titration of the excess with standard ferrous sulfate.

3. Benzoic, phthalic and salicylic acids are oxidized to a variable extent by ceric sulfate in hot sulfuric acid solution.

4. Attention is called to the possibility of using ceric sulfate in certain organic oxidations where the usual reagents, such as permanganate or dichromate, either do not act or do not produce the result desired.

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PYROPHORIC IRON. I. PREPARATION AND PROPERTIES[1]

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The pyrophoric property of properly prepared finely divided iron reacting with air at room temperatures is a well-known phenomenon.[2] It has been definitely established, moreover, that such material becomes non-pyrophoric when subjected to a high temperature.

[1] The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction. (Manuscript first received August 30, 1928.)

[2] Magnus, *Pogg. Ann.*, **3**, 81 (1825); Moissan, *Ann. chim. phys.*, [5] **21**, 199–256 (1880); Birnie, *Rec. trav. chim.*, **2**, 273–294 (1883); Smits, Kettner and de Gee, *Verslag. Akad. Wetenschappen*, Amsterdam, [II] **16**, 999 (1913); Tammann and Nikitin, *Z. anorg. allgem. Chem.*, **135**, 201–204 (1924).

Pyrophoric iron has been prepared in many ways, among which may be enumerated the thermal decomposition of ferrous oxalate, reduction of ferrous oxalate by hydrogen, reduction of ferric oxide or a mixture of ferric oxide and aluminum oxide by either hydrogen or carbon monoxide and the reduction of ferrous oxide or carbonate by hydrogen. In most cases definite conditions for the preparation of the pyrophoric materials are not mentioned in the literature nor are the pyrophoric products properly identified. Consequently the term pyrophoric iron includes any pyrophoric ferrous material containing any amount of metallic iron. The references on the preparation of pyrophoric iron indicate that such factors as temperature, length of time of heating or reduction and the condition of the starting material are exceedingly important in obtaining concordant results. To explain pyrophoric action and the inactivation of pyrophoric materials, several theories have been proposed, among which may be named Magnus'[2] theory of fineness of division; that of Moissan,[2] who believed that, in general, so-called pyrophoric iron owes its pyrophoric activity to finely divided FeO; the metastable equilibrium theory of Smits;[2] and the surface theory of Tammann and Nikitin.[2]

According to Hofmann,[3] the smaller the oxide particle, the greater will be the rate and the extent of reduction, and the greater will be the tendency for the iron particles to adhere to each other so as to diminish the surface. If pyrophoric activity is dependent upon the extent of the surface of the individual particles, the degree of dispersion of the iron oxide from which the pyrophoric iron is to be prepared should have an effect on the pyrophoric activity and also on the inactivation of the resulting iron.

To prepare the true metallic pyrophoric iron in the highest state of purity, it is advisable to avoid all organic compounds. Oxalates or carbonates upon heating or reduction tend to form finely divided carbon. Even carbon dioxide will react with finely divided iron at 500° as shown by Herschkowitsch.[4]

The present paper deals chiefly with the preparation of pyrophoric iron with the highest possible metallic iron content, the effect of the condition of the starting material and the effect of various gases on the inactivation of pyrophoric iron.

Experimental

Ferric oxide precipitated from a ferric nitrate solution by ammonia was used as a starting material in this work. Ferric nitrate was chosen in preference to ferric chloride as it was found that chlorides inhibit the formation of pyrophoric iron while the oxides of nitrogen apparently do not. It has been shown by von Weimarn[5] that if substances

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[3] Hofmann, *Z. angew. Chem.*, **38**, 715–721 (1925).

[4] Herschkowitsch, *Z. anorg. allgem. Chem.*, **115**, 159 (1921).

[5] Von Weimarn, *Chem. Rev.*, **2**, 228 (1925).

are precipitated from solutions of different concentrations, a difference in the degree of dispersion of the precipitate will result. Thus, in two samples of ferric oxide, the degree of dispersion should be greater in the one precipitated from the more concentrated solution of ferric nitrate. Ferric oxide as a colloidal sol would also be in a state of high dispersion. With this principle in mind, the ferric oxide used in this work was prepared in three ways. *Ferric oxide A* was prepared by precipitation from a hot ferric nitrate solution containing 100 g. of $Fe(NO_3)_3 \cdot 9H_2O$ per liter of water, using an excess of NH_4OH (sp. gr. 0.90). The oxide was freed from salts and ammonia by decantation and washing, dried at 110–120° and ground to a fine powder in an agate mortar. *Ferric oxide B* was prepared in a manner similar to the preparation of oxide A with the exception that the concentration of the ferric nitrate solution was 25 g. per liter. *Ferric oxide C* was obtained by hydrolysis of 10 g. of ferric nitrate per liter of boiling water, so as to produce a colloidal sol. It was subsequently dialyzed in collodion bags at 90–95° for approximately one week, after which time the sol was almost free from the nitrate ion. This method for preparation of the sol is similar to that described by Sorum.[6] The sol was slowly evaporated to dryness in an electric oven held at about 140°. Oxides A-II, B-II, etc., represent different samples of the oxides prepared in the same manner as A and B, respectively.

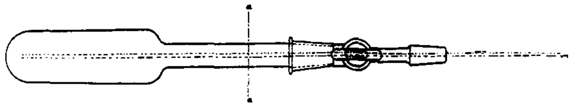

Fig. 1.—Reduction tube.

Preparation of Pyrophoric Iron.—The pyrophoric iron was prepared by hydrogen reduction of approximately two grams of iron oxide placed either in a drawn-out test-tube or in a container similar to that shown in Fig. 1. The latter consisted of a tube fitted with a stopcock and ground-glass joints which permitted it to be attached to a high vacuum apparatus for subsequent degassing of the iron. The hydrogen, previously carefully purified by passage through hot copper, soda lime and phosphorus pentoxide, was passed into the tube through a small capillary. In each case reduction was continued for three hours at 500°, using a gas flow of approximately 80 cc. per minute.

Inactivation of Pyrophoric Iron by Heating in Hydrogen, Nitrogen or Helium.—It is known that pyrophoric iron becomes inactive when heated for an extended length of time. Consequently, experiments were carried out to determine the effect of the following factors upon the pyrophoric property of iron: the length of time of heating, the method of preparation of the oxide from which the iron was reduced and the gaseous medium in which the pyrophoric iron was heated. Samples of pyrophoric iron prepared in drawn-out test-tubes as described above were placed in a furnace held at 600° for various lengths of time, after which the tubes were removed from the furnace and allowed to cool, hydrogen passing through the capsules continually. When cool, the contents of the tubes were thrown into the air and their pyrophoric or non-pyrophoric property noted.

In preparing the samples of iron to be heated in nitrogen or helium, all samples were reduced in the manner described above. After reduction, these samples were degassed at 500° for approximately one hour until the pressure dropped to at least 5×10^{-5} mm. of mercury. The

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[6] Sorum, This Journal, 50, 1263 (1928).

bulb was then filled with dry oxygen-free nitrogen or helium at approximately atmospheric pressure and heated for various lengths of time as indicated in Table I.

TABLE I

EFFECT OF HEATING PYROPHORIC IRON IN HYDROGEN, NITROGEN OR HELIUM

Oxide sample	Condition	Time of heating, hours			
		H_2 (600°)	N_2(600°)	He (600°)	He (625°)
A	Pyrophoric	1.5	6	70	..
	Non-pyrophoric	2.5–3	..	156	42
A-II	Pyro.	1	5–9	144	..
	Non-pyro.	3	11	...	..
B	Pyro.	12.5	45	...	..
	Non-pyro.	17	..	...	..
B-II	Pyro.	....	..	73.5	..
	Non-pyro.	....	..	160	..
B-III	Pyro.	....	..	...	48.5
	Non-pyro.	....	..	...	..
C	Non-pyro.	1	1	1	1

In every case the pyrophoric iron was black while the non-pyrophoric form was gray-black or decidedly gray From the results obtained by heating in nitrogen and hydrogen, it is evident that iron C loses its pyrophoric property the most rapidly, A and B following next in order. The time for inactivation was greater for heating in nitrogen or helium than in pure hydrogen. Helium required the greatest length of time.

The difference between Samples A, B and C is one of preparation or, as previously pointed out, one of dispersion. It thus appears that the oxide of the lowest degree of dispersion yields pyrophoric iron which is the most difficult to inactivate. As previously mentioned, Hofmann[3] found that the smaller the oxide particles the greater will be the extent of reduction and the greater will be the tendency for the iron covered oxide particles to adhere to each other so as to diminish the total surface. It thus appears that inactivation of pyrophoric iron consists in a decrease of the total surface. This is also in accord with Tammann's views. From Table I, it can also be seen that iron from any particular oxide sample can be more easily inactivated in hydrogen than in nitrogen or helium, the latter taking the longest time. One possible explanation for this difference is that at 600° hydrogen and nitrogen are absorbed and combine to form hydrides and nitrides with the active iron, thus causing it to become inactive, while helium is non-reactive with the iron and consequently allows it to remain pyrophoric for a greater length of time. However, it is known that iron reduced at 500° contains an abundance of absorbed hydrogen and is still pyrophoric; also, iron heated at 500 or 600° gives the α-iron x-ray diagram with no indication of swelling of crystal lattice or evidence for any new lines. Inasmuch as oxide B has the lowest degree of dispersion on the basis of von Weimarn's theory and is also the most difficult to inactivate, it might seem probable that the pyrophoric iron particle contains a small core of oxide which hinders recrystallization of the iron. Heating in hydrogen at a temperature higher than its reduction temperature (500°) should then cause further reduction and also facilitate the removal of the water vapor thus formed so as to increase coalescence of the iron atoms. The larger the oxide particle, the larger the residual oxide core and consequently the longer will be the time necessary for inactivation. On this basis, however, it seems impossible to explain the large difference found in the inactivation in nitrogen and helium.

Analysis of the Samples of Iron.—The metallic iron content of the pyrophoric and non-pyrophoric samples of iron was determined by measuring the amount of hydrogen liberated from dilute sulfuric acid solution. Approximately 0.4 g. of iron was prepared by reducing the desired oxide in hydrogen in a small tared capsule, the neck of which was slightly constricted. After reduction, the capillary, through which hydrogen was introduced into the capsule, was withdrawn and the neck of the capsule quickly sealed off while still hot, thus causing a partial vacuum upon cooling. The weight of the iron was obtained as the difference between the gross and tare weights of the capsule. The determination was carried out by breaking the capsule under pure water, which was later acidified with sulfuric acid. The hydrogen liberated was collected and measured in a buret, reduced to standard conditions of temperature and pressure and the metallic iron equivalent calculated. To check the accuracy of the results a determination was made on a sample of pure iron wire the analysis of which was known. The results are given in Table II.

TABLE II

METALLIC IRON CONTENT OF PYROPHORIC AND NON-PYROPHORIC IRON

Oxide reduced	Temp., °C.	Time, hrs.	Yield, %	Condition
B	500	3	98.5	Pyrophoric
B	500	14	98.4	Pyrophoric
B (Constantly agitated)	500	10.5	99.1	Pyrophoric
B	400	24	97.6	Pyrophoric
C	500	12.5	99.0	Pyrophoric
A	625	4	98.5	Non-pyrophoric
Standard iron wire, 99.7% Fe	...	...	99.4	....

From these results it is evident that with the sample used reduction at 500° in hydrogen for three hours is practically the optimum condition for the preparation of pyrophoric iron. It is further shown that there is no essential difference in the iron content of the various samples reduced at 500° and above, whether they be pyrophoric or not.

Microscopic examination of the pyrophoric and non-pyrophoric forms of the most easily inactivated iron, Sample C, was carried out by breaking sealed capsules of both forms of iron under paraffin oil and examining the suspension. The difference in the samples (see Figs. 2 and 3) is in the sizes of the respective clusters or lumps of iron, suggesting that adhesional forces were at play during the heating of the iron. Both photographs are of the same magnification, the distance between the two small lines in Fig. 3 representing 0.1 mm.

Fig. 2.—Pyrophoric iron.

X-Ray examination of pyrophoric iron prepared by reducing oxide C at 400° for twenty-four hours in a special tube (Fig. 4) to prevent entrance of air was carried out as follows: the reduction tube (Fig. 4) was constructed so that it could be sealed off at a-a and b-b after reducing the oxide in the bulb. The active iron was shaken into the capillary, which was then sealed off at c-c. The diffraction lines showed the iron to be of the α-variety with the same pattern as the non-pyrophoric iron which was heated to 650°. Those due to the pyrophoric material appeared slightly more diffused than those shown by iron heated at 650° in hydrogen, indicating a smaller particle size for the pyrophoric iron. Similar results have been obtained by Wyckoff and Crittenden[7] in their studies of ammonia catalysts.

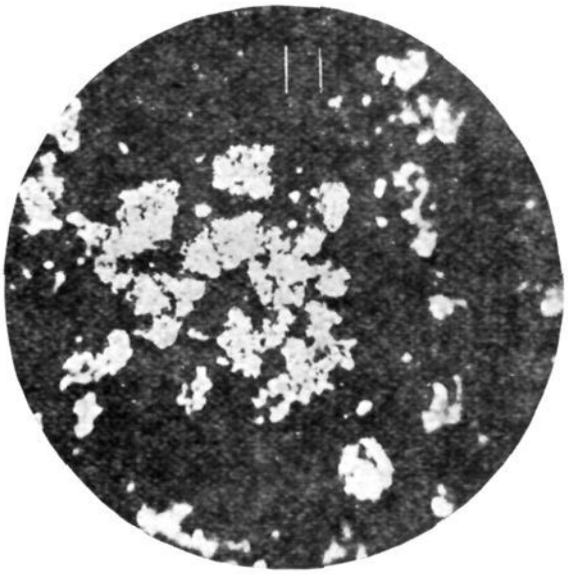

Fig. 3.—Non-pyrophoric iron.

Method for Determining the Degree of Pyrophoric Activity.—A measure of the relative pyrophoric activities of the samples of iron was obtained by determining the limiting concentration of oxygen in an oxygen–nitrogen mixture which would just cause pyrophoric action when a sample of the iron was dropped through the gaseous mixture. A gaseous mixture of the desired composition was prepared in a glass tube 30 cm. in length, one end of which was fitted with a rubber stopper through which passed a glass tube. The sealed capsule containing the prepared sample of iron was attached to this glass tube by means of a tough

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[7] Wyckoff and Crittenden, This Journal, **47**, 2866 (1925).

rubber tube which could be squeezed with a pair of pliers, thereby breaking the neck of the capsule and allowing the iron to drop through the gaseous mixture. The observations were made in the dark so that the slightest indications of pyrophoric activity could be noticed. One-gram samples of iron were prepared by hydrogen reduction at 500°, the reduction being carried out until 1.0 mg. or less of water was liberated per hour. As a check on the preparation of the sample, the iron after being dropped through the tube, was thrown into the air. In all cases, the samples which failed to ignite in the prepared oxygen–nitrogen mixture afterward took fire when dropped into the air. The results obtained by this method are given in Table III.

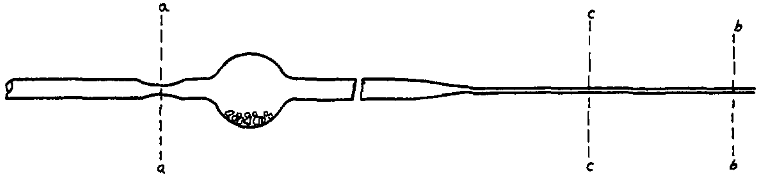

Fig. 4.—Preparation tube for x-ray sample.

TABLE III

LIMITING CONCENTRATION OF OXYGEN IN WHICH PYROPHORIC IRON IS ACTIVE

Oxide sample	A-II			B			C		
Oxygen concn., %	5	3	5	10	3	1	9.4	5	3
Condition	Pyro.	Non-pyro.	Pyro.	Pyro.	Pyro.	Non-pyro.	Pyro.	Non-pyro.	Non-pyro.

From these data, it is evident that the limiting oxygen concentrations for the various samples of iron are as follows: C, between 5 and 9.4%; A, between 3 and 5%; B, between 1 and 3%. This would put the oxides in the order of their increasing pyrophoric activity as C, A, B, an order which is just the reverse of what one would predict from a consideration of a method for preparation of the three oxides. The colloidal oxide, being the most finely divided, should yield the iron having the greatest surface per unit mass, the surface factor, according to Tammann being the criterion for pyrophoric activity. However, referring to the results obtained in heating the pyrophoric iron in hydrogen and also in nitrogen, it will be seen that C became non-pyrophoric in the shortest length of time, A followed and B remained active the longest, probably due to the degree of incompleteness of reduction of the oxides. It is very probable that the inactivation process caused by adhesion or recrystallization is operative at temperatures as low as 500°, the iron containing the most residual oxide remaining pyrophoric the greatest length of time and also being the most pyrophoric when tested by this method. In the following paper it is shown that the adsorptive capacities of the samples of iron for ammonia and carbon dioxide also increase in the order C, A, B.

Reaction of Pyrophoric Iron at −78° and with Dried Air.—A sample of oxide B was reduced in a capsule at 500° in hydrogen for three hours, after which time the neck of the capsule was sealed. The sample was allowed to drop into a glass tube 18 inches long, the sample, tube and air within the tube being cooled to −78° for one-half hour by means of carbon dioxide, snow and ether. A trigger was placed in a side-arm of the 18-inch tube to break the capsule and allow the iron to drop through the cold air. No precautions were taken to prevent the diffusion of the carbon dioxide through the side-arm and into the tube. The iron falling through the tube was exceedingly pyrophoric, heating the air in the tube to such an extent that some of the finely divided iron was blown out of the side-arm.

It was also found that properly prepared iron was pyrophoric when allowed to drop through air dried for two to three months over phosphorus pentoxide. The iron samples were prepared from oxide A, reduced at 500° by hydrogen. The capsules containing the iron were evacuated to 10^{-3} mm. pressure at 500°, filled with nitrogen and sealed.

Summary

1. Pyrophoric iron can best be prepared by reducing precipitated ferric oxide by hydrogen at 500°.
2. Ferric nitrate is a suitable starting material for the preparation of the ferric oxide. Chlorides are to be avoided as they destroy the pyrophoric property of the iron.
3. For pyrophoric iron prepared from a definite sample of oxide, inactivation is dependent not only upon the temperature and time of heating but also upon the gaseous medium in which it is heated.
4. Accepting von Weimarn's precipitation law, the time necessary for inactivation of pyrophoric iron is dependent upon the degree of dispersion of the oxide from which it is reduced.
5. Iron was found to be pyrophoric in dried air and also in air cooled to −78°.
6. A method was devised for the determination of the degree of pyrophoric activity of iron.

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