ON THE AGING OF FERROUS HYDROXIDE AND FERROUS CARBONATE.

BY OSKAR BAUDISCH AND L. A. WELO.

(From the Laboratories of The Rockefeller Institute for Medical Research.)

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Interest in the aging of metal hydroxide has increased greatly during the past few years and it is due, no doubt, mainly to the fact that certain metal hydroxides have become useful for the isolation of enzymes and vitamins. The selective adsorption properties of these hydroxides, aluminum hydroxide for example, make them suitable for these purposes. Their surface forces make it possible to separate unstable organic groups or compounds which otherwise would not be obtained at all, or only with extreme difficulty. But the theoretical interest in the aging phenomenon has also become more intense, since it is possible by modern methods, especially by that of X-ray spectroscopy, to follow the changes taking place in the hydroxides with time, and thus to come to certain conclusions as to the nature of the adsorption process. In this connection we have in mind particularly the recent work of Fricke and Wever (1) on aluminum hydroxide.

Our own work is concerned entirely with ferrous hydroxide and ferrous carbonate. These substances are widely distributed in nature, and almost certainly play a very large part in many biological processes. Our experiments were not originally planned with the purpose of getting data on the aging problem. But they led us to believe and finally convinced us that ferrous hydroxide and ferrous carbonate, at the instant of precipitation, possess properties which disappear very rapidly with time.

Since it was known that ferrous hydroxide and ferrous carbonate are exceedingly autoxidizable and, as a result of the absorption of oxygen, form a series of compounds it was necessary to adopt two distinct types of experiments in our study. The experiments had to be performed in: (1) the entire absence of oxygen;

and (2) the presence of air or oxygen. Much experimental material exists concerning the behavior of ferrous hydroxide and ferrous carbonate when oxygen has access to them, but as far as we are aware, very little is known about them when they are precipitated under conditions which exclude oxygen.

We shall first discuss, briefly, the work that Just and Günzburg (2) have done in this field. They made an exact study of the solubilities of metallic iron and ferrous carbonate. They found, among other things, that the solubility of fresh ferrous carbonate is higher than that which has been aged, and that fresh ferrous carbonate has the property of increasing the supersaturation of ferrous carbonate, whereas aged ferrous carbonate cannot do so. They concluded from this fact that "the ions of the ferrous bicarbonate must be different in their make-up than those of the aged ferrous carbonate. A further explanation of the whole question seems to demand additional experimental investigation of ferrous carbonate in its solid form."

In contrast to our very sparse information as to the chemical and physical behavior of ferrous hydroxide and ferrous carbonate in the absence of air or oxygen, we have numerous publications on the action of ferrous salts when they are in contact with oxygen. We have published some of the results obtained in such work (3), and will here limit ourselves to a brief review of the action of oxygen on ferrous hydroxide and ferrous carbonate in as far as it concerns the formation of magnetic oxides.

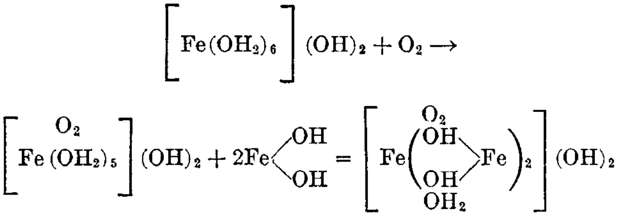
If ferrous hydroxide is oxidized under limited access of air, it can be shown in various ways that the oxidation goes mainly to the stage $Fe_3O_4 \cdot xH_2O$. In only a few cases does the oxidation proceed completely according to the scheme

$$\ddot{\mathrm{Fe}} + \oplus = \dddot{\mathrm{Fe}}$$

In by far the most cases the oxidation goes through numerous intermediate stages and we are very far from a thorough understanding of the mechanism of the oxidation. Nature itself demonstrates to us through the large number of magnetic and non-magnetic ferro-ferric and ferric oxides, with their great variety of color shades, that these oxidation processes must be exceedingly complex. Then, if the processes are further complicated by the presence of other metals than iron and by the addition of organic compounds, the possible compounds and processes become very numerous indeed.

As a working scheme we have adopted a formulation according to the theory of Werner which will be briefly described as follows:

When oxygen has access to ferrous hydroxide, the following process very probably takes place.



$$\left[\mathrm{Fe(OH_2)_6}\right](\mathrm{OH})_2 + \mathrm{O_2} \rightarrow$$

$$\left[\overset{\mathrm{O_2}}{\mathrm{Fe(OH_2)_5}}\right](\mathrm{OH})_2 + 2\mathrm{Fe}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} = \left[\mathrm{Fe}\overset{\mathrm{O_2}}{\underset{\mathrm{OH_2}}{\left(\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}{>}\mathrm{Fe}\right)_2}}\right](\mathrm{OH})_2$$

I. II.

From this graphical representation it is seen that at first an oxygen molecule reacts with ferrous hydroxide and that the resulting peroxo compound (I) can combine with the surrounding, but as yet unchanged, ferrous hydroxide molecules, and thus forms what may be called a polynuclear complex salt (II). This complex salt has, however, a very short life, and through the splitting off of the coordinatively bound oxygen there is developed a very labile, ferro-ferric compound in which the proportion of ferrous to ferric iron is 2 to 1. Hauser (4) has synthesized this weakly paramagnetic oxide $Fe_2O_3 \cdot 4FeO \cdot xH_2O$ from ferro-ferric ammonium carbonate, and has found that, on further oxidation with molecular oxygen, it is converted into the magnetite $FeO \cdot Fe_2O_3$. Actually the proportion of ferrous to ferric iron is less than this formula indicates. If one passes oxygen over this magnetite at a temperature of 200°C. it is still further oxidized, as we have found into the ferric oxide, Fe_2O_3, and becomes even more ferromagnetic. The reason why we are concerned with the magnetic properties of the oxides of iron is made clear in our previous paper (3). *From the experiments described there it became particularly clear that the properties of the oxides were really determined by conditions existing at the moment of precipitation of the hydroxide from which they were derived.* We could also conclude that the reduction of potassium nitrate with oxygen and ferrous hydroxide is a molecular reaction. As far as the present paper is concerned the important result was that the reduction of nitrate to nitrite was *extremely rapid, and that on the aging of the precipitated hydroxide of only a few seconds the reduction of the nitrate was decreased more than half.*

The foregoing observations relate to the things observed when working in the presence of air or oxygen. But we have also observed that ferrous hydroxide is subject to an aging process in the *absence* of oxygen, and the phenomena are in complete accordance with the observations and conclusions of Just and Günzburg, which have already been discussed.

To secure absence of oxygen from our solutions of ferrous sulfate and sodium hydroxide, from which the ferrous hydroxide was precipitated, it was necessary to boil each solution separately and to cover them with atmospheres of pure hydrogen previous to the mixing. This was conveniently done with the apparatus shown in Fig. 1.

We usually had the lower bulb half full of sodium hydroxide solution and the upper bulb half full of a solution of ferrous sulfate. On boiling, the air and steam escape through the barometer tubes dipping into wells of mercury. This arrangement of barometer tubes also acts as a safety valve against too high pressures while boiling. As the bulbs cool off, the pressures decrease and hydrogen is drawn in until the solutions have cooled off to room temperature. When cool, the ferrous sulfate in the upper bulb is run into the lower one, and becomes mixed with the solution of sodium hydroxide. A snow-white ferrous hydroxide is formed which remains white, even on standing several days, and apparently does not change in any way. *Nor does it decompose water or change in any way in general appearance, even if the mixture containing the precipitate is boiled for several hours.* However, if only a trace of air is admitted, the white flocculent precipitate changes to a green color which, in turn, becomes black if air is admitted in larger quantities.

If we repeat the experiment, but with the difference that the solution in the lower bulb contains potassium nitrate, in addition to sodium hydroxide, the results are exactly the same. A white flocculent precipitate is formed which, even on boiling for a long time, remains the same in color. It does not matter how much or how little nitrate is present. If oxygen is kept away, there is no change in the nitrate at room temperature, nor at the boiling temperature. The fact that the ferrous hydroxide remains white and does not change from white to green or black is convincing evidence that the potassium nitrate has not been changed. But, in order to make doubly sure, direct tests for the presence of nitrite or ammonia in the solution, which had contained the precipitate for several days, were made. There were no nitrites or ammonia, and hence no reduction product.

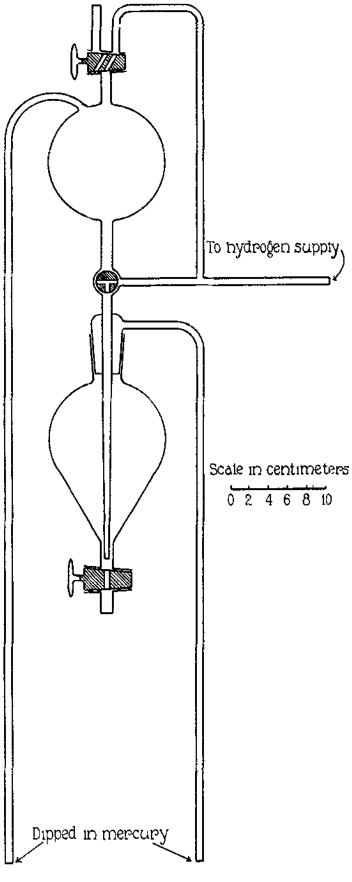


Fig. 1.

The results are entirely different if, instead of potassium nitrate, potassium nitrite is used. Even in the complete absence of oxygen, the nitrite reacts with ferrous hydroxide and forms a deep green complex compound which, on decomposition, yields ammonia as a reduction product.

Before passing to a detailed consideration of the aging process, it is well to describe some quantitative experiments on the reduction of nitrates with oxygen and ferrous hydroxide. The usual procedure was as follows, using the apparatus shown in Fig. 2.

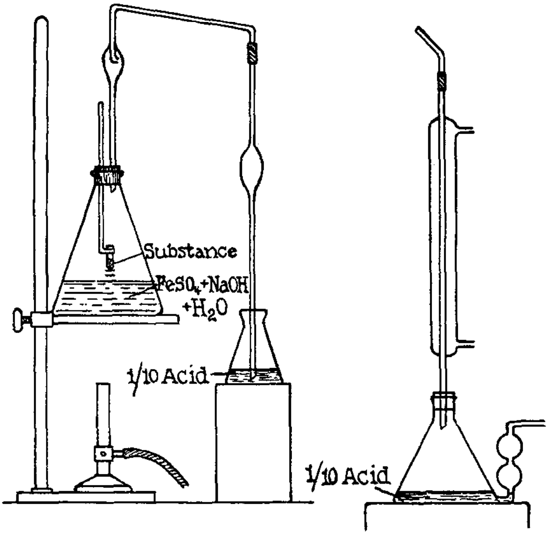


FIG. 2.

In the flask were put 400 cc. of distilled water, in which had been dissolved known quantities of sodium hydroxide and of the potassium nitrate to be reduced.[1] Then 100 cc. of a solution of ferrous sulfate were added. The solutions were thoroughly mixed by shaking. The mixture was then distilled until the

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[1] With the simple apparatus shown in Fig. 2, we can also show that potassium nitrate is not reduced in the *absence* of oxygen. The oxygen being first excluded by boiling the mixture of ferrous sulfate and sodium hydroxide, the potassium nitrate is added afterwards by means of the small test-tube suspended from the stopper and indicated in the drawing as "substance."

TABLE I.*

Reduction of Alkali Nitrate by Ferrous Hydroxide.

Amounts used: 0.1702 gm. of $NaNO_3$ in 500 cc. of water. Complete reduction would give 0.0340 gm. of NH_3.

Experiment No.	$FeSO_4$	NaOH	Equivalent.		Concentration of free NaOH.	NH_3 formed.	
			$Fe(OH)_2$	Free NaOH.		Amount.	Theoretical amount.
	gm.	gm.			per cent	gm.	per cent
1	4.8	2.6	2	0 (neutral).	0 (neutral).	0.0340	100
2	4.8	3.2	2	0.5	0.12	0.02244	66
3	4.8	3.9	2	1	0.26	0.01309	38.5
4	4.8	5.2	2	2	0.52	0.00952	28
5	4.8	6.5	2	3	0.78	0.00544	16
6	4.8	7.8	2	4	1.04	0.00476	14
7	4.8	9.1	2	5	1.30	0.00425	12.5
8	4.8	18.0	2	11.8	3.08	0.00344	10
9	4.8	20.0	2	12	3.10	0.00323	9.5
10	4.8	23.2	2	15.8	4.14	0.00306	9
11	4.8	27.0	2	18.7	4.88	0.00289	8.5
12	4.8	35.1	2	25	6.50	0.00187	5.5
13	4.8	36.0	2	25.7	6.68	0.00153	4.5

* From Baudisch, O., and Mayer, P., *Biochem. Z.*, 1920, cvii, 1.

TABLE II.*

Reduction of Alkali Nitrate by Ferrous Hydroxide in the Presence and Absence of Oxygen.

0.1702 gm. of $NaNO_3$, 4.8 gm. of $FeSO_4$, 500 cc. of H_2O.

Experiment No.	NaOH	Equivalent.		Amount of nitrate reduced.	
		Free.	NaOH	With oxygen.	Without oxygen.
	gm.		per cent	per cent	per cent
14	2.6	0 (neutral).	0	100	0
15	4.0	1	0.28	38.5	0
16	9.1	5	1.38	12.5	0
17	20.0	12	3.1	9.5	0

* From Baudisch, O., and Mayer, P., *Biochem. Z.*, 1920, cvii, 1.

Nessler reagent no longer showed a yellow color, the distillation being usually complete when 150 cc. of liquid had been boiled off. The results are exhibited in Tables I and II and in Fig. 3.

From the tables and the figure it is seen that, when the nitrate is reduced by ferrous hydroxide, in the presence of air, through potassium nitrite, to ammonia, the behavior is quantitatively regular. With increased concentration of free alkali in the solution, that is, with increasing amount of alkali not used by the ferrous sulfate, the yield of ammonia and hence the amount of nitrate which is reduced falls off in a manner entirely quantitative. If the same experiment is carried out in such a way as to exclude air or oxygen, the nitrate remains absolutely unchanged. We regard the action of the alkali as being that of an "Anlagerung" of NaOH to the molecules of ferrous hydroxide, similar to that which Miolatti and Bellucci (5) have shown to take place between potassium hydroxide and platinum hydroxide. Their results may be expressed by the reaction

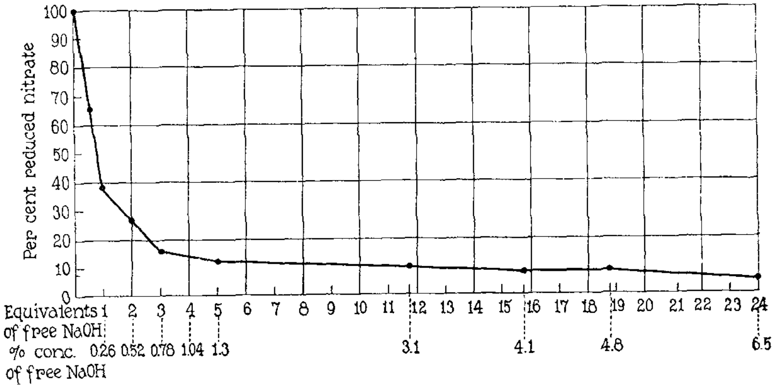


FIG. 3.

$$Pt\ (OH)_4 + 2KOH \rightarrow (OH)_4\ Pt \genfrac{}{}{0pt}{}{OHK}{OHK} \rightarrow \left[Pt\ (OH)_6\right]K_2$$

What may here be considered as the "blocking" action of the alkali is in complete harmony with our previous explanation of the mechanism of nitrate reduction. We are dealing with a competition between the oxygen and the alkali molecules for the unsaturated ferrous hydroxide molecules. If the solution is neutral all of the ferrous hydroxide molecules can combine with the oxygen dissolved in water and form the peroxide

$$[FeO_2]\ (OH)_2$$

Each peroxide molecule reacts with a nitrate molecule and on the splitting off of an oxygen atom from the latter a nitrite is formed. On the other hand, if free alkali is present in the solution, ferrous hydroxide presumably combines with this according to the reaction

$$\mathrm{Fe\ (OH)_2 + NaOH \rightarrow [Fe\ (OH)_3]\ Na}$$

and the ferrous hydroxide is no longer available for the reduction of nitrate.

It was found that the oxygen which becomes coordinatively bound to the ferrous hydroxide can be used not only for the reduction of nitrate, but it is also capable of oxidizing certain inorganic and organic compounds. A complete discussion will be made the subject of another paper. We shall only point out here that our view of the special properties of ferrous hydroxide-peroxide is completely valid in this case. As more and more molecules of the substance to be oxidized, lactic acid, for example, combine with the nascent ferrous hydroxide-peroxide molecules, there is a corresponding increase in the yield of pyruvic acid.

From all of the foregoing it can be seen that the study of the reduction of nitrate has enabled us to gain a considerable insight into the mechanism of this peculiar action of ferrous hydroxide and oxygen. But the study has, in addition, provided us with a foothold from which the investigation of the aging of the ferrous hydroxide or carbonate may be carried out in the absence of oxygen.

If ferrous hydroxide is precipitated in the absence of oxygen, the white voluminous precipitate formed in the lower bulb of Fig. 1 settles gradually to the bottom with no apparent change in its properties. If the experiment is again carried out with the difference that potassium nitrate is also present during the precipitation, no visible change in the precipitate with time is observed. There is, then, no obvious reason for believing that any change has taken place in the hydroxide, even after it has become several hours, or even days, old. If air is admitted through the slender tube extending down into the lower bulb, and allowed to bubble through the mixture, the ferrous hydroxide changes through several intermediate stages into the red ferric hydroxide,

$Fe(OH)_3$, so that there seems to be no difference between fresh and aged ferrous hydroxide, as far as the property of absorbing oxygen is concerned. This may, indeed, be the reason that the rapid aging of ferrous hydroxide has heretofore escaped detection. However, although the aged hydroxide or ferrous carbonate retains its marked property of being autoxidizable, it *has lost completely the property of being able to reduce nitrate or to oxidize organic compounds such as uracil and lactic acid.*

Several experiments have been made to illustrate this.

Experiment 1.—If ferrous carbonate (10 gm. of Na_2CO_3 and 3 gm. of $FeSO_4$) is precipitated in the presence of 0.1 gm. of sodium nitrate in a sealed tube, preventing entrance of air, and keeping at room temperature, there is formed a snow-white product which does not change in appearance after standing for over 6 hours. If the tube is then opened to the air, and is shaken, the white ferrous carbonate takes on a deep blue-green color in a minute or two, as a result of autoxidation. In spite of continued shaking, and addition of oxygen, the nitrate is not reduced and not a trace of nitrite or ammonia is found in the filtrate.

Ferrous hydroxide was tested in a similar manner, with similar results, only that the nitrate was added to the mixture after the ferrous hydroxide had been aged.

Experiment 2.—1.3 gm. of sodium hydroxide were dissolved in 500 cc. of water, and the solution was boiled to drive off oxygen. Taking care that no air entered, a solution containing 4.4 gm. of ferrous sulfate was added and the precipitate was left in the sealed flask to age for 8 hours. Then the flask was opened, nitrate added, and the mixture shaken with air. The white precipitate was still autoxidizable, turning first dark green, and finally red as the iron became oxidized. The nitrate, however, remained unchanged, the tests for nitrite and ammonia being all negative.

These experiments prove that ferrous carbonate and ferrous hydroxide, *when aged out of contact with oxygen, lose the property of reducing nitrates to nitrites, althouth they retain their ability to absorb oxygen from the air and can be oxidized to ferric compounds.*

This fact becomes even more striking if an attempt is made to use the ferrous hydroxide or ferrous carbonate, which has been aged for a few hours, for the purpose of oxidizing certain organic compounds, let us say, uracil or lactic acid. These organic compounds can, as has been mentioned, easily be oxidized by *freshly* precipitated ferrous hydroxide or ferrous carbonate if air has access. On the other hand, if the ferrous hydroxide or ferrous carbonate be left to age for a few hours, they remain autoxidizable, but the molecular oxygen then absorbed can no longer oxidize the uracil or the lactic acid which may be present.

The following experiments sustain this conclusion.

Experiment 3.—0.015 gm. of uracil and 5 gm. of sodium bicarbonate are dissolved in 400 cc. of water. This may be called Solution *A*. To this is added a solution containing 5 gm. of ferrous sulfate and the mixture is shaken with air until all of the iron is oxidized to Fe $(OH)_3$. The filtered solution shows every reaction characteristic of oxidized uracil.

Experiment 4.—Experiment 3 is repeated with the difference that Solution *A* is first boiled to drive off oxygen. Ferrous carbonate is added to the cooled Solution *A*, care being taken to keep air away, and the mixture is allowed to stand for 4 hours. Then the flask is opened and shaken with air until the iron is oxidized to Fe $(OH)_3$. The filtrate obtained in this experiment showed no oxidized uracil. It contained only unchanged uracil. Although the precipitation of ferrous bicarbonate took place in the presence of uracil, there was no oxidation on the subsequent admission of oxygen. The ferrous bicarbonate had been aged, and was ineffective as an aid to the oxidation.

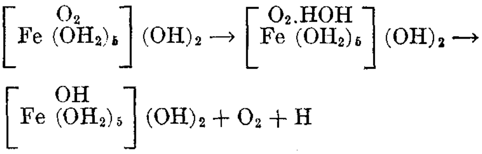
Similar results were obtained on the oxidation of lactic acid to pyruvic acid. Here, too, it is true that it is only the *freshly* precipitated ferrous bicarbonate which is able to bring about oxidation when oxygen is admitted. After the bicarbonate has aged for a few hours, it is still, indeed, autoxidizable, but it is not able to aid the oxidation of lactic acid.

From the experimental results we have here described, and from our previous work, there appears a whole series of facts which will now be briefly analyzed.

Freshly precipitated ferrous hydroxide alone does not react with potassium nitrate nor with the alkali salts of, say, lactic acid or succinic acid, nor does molecular oxygen alone react with these same compounds. However, if one gives both of the substances, ferrous hydroxide and molecular oxygen, the opportunity to react with each other, there is formed a chemical compound having an extraordinarily great reactive tendency which can change the potassium nitrate, if simultaneously present, to potassium nitrite. This strongly reactive ferrous hydroxide-peroxide can also oxidize lactic acid into pyruvic acid. Both of these reactions, the oxidation, as well as the reduction, are a direct function of the oxygen dissolved in the water which contains the reacting substances. This molecular oxygen in solution is activated as a *molecule.* If it is still a molecule when it performs the oxidation, or if it is first split up into the atoms, we are not able to decide with our present experimental material. But the fact remains that under the given conditions, namely attachment to the iron atom, the oxygen has gained a markedly great chemical activity. This activity is so great that even in the strongly reducing medium formed by an excess of unchanged ferrous hydroxide molecules it is able to oxidize such substances as lactic acid or succinic acid, which are ordinarily so difficult to oxidize.

This great oxidizing ability belongs, however, only to the oxygen which has been activated by the *freshly precipitated* ferrous hydroxide or ferrous bicarbonate. If the freshly precipitated ferrous hydroxide or ferrous bicarbonate is rapidly centrifuged out and then used for autoxidation in the presence of the substances mentioned, there is not the slightest trace of any chemical change in them. The coordinatively linked oxygen attached to the iron atom of the ferrous hydroxide which has been aged for so short a time possesses no longer such a high oxidation potential. It is only able to oxidize those substances having very labile hydrogens, such as they are in para-phenylenediamine, or in benzidine. This oxygen can also no longer reduce potassium nitrate.

These results of our investigations furnish a striking proof of the fact that compounds or atoms in their nascent states have very different properties than they have after they have been aged. With an appreciation of this fact, many of the mysteries connected with some of the intensive chemical reactions occurring in living cells at the ordinary body temperatures disappear entirely. We shall not discuss here the mechanisms of the oxidation and reduction, as they occur in the natural processes, with any great detail. It is most probable that, at the moment of formation, the ferrous hydroxide-peroxide acts so as to dissociate water, and forms a strongly activated oxygen and atomic hydrogen. This process of activation may be represented by



$$\left[\overset{O_2}{\mathrm{Fe}}\,(OH_2)_5\right](OH)_2 \longrightarrow \left[\overset{O_2.HOH}{\mathrm{Fe}}\,(OH_2)_5\right](OH)_2 \longrightarrow$$

$$\left[\overset{OH}{\mathrm{Fe}}\,(OH_2)_5\right](OH)_2 + O_2 + H$$

If we assume this we have a natural explanation of the double rôle played by the freshly precipitated ferrous hydroxide-peroxide in its strong oxidizing action and its strong reducing action.

An analogous chemical action takes place when molecular oxygen comes in contact with the *aged* ferrous hydroxide or ferrous bicarbonate. But there is a difference in the degree of the activation. In this case the activated oxygen which is formed does not have such a high oxidation potential and can only oxidize those compounds having hydrogen which is labile and which is easily removed.

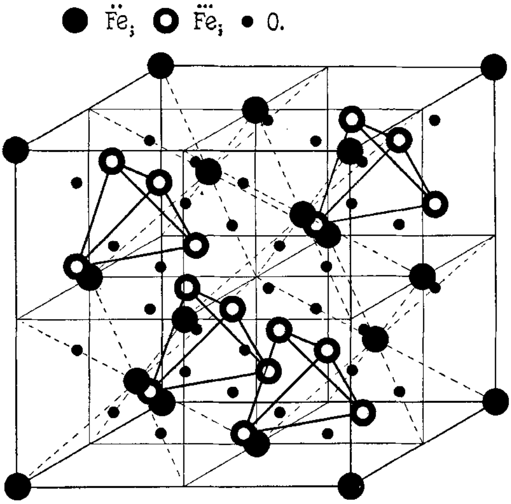
Similar relations can be followed for the stages of activation of hydrogen. There are many examples to show that when one dissociates water one obtains hydrogen of a very wide range of reducing power, according to the chemical or physical condition of the metal used for the dissociation. The chemical activity of hydrogen obtained by the dissociation of water varies enormously and the process is very complicated.

If aged ferrous hydroxide or the magnetite obtained therefrom is autoxidized in the presence of lactic acid or of potassium nitrate, both of these substances remain unchanged, although molecular oxygen is activated in some degree. There exist, between the fresh and the aged ferrous hydroxide, differences which are analogous to the differences found between the "active" and the "inactive" forms of ferric oxide, Fe_2O_3. We have found that active ferric oxide decomposes hydrogen peroxide, yielding an active oxygen which oxidizes benzidine. The inactive ferric oxide, on the other hand, on decomposing hydrogen peroxide, yields only the molecular oxygen which does not oxidize the benzidine. Ferrous hydroxide freshly precipitated in the presence of oxygen can oxidize lactic acid by the removal of its hydrogen. Aged ferrous hydroxide, on the other hand, can remove only labile hydrogen atoms, such as are found in paraphenylenediamine, for example.

It is our intention to study certain of the physical properties of those iron compounds which activate oxygen, and to attempt to correlate the activation to their molecular and atomic structure. At the present time we really know very little about the adsorption and the activation of gases. This statement is particularly true of those with which we are concerned here, oxygen and hydrogen. It is to be expected that with more detailed information as to the structure of these iron compounds we can come to an understanding as to their adsorbing action towards various gases. The activation of the gases is, however, most probably a complex change taking place in the atoms themselves and just beyond the reach of the present experimental methods. Just now the prospects are very poor for getting the information which will enable us to understand the several degrees of activation and the selective behavior of the activated oxygen or hydrogen towards other compounds. From our experiments and investigations we believe we can safely say that there are *several different kinds* of activated oxygen, and that the hitherto recognized active forms of oxygen, such as atomic oxygen or ozone, represent only the more stable forms.

Now, as to the nature of the changes taking place in the ferrous hydroxide or ferrous bicarbonate, or the ferrous hydroxide-peroxide, during the time of aging we have little or no information which has been obtained from these substances themselves. But they may be expected to be of the same nature as those which have been found to take place in aluminum hydroxide; namely, a gradual passing, during the aging, from an apparently amorphous to a very definite crystalline form. During the aging process there occurs an ordered arrangement of the forces among the iron atoms and the hydroxyl groups, and small crystals are formed which retain some of the properties that the substances had in the amorphous state, but have lost others. The ferro-ferric oxide, Fe_3O_4, which has so often been mentioned, is a known and striking example of such a case. If the attempt is made to use the newly prepared oxide, Fe_3O_4, for the purpose of reducing potassium nitrate, the result is always absolutely negative. *But it can absorb more oxygen,* although it already has a perfectly definite crystal structure (6), such as is shown in Fig. 4; and the structure is not disarranged during this increase of the crystal's oxygen content. On examination of the interatomic dimensions involved, it was found that room can actually be found in the structure, shown in Fig. 4, for sufficient oxygen to convert the magnetite, Fe_3O_4, into the ferric oxide Fe_2O_3, without changing the arrangement of the iron and oxygen atoms already in place.

It is noticed that the unit cube (Fig. 4) contains 8 molecules, so that Fe_3O_4 may be written $Fe_{24}O_{32}$. After oxidation to Fe_2O_3 the corresponding composition would be $Fe_{24}O_{36}$. We must find room for 4 additional oxygen atoms in the cube. The first places to suggest themselves are the centers of the tetrahedra formed by the trivalent iron atoms, and they are thus shown in Fig. 5. In view of the uncertainties as to the actual radii of combination, it is quite possible that the extra oxygen atoms are placed, as shown, without undue distortion of the system. The edge of the unit cube has a length $a = 8.30$ Å. u. and the distance from the center of the tetrahedron formed by trivalent iron atoms to each corner is



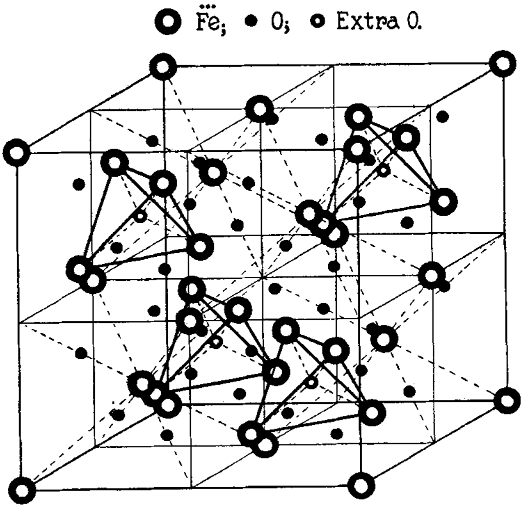
MAGNETITE

FIG. 4.

$$\frac{a}{8}\sqrt{3} = 1.795 \text{ Å.u.}$$

The radius of the oxygen atom is usually taken to be 0.65 Å. u. This leaves 1.145 Å. u. as a remainder for the radius of the iron atom. The radius of the iron atom appears to be variable and values as low as 1.25 Å. u. have been found in the case of pyrites (7) and in iron itself.

An alternative and equivalent arrangement would be to place an oxygen atom at the middle of each edge of the cube and one in the center. The room at our disposal would be the same. The question is not considered here. We are here concerned only with the possibility of putting more oxygen in Fe_3O_4 so as to convert it to Fe_2O_3 without changing the existing arrangement of the atoms. And we are especially concerned with the fact that we are dealing with a known substance which has the property we have assumed for the precipitated ferrous hydroxide and ferrous carbonate. It is that, while becoming crystalline, it loses certain specific properties, such as its reducing and oxidizing powers, and yet remains capable of absorbing still more oxygen.

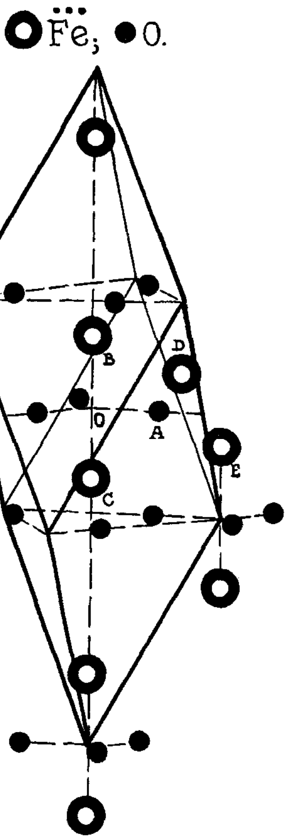


OXIDIZED MAGNETITE

Fig. 5.

It must be explained here that the structure of Fe_2O_3 in Fig. 5 is not the most stable form. Fe_2O_3 of that structure is obtained by oxidizing Fe_3O_4 in oxygen at a temperature of about 200°C. On reaching a temperature of 550°C. or more the structure becomes unstable and goes over into the more stable calcite-like structure usually found for Fe_2O_3 as shown in Fig. 6. The most recent determination of this stable structure is that of Pauling and Hendricks (8).

It is our intention to proceed further with this work on the aging of ferrous hydroxide and ferrous carbonate. In particular it is our plan to follow by X-ray analysis the conversion of the hydroxide or the carbonate from the apparently amorphous to the crystalline condition.



Hematite

Fig. 6.

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