

tities of fluid and for starch mass which must be prevented from setting. This equipment, with the moderate water pressure available, will develop an air pressure of ten pounds, though two to five are all that are usually needed. It will deliver one liter of air per minute at five pounds pressure and over four liters at atmospheric pressure. It will maintain an even pressure without attention unless the air is suddenly released or the water pressure varies. This apparatus, in comparison with the gravity apparatus formerly used, saves time and necessitates less handling of unpleasant fluids and less moving of heavy bottles.

The same equipment can also be used for operating a small blast burner, for stirring with air, for aerating aquaria, etc. It is especially useful for salt water aquaria where running sea water is not available. Fresh air may be secured from out of doors by running a tube to the pump from any desired point, and the air delivered to the aquarium is washed, cooled and moistened. The writer has aerated fourteen aquaria at one time with one pump. The tube to each aquarium must be provided with a clamp to regulate the flow of air and to maintain some pressure in the system. Especial care must be taken that water from the pump does not get through the air line into the aquaria.

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SPECIAL ARTICLES

CERTAIN OXIDES OF IRON IN SOME NEW CATALYTIC ACTIONS¹

IN current numbers of the *Philosophical Magazine* and the *Journal of Biological Chemistry* detailed accounts of our work with synthetic iron oxides and their use in catalyzing certain reactions of biological interest will be presented. The results appear to be of sufficient general interest to justify a brief description in this journal.

The oxide with which we start is the magnetite which is formed when a solution containing one mol of ferrous sulphate and two mols of ferric sulphate is poured into a boiling solution of sodium hydroxide of sufficient strength to remain alkaline after the addition of the sulphates. The black, micro-crystalline precipitate is washed to remove the sulphate, and it is then filtered off and dried. Two distinct ferric oxides can be derived from this magnetite. One, which we call "oxidized magnetite," is obtained by oxidation of the magnetite in a stream of oxygen at

a low temperature of say, 300° C. The oxidized magnetite is ferric oxide of the composition Fe_2O_3 but it retains the ferro-magnetic properties of the magnetite Fe_3O_4 , with which we started, and it retains also the original cubic crystal structure. If, now, the oxidized magnetite, which is completely oxidized to Fe_2O_3 , is heated to 550° C. or more, it loses its ferro-magnetic properties, and the crystal unit takes on the rhombohedral form usually found in hematite, Fe_2O_3 . This transformation of oxidized magnetite into hematite is non-reversible, for the oxide remains permanently non-magnetic and the structure does not change back to cubic when the oxide cools. These physical properties of the magnetite with which we begin, of the oxidized magnetite, and of the hematite are compared in the first three rows of Table I.

TABLE I

	Fe_3O_4 (Magnetite)	Active Fe_2O_3 Fe_3O_4 oxidized at 330° C. (Oxidized magnetite)	Inactive Fe_2O_3 Fe_3O_4 oxidized at 330° C., then heated to 550° C. (Hematite)
Prussian blue test for ferrous iron	+	—	—
Maximum mag- netic suscepti- bility, k.	0.152	0.182	0.0036
Crystal unit	cubic	cubic	rhombohedral
Absorption o f water, average per cent.	27	27	21
Blood test. Oxi- dation of benzi- dine by H_2O_2 in presence of —	good	good	none
Growth of <i>B. lepi- septicum</i> in broth and in presence of —	good	good	none
Absorption o f oxygen, average initial rate, Cm ³ gr. hr.	0.0044	0.0080	0

The table brings out the marked tendency to absorb water which is characteristic of the oxides if prepared in the way we have described. The table shows, too, that the appearance of ferro-magnetism in an oxide

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of iron is not dependent on the presence of ferrous iron.

Each of these three oxides have been submitted to two tests of a catalytic nature. One is the well-known benzidine test for blood. Both the magnetite and the oxidized magnetite, which we will hereafter call "active Fe_2O_3 ," gave positive benzidine tests, just as if we had used blood instead of the oxides as a catalyzer. When the test was made with the hematite, "inactive Fe_2O_3 ," the result was absolutely negative. The other test we used was that of promoting the growth of *Bacterium lepi-septicum*.² Under aerobic conditions this organism does not thrive and soon loses its virulence if one attempts to grow it in broth alone. But it thrives and remains virulent if grown in broth plus a small quantity of blood. The organism will also thrive and remain virulent when a small quantity of magnetite or of oxidized magnetite (active Fe_2O_3) is added to the broth culture. However, when the organism is seeded in a culture of broth plus hematite (inactive Fe_2O_3) it does not thrive and it becomes non-virulent just as if broth alone were used. In these tests with bacteria we usually employed 100 milligrams of oxide per cubic centimeter of broth.

The fact that *Bacterium lepi-septicum* requires the presence of a suitable substance in addition to the broth, if growth is to take place under aerobic conditions, whereas growth takes place in broth alone under anaerobic conditions, suggests that the function of the blood or of the oxides is to absorb oxygen, and thus bring about the equivalent of anaerobic conditions. The oxygen absorption of each of the three oxides, when covered with broth, was therefore measured. The results are shown in the table.

It is not the purpose of this paper to consider the question of whether the function of the active oxides is that of creating anaerobic conditions in the broth, or whether we are dealing with some other chemical phenomenon which is associated with the absorption of oxygen. The object is to bring out the fact that the activity or inactivity of Fe_2O_3 as a catalyzer is dependent on its *crystal structure*. Likewise, the property of ferro-magnetism is closely connected with the structure, as it may be present or absent in oxides of identical composition according as the crystal unit is cubic or rhombohedral.

The questions may now be asked: Are these true phenomena of catalysis? Does anything happen to the oxide when it is used to promote the benzidine reaction or to promote the growth of *Bacterium lepi-septicum*? There seems to be no chance of any chemical change in the active Fe_2O_3 , which is already completely oxidized. But we meet with one extremely

tempting and attractive possibility when we consider the relative lattice energies of the crystals of active and of inactive Fe_2O_3 . Crystals of the former are evidently less stable than those of the latter, since the transformation which can take place at a high temperature is non-reversible. The possibility before us is that the transformation of active Fe_2O_3 into inactive Fe_2O_3 can, in some way, take place during the catalysis, and that the difference in the lattice energy becomes available for the activation of the atoms or molecules taking part in the reactions.

The hypothesis can be tested in two ways. We may examine the X-ray diffraction pattern given by active Fe_2O_3 , after it has been used as a catalyzer, for lines which are given by inactive Fe_2O_3 . A more sensitive test would be to look for a decrease in the ferro-magnetism which is known to disappear when active Fe_2O_3 becomes inactive. We have done this, with negative results, as shown in Table II. In the case of the benzidine reaction it was necessary to take account of the products of the reaction which formed a coating on the

TABLE II

	Pull in mag- netic field mg./gr.	Analysis for Fe_2O_3 and non-combustible impurities (per cent.)	Pull in mag- netic field mg./gr.
Active Fe_2O_3 (control)	2403	100	2403
Active Fe_2O_3 after support of benzidine reaction	1380	57.5	2400
Active Fe_2O_3 after support- ing growth of <i>B. lepi- septicum</i> in broth for 10 days	2400	100	2400

oxide particles which could not be washed off. This was done by burning the reaction products in oxygen at 800° C. and recalculating the magnetic pull per unit of mass. After being used as catalyzers the oxides seem to be as strong magnetically as they were originally. They function as true catalyzers in the usual sense that they undergo no permanent change. Apparently their action can not be explained on the assumption that the excess energy of the lattice becomes available for the activation of the constituents taking part in the reactions.

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