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A CRITICAL STUDY OF THE LEDEBUR METHOD  
FOR DETERMINING OXYGEN IN  
IRON AND STEEL

BY

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*Bureau of Standards*

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# A CRITICAL STUDY OF THE LEDEBUR METHOD FOR DETERMINING OXYGEN IN IRON AND STEEL

By J. R. Cain and Earl Pettijohn

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## I. INTRODUCTION

Oxygen in steel and iron is believed by most investigators to be present in the combined form. Indeed, it is difficult to conceive of elemental oxygen remaining as such in equilibrium with an excess of a solution of carbon in molten iron. The exact form of combination can only be conjectured. Metallographic methods for differentiating oxides in steels have not been developed, except

in a few special cases, and chemical methods dependent upon separating the oxides by selective solubility have proved unsatisfactory. Solutions of iodine, ferric chloride, cupric salts, and other solvents have often been proposed and tried for such separations, but the difference in solubility of metallic iron and of the oxides concerned has not been sharp enough to enable satisfactory results to be obtained.<sup>1</sup>

Oxides with known or unknown formulæ of the following elements may exist in steel: Class 1, iron and manganese; class 2, silicon (silicates), aluminum, chromium, vanadium, and titanium; class 3, copper, nickel, and tungsten; class 4, phosphorus and sulphur; class 5, carbon. Class 1 consists of metals present in quantity relatively large to that of the reducing agent (carbon). The corresponding oxides would, therefore, probably be present in steel. Oxides of metals in class 2 have very high heats of formation; hence are difficult to reduce by carbon except at temperatures higher than those usual in steel or iron furnaces, and are therefore probably present to some extent in the steels which contain these metals as essential ingredients. Oxides of metals in class 3 are, on the contrary, very readily reduced by carbon at temperatures prevailing in steel furnaces, and are probably never present in steel. Oxides of class 4 are volatile or decomposed at steel-melting temperatures and are not to be expected in the metal. Class 5 contains the oxides of carbon. These have been reported by numerous investigators, and it is almost certain that carbon monoxide, at least, is present.

Ideal methods for determining oxygen in steel should permit the separate determination of each form of combination. There is a theoretical possibility of accomplishing this, but there would be many practical difficulties. Some work of this kind has been done by the differential reduction of the oxides with various reducing agents and varying reduction temperatures, or by both. Thus, Pickard<sup>2</sup> has investigated in this connection the reducibility by hydrogen of manganous oxide, iron oxides, and oxide of carbon. Walker and Patrick<sup>3</sup> state that reduction by carbon in an Arsem vacuum furnace under the conditions prescribed by them gives the total oxygen content of steel, in contrast with the Ledebur method (reduction with hydrogen at 900 to 1000°), which, they claim, gives only the iron oxide content.

<sup>1</sup> Pickard; Carnegie Scholarship Memoirs, Iron and Steel Inst., 5, pp. 73-76.

<sup>2</sup> Cf. Carnegie Scholarship Memoirs, Iron and Steel Inst., 5, pp. 81-82.

<sup>3</sup> Proc. Eighth Internat. Cong. Applied Chem., 21, p. 139.

It seemed advisable to make a study of the Ledebur<sup>4</sup> method for determining oxygen in steel and iron, since this method has been used more extensively than any other proposed. The method as described by its originator, consists in heating drillings or chips of the metal in a current of pure hydrogen to about 1000°, collecting the water formed by reduction of the oxides and weighing it. The apparatus used by Ledebur consisted of generators for nitrogen and hydrogen followed by appropriate purifying apparatus for each. Generators and purifying apparatus were attached to one end of the combustion tube. To the other end of the combustion tube weighed phosphorus pentoxide tubes were attached, in which the water formed as a result of the reduction was collected. The procedure consisted in inserting the boat containing the chips into the cold combustion furnace, passing pure dry nitrogen over it to replace air, and heating the chips in nitrogen to remove moisture and organic matter. After cooling, the nitrogen was replaced by purified dried hydrogen, the temperature raised to the proper point, and the heating and passage of the hydrogen continued for 30 or 40 minutes. The phosphorus pentoxide tubes were then disconnected and weighed and the oxygen content of the steel calculated from their increase of weight.

Variations in the method introduced by others have been mainly in details, such as omission of the use of nitrogen,<sup>5</sup> weighing phosphorus pentoxide tubes filled with air instead of hydrogen,<sup>6</sup> electric instead of gas furnaces for heating,<sup>7</sup> improved forms of hydrogen generators, absorption tubes, etc. Very special changes in Ledebur's procedure and apparatus were introduced by Pickard,<sup>8</sup> who used a definite volume of hydrogen at less than atmospheric pressure in a confined space instead of passing a current of the gas through the combustion tube. He used a weighed boat as container for the phosphorus pentoxide.

In our study we have given special consideration to: (1) Apparatus, with a view to simplicity, reliability, small blanks in determinations, and durability; (2) sources of error; (3) preparation of samples for determinations; (4) reducibility, under the conditions of the Ledebur method, of various oxides likely to be present in steel; and (5) accurate determination, by the Ledebur method, of oxygen in some typical American irons and steels.

<sup>4</sup> Leitfaden für Eisenhütten Laboratorien, 9th ed., p. 154.

<sup>5</sup> Cushman, J., *Ind. and Eng. Chem.*, 3, p. 372.

<sup>6</sup> *Ibid.*

<sup>7</sup> McMillen, J., *Ind. and Eng. Chem.*, 5, pp. 123-125.

<sup>8</sup> Carnegie Scholarship Memoirs, *Iron and Steel Inst.*, 5, p. 77.

## II. APPARATUS AND REAGENTS

### 1. HYDROGEN GENERATORS AND PURIFICATION OF HYDROGEN

One of the hydrogen generators used for our work is shown in Fig. 1. It is similar in design to generators that have for some time been successfully used in the section of gas chemistry at this Bureau. To operate the generator, fill the bottle *F* with zinc (see Fig. 1) and replace the stopper, closing the bottle. Fill the reservoir *B* with dilute sulphuric-acid mixture 1 to 6, containing 5 g.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per 100 cc. Open the cocks *C* and *H*, which permit hydrogen to escape (usually through the train) and apply air pressure to the acid reservoir, *B*. Acid is thus driven over into

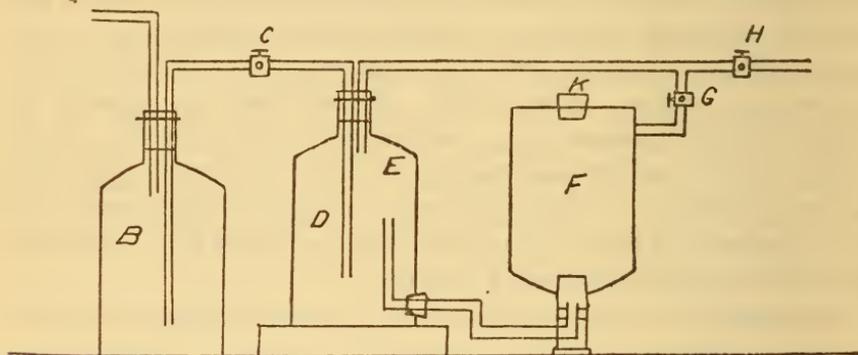


FIG. 1.—Hydrogen generator

*D*. When sufficient acid has been forced into *D*, stopcock *C* is closed and the air pressure released. A constant, regulated current of hydrogen is then obtained by manipulating cock *G* (*H* being, of course, open). To stop the generation of gas, close the cocks *G* and *H* and open cock *C*. The pressure of the hydrogen being generated in *F* forces the acid out of *F* and *D*, partially. As soon as the acid is all driven away from the zinc, gas ceases to be generated.

This generator has been found very convenient in use and has advantages over others that have been proposed for this kind of service. After being filled with reagents and freed from air (by displacement or evacuation, or both) spent acid can be replaced without any air being introduced into *D*. *F* holds enough zinc to suffice for about 30 determinations. The flow of hydrogen can be well regulated without much variation of pressure inside the apparatus. The position of the acid inlet at *E* insures fresh acid being in contact with the zinc, the spent acid, because of its

greater density, settling to the bottom of *D*. Because the generator is left under atmospheric pressure there is minimum danger from overflow or loss of acid or from blowing out the rubber stoppers in the generator or apparatus.

The impurities to be removed from hydrogen generated in this manner are: Water vapor, oxygen (from air), carbon dioxide, carbon monoxide, and some hydrogen sulphide. The possibility of carbon monoxide being present seems to have been overlooked by others, since we find no reference to it in the literature. Its absence in the gas entering the combustion tube by way of *G* (Fig. 3) is desirable, since hydrogen slowly reduces carbon monoxide (see pp. 28 and 29) under the conditions of the Ledebur method, and the water vapor resulting from this would give high results for oxygen in steel samples. It is less desirable to correct this error by a blank than it is to eliminate the carbon monoxide altogether; hence we have adopted the latter method. Both the carbon dioxide and monoxide come from the zinc, and it is interesting to note that samples tested from three different sources all contained both gases, and only one, a zinc from an English source unknown to us, was free from this gas. Since we happened to have an abundant supply of this zinc, it was used in all of our work with this generator. Consequently, the apparatus shown in Fig. 1 does not provide for the removal of carbon monoxide. Probably the simplest method for accomplishing this would be to pass the hydrogen through a U tube (both limbs sealed at the top, no rubber stoppers or lubricated stopcocks being permissible) filled with iodine pentoxide and heated by an oil bath to 150°. This would oxidize the carbon monoxide to dioxide, which would be absorbed by soda lime. Hydrogen would not be oxidized under such conditions. Since, as stated, we used carbon-monoxide-free zinc, no iodine pentoxide tube such as proposed is shown preceding the tube *G* (Fig. 3), whose function is to remove the carbon dioxide always present in the hydrogen. If a carbon-monoxide purifier of the type described is used, it should be inserted between the hydrogen generator and *G* (Fig. 3). The soda-lime tube *G* also serves to remove any hydrogen sulphide. The removal of the traces of oxygen always likely to be present from air, even when the greatest care is used in freeing the generator of air, is secured by the catalyzer. This consists of a  $\frac{1}{4}$ -inch bore tube of porcelain, glazed in this case inside and out, heated to 600° for 6 inches in the middle by the electric furnace *F* (Fig. 3). This tube is

filled loosely in the heated part with platinized quartz. The phosphorus pentoxide tube, *D*, removes the water vapor formed

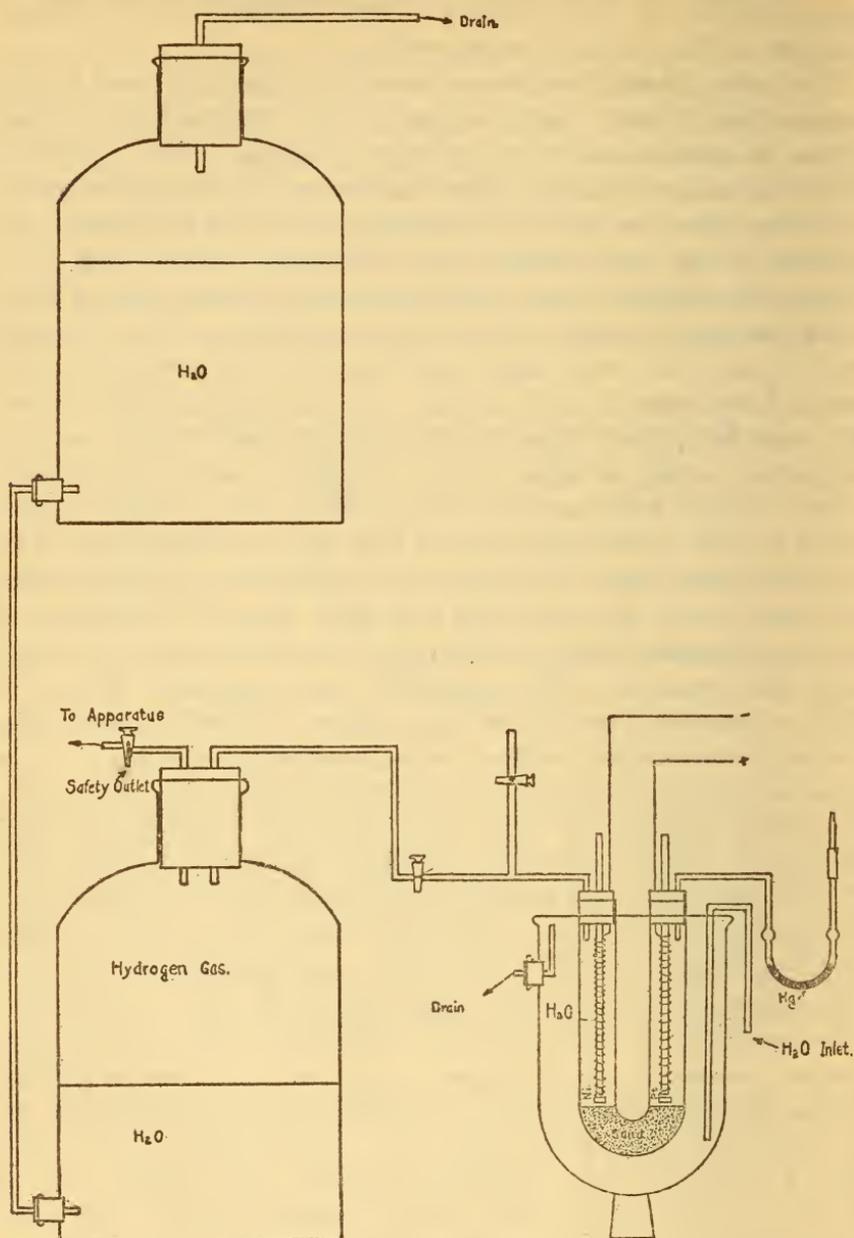


FIG. 2.—Electrolytic hydrogen generator

by combustion of the oxygen present as impurity, as well as the water vapor originally present in the gas.

*Electrolytic Hydrogen Generator and Reservoir.*—Hydrogen gas was generated by the electrolysis of a saturated solution of barium-hydroxide mixed with a 25 per cent solution of sodium hydroxide in a large pyrex glass U tube, using a platinum anode and a nickel cathode. Platinum and nickel were used as the electrode materials because they have a low oxygen and a low hydrogen overvoltage, respectively. The generator (Fig. 2) consists of a U tube containing the electrolyte and submersed in a jar through which flows cold water. The bottom of the U is filled with sea sand to hinder the passage of dissolved gas from one limb of the U to the other, as suggested by Lewis, Brighton, and Sebastian.<sup>9</sup> The current passing through the generator is regulated by means of a rheostat in the circuit. During the course of the investigation the current used by the operator was 3.3 amperes, which liberates about 1.5 liters of hydrogen gas per hour.

The hydrogen gas reservoir and pressure-maintaining bottle is connected to the cathode side of the generator, and to the anode side a small U tube of 10 mm inside diameter is attached which contains mercury to balance the pressure in the receiving system. With this arrangement the generator operates automatically. As hydrogen is generated and delivered to the gas reservoir water is displaced from the gas reservoir and forced into the water bottle above. The increased pressure thus produced forces down the liquid in the cathode side of the generator an amount approximately equal to the height to which the water level in the water bottle is raised. After a certain volume of hydrogen gas has been generated and stored in the reservoir, the level of the electrolyte on the hydrogen side of the generator will be forced down out of contact with the cathode, thus automatically breaking the circuit. The pressure of the hydrogen that is desired for the experiment is regulated by adjusting the height of the water bottle, which then determines the amount of mercury that must be added to the U tube on the oxygen side of the generator. The hydrogen gas as it is drawn off from the reservoir for use is passed through the catalyzer and purifying train.

The electrolytic hydrogen generator is followed by the same type of purifying train as shown for the zinc generator. No carbon monoxide need be feared in using this method of generating hydrogen.

<sup>9</sup> J. A. C. S., 39, 1917, 2248.

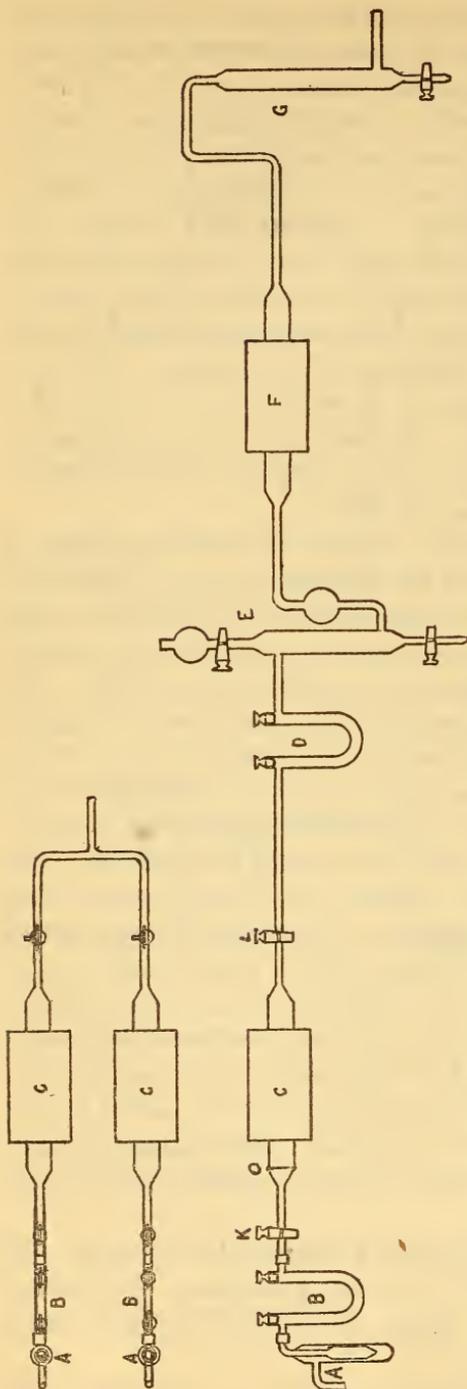


FIG. 3.—Apparatus used for determination of oxygen

## 2. FURNACES, COMBUSTION TUBES, AND TEMPERATURE CONTROL

(a) *Furnace*.—An electric furnace is very greatly to be preferred for Ledebur oxygen determinations. Gas furnaces may be and have been used, but they are much harder on tubes, and in case of porosity or minute cracks in the latter the danger from inwardly diffusing water vapor from products of combustion is very great, a difficulty which is entirely obviated by electric heating, which we have used in our work. The type of furnace shown at *c* in Fig. 3 and in detail in Fig. 4 was used. Obviously, in work of this kind another combustion can not be begun until the entire apparatus has cooled practically to room temperature after the preceding combustion. But since, in general, for efficiency in heating the thermal insulation of an electric furnace should be made very effective, it follows that cooling is correspondingly slow. The difficulty of a slow-cooling furnace can be obviated by (a) fitting the furnace with a removable heat-insulating jacket; (b) by using a combustion tube closed at one end, thereby dispensing with a rubber stopper and connections at that end, so that the hot furnace may be

slid on and off there; (c) by providing heat insulation incased in a sheet-iron jacket split and hinged in the medial horizontal plane, so that the hinged halves may be opened and the furnace removed from the tube without interrupting the heating current. Method (c) was considered the most convenient, and the hinged furnace shown in Fig. 4 was built according to our specifications for this work.<sup>10</sup> This furnace is satisfactory and by its use with a porcelain tube a new determination may be begun

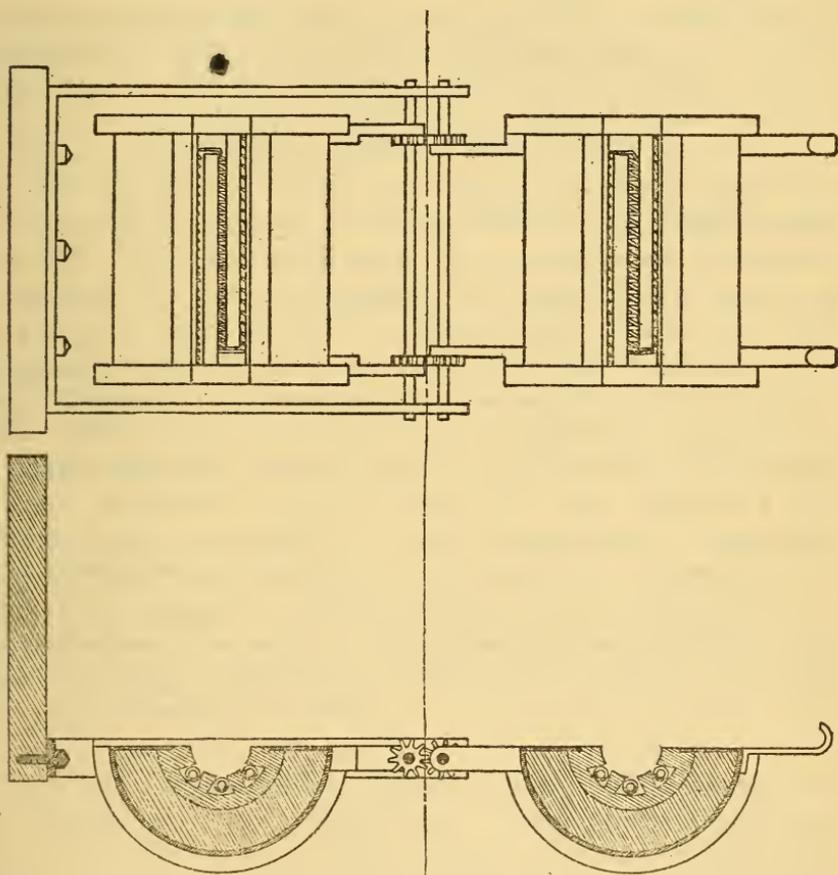


FIG. 4.—*Special electric furnace for oxygen determinations*

within 20 minutes after completing the preceding one. With most porcelain tubes the opening of the furnace and the closing of the hot sections upon the cold tube for heating must be done rather gradually, owing to the danger of rupturing the tube by sudden temperature change. This is particularly true with the somewhat inferior porcelain now available. If fused silica tubes are used,

<sup>10</sup> A great deal of work was also done in the ordinary nichrome-wound electric furnaces without removable heat insulation such as are in general use at the Bureau.

this condition is much improved. However, as will be seen later, the fused silica tubes which we have tried for the work are open to certain objections.

(b) *Boats.*—Boats may be made of quartz, porcelain, nickel, or iron, the order of preference being as given. We find statements in the literature on the Ledebur method to the effect that quartz reacts with iron or hydrogen at the working temperatures of the Ledebur method, but these statements are not confirmed by our experience. Porcelain boats are less desirable than quartz, owing to the greater liability to fracture by sudden temperature changes. Nickel and iron boats, the latter in much greater degree than the former, are liable to oxidation if removed from the furnace when they are at all hot. In fact, even at ordinary temperatures there is some oxidation of both metals on long standing, so that they must be prepared for use by preliminary reduction in hydrogen if the operator is to feel safe on this point. The size of the boat is governed by the physical form and the amount of chips used for each determination. We have found 20 to 30 g of chips a suitable weight, and if the size of chip recommended later (p. 19) is used, a boat of about 15 cc capacity is required. Our quartz boats measured 15.0 cm by 1.3 cm by 1.3 cm inside. The bottoms were flat and slightly concave inside toward the edges.

(c) *Combustion tubes.*—The use of proper combustion tubes is imperative if reliable results are to be expected. The desirable qualities for work of this kind are: Freedom from tendency to oxidize, mechanical strength, impermeability to oxygen or to water vapor, inertness toward hydrogen at 900 to 1000°, resistance to temperature changes, and absence of structural changes by heat, with consequent development of porosity. Platinum tubes are perhaps best, but are expensive. Fused silica tubes are good until they become opaque, due to the gradual formation of tridymite, when they develop porosity. (See Table 1 (1).) The useful life of quartz tubes is, on this account, rather short. Opaque or semi-transparent quartz tubes, so far as our results show, are very dangerous unless they are thoroughly glazed. Blanks to ascertain the condition of tubes should be run every few days, as deterioration is sometimes quite rapid. When the blank per one-hour heating exceeded 0.0003 g, we put in new tubes for our most accurate work<sup>11</sup> unless the blank was found to be due to other causes. Porcelain tubes now available are of variable quality. Royal Berlin tubes, some with inside glaze only, others with both inside and

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<sup>11</sup> See footnote under Table 1.

outside glaze, were used, and, in general, were found quite satisfactory. Occasionally defective porcelain tubes from the most reliable sources are found (Table 1 (2, a).) The only safe way is to test each tube thoroughly before installing and to run frequent blanks afterwards until failure is detected. In more recent work Copenhagen porcelain tubes and Imperial porcelain tubes have been used with fair satisfaction. No American-made tubes yet submitted to us have proved at all reliable. The outstanding objection to porcelain is the poor resistance to sudden temperature changes, an objection which is probably inherent and which sets the limit on the time required for an individual determination.

TABLE 1.—Data on Combustion Tubes

Kind	Dimensions	Blank (boat present)	Time of each heating	Blank when discarded <sup>a</sup>	Life hours, at 1000°
	cm	g	hours	g	
(1) Quartz.....	60 by 2.2	.0010 .0014 .0017	1 2 3½	0.0088	250
(2) Porcelain:					
(a) Royal Berlin.....	60 by 2.2	0.0020-0.0024	4	.0045	150-200
	60 by 2.2	.0010	1		
		.0040	4	Not used	
(b) Royal Imperial.....	60 by 2.2	.0010	1	.0040	120 b 70 b 166
(c) Royal Copenhagen.....	60 by 2.2	.0010	1	.0050	66
(d) Fused silica (unglazed).....	60 by 2.5	.0036- .0044	4	Not used	

<sup>a</sup> The blank denotes increase in weight of the phosphorus pentoxide tube. The increase in blank noted when the tube is discarded occurs all at once and is not a gradual increase from 0.0010 g per hour to the figure given in this column. The normal blanks indicated here were obtained during the first stages of our work, and were later reduced to 0.0003 g per hour. The values are given because they show the quality of the varieties of tubes used. See Blanks, p. 17.

<sup>b</sup> Still in use.

(d) *Temperature Control.*—The usual working temperature in Ledebur determinations is 900 to 1000°, at which temperatures the oxides of classes 1, 3, and 5 (see p. 4) are reduced wholly or partially.<sup>12</sup> No advantage is to be gained by carrying the working temperature to the maximum practicable when working with glazed porcelain tubes (1200 to 1400°), since these temperatures are still below the temperature range where the lower oxides of class 2 are reduced to metal by hydrogen but are above the temperature range where porcelain tubes have a long life. The most convenient method for measuring the working temperature is by base metal or by platinum-rhodium thermocouples connected to

<sup>12</sup> Some work showed that a very considerable reduction takes place at temperatures as low as 500 or 600°.

direct-reading millivoltmeters. In our work both types of couple were used. The temperature of the furnace should be measured every three or four days of actual service. A steady temperature drop not caused by change in voltage of the current supplied the furnace is probably due either to oxidized terminal connections or to deterioration of the resistor, and should immediately be remedied.

### 3. WEIGHED ABSORPTION TUBES

Glass-stoppered U tubes of the type usually employed for carbon determinations were used and found satisfactory. The limbs of our tubes were 12.5 cm long and 0.90 cm in bore. They were fitted with well-ground stoppers kept well lubricated with a good quality of stopcock grease. They were filled with alternate layers of phosphorus pentoxide and glass wool in such manner that free passage of gas was not impeded. Counterpoises of the same approximate shape and size were used in weighing. A guard tube A (Fig. 3) containing concentrated sulphuric acid was used at the end of the train to prevent access of moisture from the air to the weighed tube.

## III. SOURCES OF ERROR IN OPERATION OF APPARATUS AND BLANKS

### 1. SOURCES OF ERROR

The principal sources of error in Ledebur oxygen determinations other than those already described and the errors resulting from faulty preparation of the sample (see next section) are: (1) Impurities in the hydrogen; (2) too low temperature; (3) failure completely to remove air from the combustion tube after inserting the boat containing the sample, (4) moisture condensed on the sample; (5) too short a period of heating during the determination; (6) weighing phosphorus pentoxide tubes; (7) rate of passage of hydrogen.

Errors (1) and (2) have been dealt with in Section II.

(a) *Removal of Air.*—Completeness of removal of air from the apparatus was tested by taking successive samples of the gas from the exit end of the combustion tube in a test tube during rapid passage of the hydrogen until a sample no longer exploded, tests being made every two minutes.<sup>13</sup> An oxygen content of less than 4 per cent was thus indicated, and passage for 10 minutes longer

<sup>13</sup> Some experiments were made in which air was removed by evacuation with a good water aspirator, refilling with hydrogen and again evacuating. This method was very effective.

assured an error of less than 0.001 per cent oxygen on a determination from this cause, assuming a weight of 30 g of steel to be used. This value has been checked by numerous blank determinations, detailed later.

(b) *Removal of Moisture.*—Since the incoming hydrogen is dried over phosphorus pentoxide, the simultaneous removal of any moisture in the air being displaced, or of any condensed moisture on the sample is assured. Our method of preparing samples also practically excluded the possibility of surface moisture.

(c) *Time of Heating.*—(See Table 2.) By varying the time of heating of several samples of steel taken from the same bar (Bureau of Standards sample No. 23, Bessemer, 0.8 per cent carbon) from one to four hours at 1000°, we found a one-hour period sufficed for complete removal of all oxygen determinable by the Ledebur method. This was checked on several samples. After the one-hour heating period the sample was heated without removal from the furnace for an additional hour in a great many cases and showed a negligible amount of oxygen, i. e., less than 0.001 per cent on 30 g from the second hour's heating.

TABLE 2.—Oxygen Results when Amount of Sample and Time of Heating are Varied

Sample	Time of heating	Weight	Oxygen
	Hours	g	Per cent
Source unknown.....	1	15	0.041
	1	20	.041
B. O. H., 0.6 per cent carbon.....	1	30	.013
		25	.012
B. O. H., 0.2 per cent carbon.....	1	30	.015
		15	.016
		15	.015
Ingot iron.....	1	15	.036
		20	.035
		30	.035
Chrome vanadium steel.....	1	30	.009
		25	.009
Bessemer, 0.8 per cent carbon.....	1½	30	.011
	1	30	.011
	4	30	.010
	4	30	.012
	4	30	.010
	1	30	.011
	1	50	.012

(d) *Weighing Phosphorus Pentoxide Tubes.*—Two methods have usually been employed by others for weighing phosphorus pentoxide tubes: (a) Filled with air by an aspirator connected with

phosphorus pentoxide drying tubes; (b) filled with hydrogen, i. e., as they are when disconnected from the combustion apparatus. Objections have been raised to the latter method because of the fear that hydrogen would be too readily lost by diffusion through stopcocks or stoppers. We have had no difficulty of this kind when using the tubes and stopcock lubricants previously described, and hence have used this method for all our work. Tubes were allowed to stand a half hour near the balance before final weighing. For comparison the initial weight just after disconnecting from the combustion tube was also recorded. The weight the following morning and the weight after a half hour differed usually by not more than 0.3 mg, a change which may be largely attributed to external atmospheric causes, since tubes filled with air will show under the same circumstances almost the same variation. This slight change in weight after 12 hours' standing shows how effectively the hydrogen is held within the tube. Table 3 shows further experimental data on this point. As previously stated, counterpoises of the same approximate weight and size as the tubes themselves were used in weighing.

TABLE 3.—Successive Weights of Absorption Tubes Filled with Hydrogen

Time	Weight of tube 3 <sup>a</sup>	Weight of tube 2 <sup>a</sup>
	g	g
Gas passed 2 hours.....	2.0224	0.2711
Stood ½ hour.....	2.0221	.2706
Stood 48 hours.....	2.0217	.2701
Stood 72 hours.....	2.0214	.2697
Stood 96 hours.....	2.0212	.2695
Stood 120 hours.....	2.0215	.2697
Stood 144 hours.....	2.0212	.2696
Stood 168 hours.....	2.0212	.2694
Increase in weight in 168 hours.....	.0012	.0017

<sup>a</sup> These columns give the weights that were placed on the pan with the absorption tube to balance the counterpoises used.

## 2. BLANKS

Blanks were run with the empty boat inserted, the furnace and catalyzer being kept at the usual working temperatures. Before heating the test for complete removal of oxygen was made as already described.

Under these conditions a blank of from 0.0010 to 0.0015 g of water has been found by those who have made use of this method.

Our early work, including that done on testing the various grades of porcelain tubes (Table 1) showed the same blank.

It was found that if the preheater was kept hot for an hour with the gas flowing through the train before the furnace tube was heated, the blank dropped to 0.0006 g of water. On replacing the rubber stoppers originally used to close the open end of the combustion tube, with glass caps sealed on with Khotinsky wax, the blank again dropped, the increase in weight for an hour at red heat being from 0.0001 to 0.0002 g. Since this represented less than 0.001 per cent oxygen on a 30 g sample, it was considered satisfactory.

The average frequency of our blank determinations was about 1 per 6 or 7 determinations unless there was reason to suspect the presence of defects in tubes, boats, or other parts of the apparatus. As soon as a blank greater than 0.0003 g was obtained in the later work and was found to be irremediable, the tube giving it was replaced by a new one.

Some of the blanks obtained by the original method and by the method as finally used are shown in Table 4.

TABLE 4.—Blanks on Furnace Tube with Empty Boat Present. Period of Blank 1 Hour <sup>a</sup>

1. Original method	2. Preheater hot for 1 hour	3. Preheater hot for 1 hour; glass caps
0.0012	0.0004	No blank
.0011	.0005	No blank
.0010	.0006	0.0001
.0008	.0007	.0002
.0010	.0005	.0001
.0008	.0006	.0001
.0010	.0006	

<sup>a</sup> The values are expressed in grams of water obtained.

(a) *Rate of Passage of Hydrogen.*—Work done at the Bureau on the equilibria between hydrogen, carbon, and oxide of iron referred to later in this paper (p. 28), shows that unless a rate of passage of hydrogen not less than 60 cc per minute is maintained part of the oxide is reduced by the carbon with formation of CO or CO<sub>2</sub>, and consequently an equivalent amount of oxygen is lost in the Ledebur method, which, of course, measures only the oxygen liberated as H<sub>2</sub>O. With very slow rates of hydrogen passage the error may be very serious.

#### IV. SOURCES OF ERROR IN PREPARATION OF SAMPLES

By far the greatest possibilities for error in Ledebur determinations lie in the preparation of the sample. Unless necessary precautions are taken in this regard, the results are liable to be worthless. (See Tables 5 and 6.) Errors may be due: (a) To improper choice of places for taking the sample, such as localized rust or oxide spots, slag streaks, and oxidized blowholes, or to improper sampling of the mass of metal itself; (b) too large chips; (c) surface oxidation during cutting of chips, because of too high tool speed, hard metal, dull tool, etc.; (d) discarding fine parts of the sample, as often recommended, because of the fear that the fine parts are most liable to be surface-oxidized during cutting; (e) moisture condensed on the sample, or contamination by other substances containing oxygen, e. g., scale.

##### 1. SAMPLING

In our opinion not enough work has been done on the question of oxygen distribution in steel to enable any rules for sampling to be formulated. The only recommendation that can be made at present is to follow the procedure used in sampling when other constituents are to be determined and to avoid the localized oxygen zones just mentioned, unless definite information regarding these is sought. Two of our samples (standard sample 8a and an ingot iron) have been analyzed for oxygen a number of times, so that the results show oxygen values over a considerable volume of the original material. These results check to 0.002 per cent. On duplicate determinations as usually made we have not found the oxygen content to vary more than the error of the determination (0.002 per cent oxygen) throughout volumes of 16 to 20 cc of the various (forged or rolled) steels mentioned in Table 9.

##### 2. SIZE OF CHIPS

We have conducted several experiments to determine the thickest chip permissible. Pickard<sup>14</sup> concluded from his work that chips should not exceed 0.2 mm in thickness. However, Pickard's samples were cut in air, and there is therefore some slight uncertainty on this account, since he gives no indication of the probable error from surface oxidation. Table 5 shows the results obtained by us with various thicknesses of chips from the same sample, all cut under oil, as described subsequently. From this we conclude

<sup>14</sup> Carnegie Scholarship Memoirs, 5, pp. 83-84.

that chips should not be thicker than 0.15 mm. Any advantage gained by using a thinner chip (such as possible shortening of time required for a determination) is likely to be offset by the longer time required in the shop to prepare a sample.

TABLE 5.—Variation in Apparent Oxygen Content with Thickness of Chips

Sample	Thickness of chip	Oxygen	Result by—
		Per cent	
Bessemer, 0.4 per cent carbon (No. 10B).....	0.015 cm.....	0.014	Authors
	Coarse from same.....	.007	Do.
	Fine from same.....	.019	Do.
A. O. H., 0.4 per cent carbon (No. 20A).....	0.015 cm.....	.023	Do.
	Coarse from same.....	.020	Do.
	Fine from same.....	.029	Do.
Unknown.....	0.015 cm.....	.034	Do.
	Coarse from same.....	.024	Do.
	Fine from same.....	.035	Do.
Ingot iron.....	0.005 cm.....	.036	Do.
Do.....	0.015 cm.....	.035	Do.
Do.....	0.030 cm.....	.033	Do.
Do.....	0.045 cm.....	.031	Do.
Do.....	0.055 cm.....	.030	Do.
Do.....	0.075 cm.....	.027	Do.
Do.....	0.100 cm.....	.017	Do.
Basic open-hearth, billet I.....	0.010 cm.....	.019	Pickard
		.020	Do.
	0.015 cm.....	.019	Do.
		.017	Do.
	0.070 cm.....	.013	Do.
		.008	Do.
	Fine material.....	.020	Do.
Basic open-hearth, billet II.....	Average.....	.014	Do.
	Finest.....	.027	Do.
	Thickest.....	.002	

### 3. SURFACE OXIDATION

We recognized from the first that the surface oxidation of samples during cutting might be very serious. This point has been mentioned many times by others, but the methods given for obviating the difficulty have seemed to us either inadequate or the descriptions of these methods lacking in necessary detail. It has just been shown by the results of Table 5 that a very thin chip is necessary. This causes the surface of the cut sample to be very large. The work done in cutting it, and consequently the heat generated during cutting, is very great compared with the surface exposed and heat generated when cutting the larger-grain samples recommended by some authors. Consequently the liability to surface oxidation was greater with us than with those who used

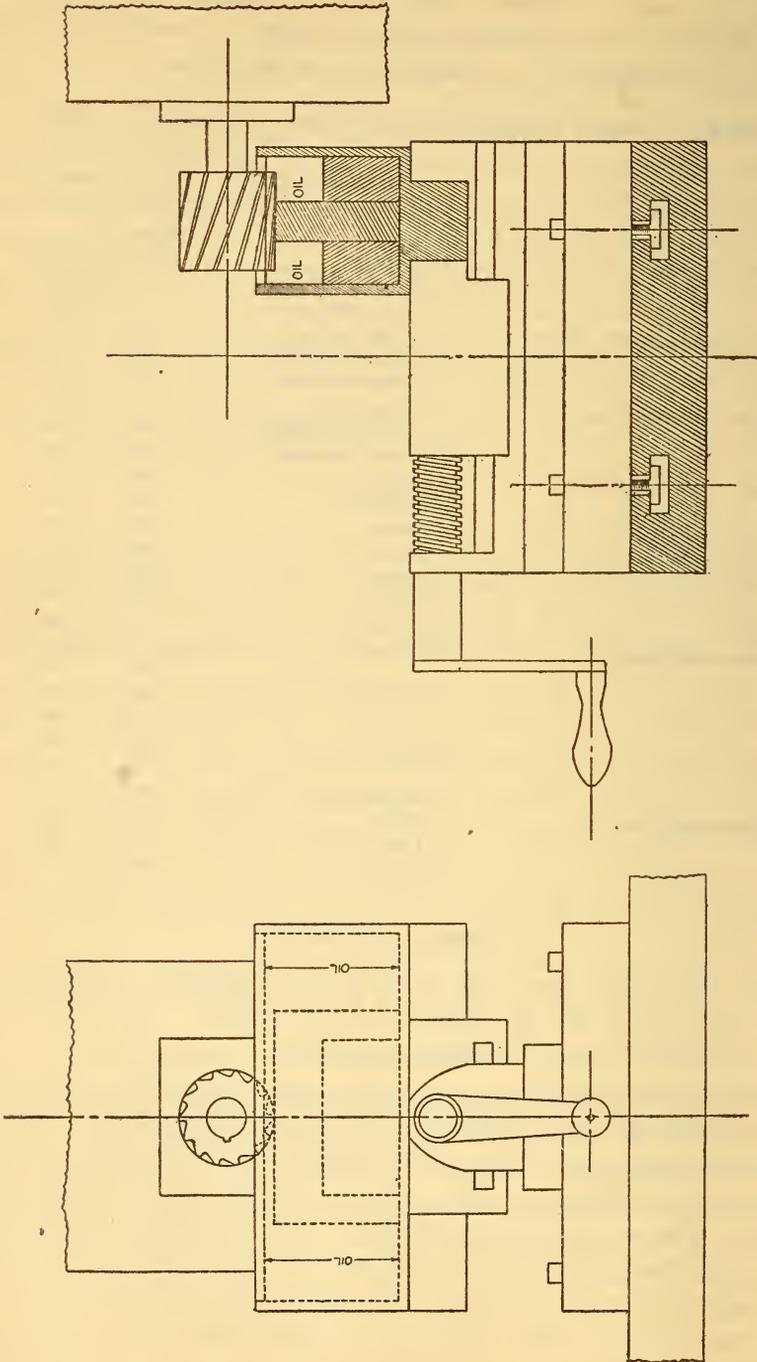


FIG. 5.—Apparatus for cutting samples under oil

larger chips. To avoid errors from this cause we tried various methods of cutting the samples under nonoxidizing, noncorroding liquids, in order to exclude air and at the same time to reduce local overheating at the point of contact of the tool with the work through the cooling effect of the large mass of liquid under which cutting was done. Mercury seemed at first to be ideal for this purpose, but practical difficulties were encountered in its use, because of its peculiar tendency to become coated, after the cutting operation has continued for a minute or so, with a scum which gradually increases in amount and from which the chips can not be freed. Even the purest mercury at our disposal showed this peculiar phenomenon. Another difficulty was the tendency of the chips to float to the surface of the mercury where they are liable to oxidation. Pure benzene was substituted as protecting liquid, but although successful, was too volatile to be convenient. Of course, the portion volatilized was lost beyond recovery and the method was therefore expensive. Pure transformer oil (H. F. grade, Westinghouse Electric & Manufacturing Co.) was next tried, and found entirely satisfactory after a suitable procedure for washing the chips free from it was developed. Fig. 5 shows the device used for cutting under oil. The chips were taken on an ordinary milling machine, a metal box being clamped between the jaws of the vise. After cutting a sufficient amount of sample from the piece of metal (which had previously been freed from surface oxide, dirt, etc.), the box is removed by opening the jaws of the vise on the milling machine, the excess of oil drained off into a suitable container, the sample poured into a bottle and kept covered with the transformer oil until ready to be washed free from oil. Very fine particles of iron tend to remain suspended in the used oil, and, because of their minute state of division, they will oxidize after the oil has stood for some time; hence it is not advisable to use the oil repeatedly unless it is filtered through a sand column or otherwise freed from this contamination.

The chips are washed free from oil by transferring them to a glass-stoppered bottle, and covering them with benzene. After shaking, the benzene is decanted off and a fresh portion added. After six washings, the benzene shows no discoloration from oil. The chips are then thrown on a Büchner funnel and washed three times with pure benzene, suction being applied, and the excess liquid removed, after each addition.

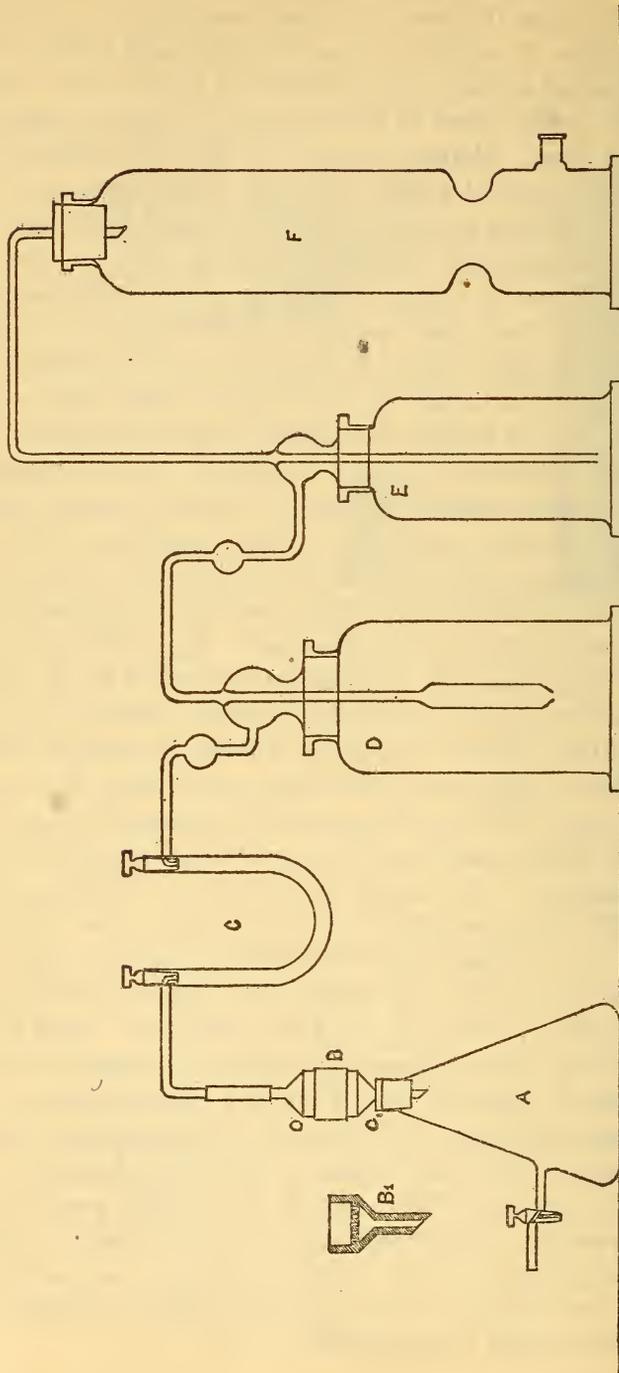


FIG. 6.—Apparatus for drying samples

## 4. DRYING AND PRESERVATION OF CHIPS

The final operation of preparing a sample for analysis is carried out in the apparatus shown in Fig. 6, and consists in fitting cover  $O$  to  $O_1$  and drying the sample by sucking dry air through it. The air passed through a plug of cotton,  $F$ , then successively through alkaline permanganate,  $E$ , concentrated sulphuric acid,  $D$ , phosphorus pentoxide,  $C$  (right limb), and a short column of reduced steel,  $C$  (left limb). Fig. 7 shows another form of apparatus which was used for drying many of our samples after they had been washed as described. The used benzene can, of course, be recovered by distillation.



FIG. 7.  
Drying  
tube

Experiments with ether and gasolene as washing agents were unsuccessful, owing to large blanks introduced into the analysis by their use. These may be due to the retention on the chips of nonvolatile organic impurities containing oxygen. It is absolutely necessary that dry air be used in aspirating, otherwise the cooling of the sample below room temperature by the rapid evaporation of the benzol causes the condensation on the sample of atmospheric moisture.

After the samples have been washed and dried as described, an operation that should not be delayed for more than a few hours after cutting, they are put in glass containers and kept in a desiccator over sulphuric acid or phosphorus pentoxide until oxygen is determined in them.

Table 6 giving comparative results on the same samples milled in air and under oil, respectively, shows the necessity of cutting under oil to insure freedom from errors arising from surface oxidation. Such errors are variable and may, as shown in the table, range from 15 per cent to 170 per cent of the oxygen present.

TABLE 6.—Comparative Values for same Samples Milled in Air and Under Oil

Sample	Under oil, in per cent oxygen <sup>a</sup>	In air, cut at low speed, in per cent oxygen <sup>a</sup>	Increase in air, per cent
B. O. H., 0.2 carbon.....	0.014	0.021	50
A. O. H., 0.2 carbon.....	.023	.034	48
Bessemer, 0.4 carbon.....	.014	.022	57
B. O. H., 0.4 carbon.....	.012	.017	42
A. O. H., 0.8 carbon.....	.010	.027	170
Ingot iron.....	.035	.042	20
Bessemer, 0.1 carbon.....	.020	.023	15

<sup>a</sup> The chips cut in the air and under oil were of the same size.

We have found a uniform blank due to preparation of sample and equivalent to 1.2 mg of oxygen per 30 g sample on all chips cut under oil as described. This is equivalent to 0.004 per cent oxygen. The size of the blank was determined by subjecting a sample of steel previously reduced in hydrogen to the same treatment employed in washing and drying the ordinary samples. An investigation of the source of this blank and of the possibility of eliminating it was also made.

There were a number of factors that might account, wholly or in part, for the observed blank. It might be due to impurities in the oil or in the benzene. An oxidation of the sample might take place inside the furnace, either through leakage of oxygen when rubber stoppers were used, or through oxygen passing the pre-heater while it is cooling and then uniting with the cooling, reduced iron in the furnace. Dry air might also form an oxide film on the surface of the reduced steel during the drying.

To investigate the source of the blank, parallel determinations on the same reduced samples were carried out, oil being used in the first, followed by benzene washing and air drying, and only the benzene washing and air drying in the second. The same blank was obtained in both cases for several different samples, which showed that the oil was not the source of the blank. (Table 7 (1).)

When glass caps were substituted for rubber stoppers at the end of the combustion tube, it was possible to reduce a sample, cool it in the furnace, and repeat the reduction the next day without danger of exposing to air. A sample so reduced gave a blank of less than 0.0003 g of water or less than 0.001 per cent on a 30 g sample. Moreover, this completely reduced sample showed the same blank on reduction after again washing it with benzene and drying it.

In view of these results it was concluded that the blank must be due either to impurities in the benzene or to oxidation by dry air. Parallel blank determinations were again carried out, (1) washing a reduced steel sample with benzene and drying as usual, and (2) passing dry air over another portion of the reduced sample for the same length of time as was required to dry a washed sample. Blanks obtained by reducing samples treated in these two ways again were of the same magnitude (Table 7 (2)). This led to the belief that the reduced steel took up oxygen from dry air to the extent of 0.004 per cent.

To test this, dry hydrogen was substituted for dry air to carry away the benzene and dry the sample. The results were very slightly lower, but still gave 0.003 per cent or 0.004 per cent, showing that the use of hydrogen did not eliminate the blank,

probably because the sample was exposed to the air in transferring from the drying apparatus to the furnace.

Finally, the completely reduced sample was exposed to air for a short time in the cold furnace. This was done by evacuating the furnace somewhat and allowing air to flow in and take the place of the hydrogen removed. The air was then removed, hydrogen admitted, and the same subsequent heating procedure followed as was used when the empty furnace gave a negligible blank. Samples so treated and kept in contact with air for only five minutes gave a blank of 0.003 per cent (Table 7).

Variation in the weight of the reduced sample used changed the weight of water obtained correspondingly, so that the oxidation of the sample was proportional to its weight, and the percentage of oxygen obtained was the same whether 10 g were used or 30 g.

Large samples were sifted, so as to remove the finest chips present. A 60-mesh copper sieve was used for this purpose. Fine and coarse material from the same sample was reduced, the fine portion giving the larger amount of oxygen. The reduced sample was removed from the furnace, crushed in a clean agate mortar (since it sinters together in the furnace), and then returned to the furnace. On repeating the reduction, the fine material again showed a larger amount of oxygen. The samples used show the oxygen content of the coarse material to be about half of that of the fine (Table 7 (5)). This verifies the assumption we made when the oxygen was found to vary with the weight of sample taken, and proves that the oxidation is a surface phenomenon.

TABLE 7.—Blanks Obtained on Washing Reduced Samples with Oil and Drying  
(1) EFFECT OF USE OF OIL

Blank (oil used), in per cent oxygen	Blank (no oil used), in per cent oxygen
0.004	0.004
.005	.005
.005	.005

(2) EFFECT OF USE OF BENZENE

Benzene washing and air drying, in per cent oxygen	Air drying for same time, in per cent oxygen
0.004	0.004
.005	.005
.004	.006
.004	.005
.005	.004
.003	
.005	

## (3) EFFECT OF DRY AIR AND OF DRY HYDROGEN

Dry air, in per cent oxygen	Dry hydrogen, in per cent oxygen
0.004	0.004
.005	.0035
.006	.003
.005	
.004	

## (4) EFFECT OF EXPOSING TO AIR IN THE COLD FURNACE

Per cent oxygen
0.0027
.0029
.0030

## (5) OXIDATION OF COARSE AND FINE REDUCED MATERIAL FROM THE SAME SAMPLE

Sample	Coarse portion, in per cent oxygen	Fine portion, in per cent oxygen
Electrolytic iron.....	0.002	0.0055
Steel.....	.003	.008
Ingot iron.....	.004	.008

The conclusion reached as a result of this work on the blank is, therefore, that steel chips as we prepare them for Ledebur oxygen determinations are oxidized slightly and almost immediately on contact with air after the benzene is removed, the amount of the oxidation for the materials we used being about 0.004 per cent oxygen. The experimental work done also shows that it is impossible to avoid this oxidation unless a method is employed which entirely prevents exposure to the air from the time that the sample is milled. Such a method seems too difficult to have any practical value. It is also evident that samples cut in contact with air, as has been the usual practice heretofore, must be subject to a very much greater oxidation than by our method, which reduces this error to the practicable minimum. Such conclusion is amply confirmed by the results in Table 6. The speed of cutting these samples in air was probably lower than has been commonly used.

## 5. DISCARDING FINE PARTS OF SAMPLES

We regard this practice, so universally recommended, as inadmissible, because of possible segregation of oxides in the fine parts of the sample in certain cases. This is balanced to an extent by

the greater air oxidation of very fine particles during preparation of the sample (see Table 8), but such error is probably less than would be caused in many cases by rejection of the fine part of the sample. All of our work on coarse and fine samples (see preceding section) supports the assumptions made above and leads to the conclusion that in general the finer chips of the milled samples are higher in oxygen than the coarser ones. See also results on Johnson pig iron, in Table 10.

## V. REDUCIBILITY OF OXIDES LIABLE TO BE IN STEEL

This subject has already been referred to in the introduction to this paper. Experimental work has been carried out by Pickard,<sup>15</sup> and Table 8 gives the results obtained by Pickard and ourselves.

TABLE 8.—Reducibility of Oxides Liable to be Present in Steel

Oxide reduced	Water calculated for complete reduction	Water found	Indicated reduction to—	Time of heating, in hours	Determination by—
Magnetite ore <sup>a</sup> .....	0.0135	0.0135	Fe	4	Authors
	.0177	.0174			
Fe <sub>2</sub> O <sub>3</sub> , pure.....	.0284	.0282	Fe	.....	Pickard
	.0245	.0241			
Manganese ore <sup>b</sup> .....	.0186	.0097	MnO	4	Authors
	.0076	.0038			
	.0610	.0298			
	.0380	.0208			
	.0512	.0278			
Manganese ore and magnetite ore..	.0169	.0086	MnO and Fe	6	Do
	.0312	.0312			
	.0114	.0055			
	.0521	.0521			
MnO <sub>2</sub> .....	.1144	.0558	MnO	.....	Pickard
	.1052	.0515			
	.0742	.0368			
Tungstic oxide, WO <sub>3</sub> .....	.0197	.0200	W	2	Authors
	.0233	.0223			
H <sub>2</sub> WO <sub>4</sub> .....	.0289	.0277			
	.0329	.0322			
Chromic oxide, Cr <sub>2</sub> O <sub>3</sub> .....	.0863	.0015		4	Do
Chromic oxide and steel.....	.0186	None	(c)		
	.0040	.0040	(c)		
	.0268	None	(c)		
	.0040	.0040	(c)		
Vanadic oxide, V <sub>2</sub> O <sub>5</sub> .....	.0120	.0042	V <sub>2</sub> O <sub>5</sub>	4	Do
	.0440	.0160			
Vanadic oxide and steel.....	.0651	.0165			
	.0040	.0040			

<sup>a</sup> Bureau of Standards standard sample No. 29, FeO—24.78 per cent and Fe<sub>2</sub>O<sub>3</sub>—52.20 per cent.

<sup>b</sup> Bureau of Standards standard sample No. 25, MnO<sub>2</sub>=87.11 per cent, Fe<sub>2</sub>O<sub>3</sub>=0.67 per cent and H<sub>2</sub>O=1.43 per cent.

<sup>c</sup> No reduction of Cr<sub>2</sub>O<sub>3</sub>; the water observed came from reduction of oxides in the steel.

<sup>15</sup> Carnegie Scholarship Memoirs, Iron and Steel Inst., 5, pp. 81-82.

Summarizing these results, it is seen that the Ledebur method determines all oxygen present in steel as  $\text{FeO}$ ,  $\text{Ni}_2\text{O}$ , and  $\text{WO}_2$ <sup>16</sup> or higher oxides of these metals, in oxides of manganese higher than  $\text{MnO}$  (if such can be imagined to be present in steel) and in oxides of titanium and vanadium above  $\text{Ti}_2\text{O}_3$  and  $\text{V}_2\text{O}_3$ , respectively, but none of the oxygen present in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{Cr}_2\text{O}_3$ .

The reducibility by hydrogen of carbon monoxide and carbon dioxide was also investigated by Pickard. He heated known amounts of pure calcium carbonate, using the same procedure as when he determined oxygen in steel. The carbonate was thus dissociated, and the carbon dioxide liberated was subjected to the reducing action of hydrogen at 900 to 1000°, the whole mass of gas being in a confined space. Pickard thus converted 60 to 100 per cent of the oxygen present in the carbon dioxide to water. The yield of water varied according to the relative quantities of hydrogen and carbon dioxide present, the time of heating, and other factors.

We have repeated Pickard's work under our own conditions for carrying out the Ledebur method, viz, heating in a current of hydrogen instead of in contact with a definite amount of that gas in a confined space. The percentages of unreduced carbon dioxide in four such experiments were, respectively, 57.0, 56.0, 56.0, and 25.0.

From Pickard's results and our own we concluded that the reducibility of carbon monoxide and dioxide would vary according to conditions, and a separate research was carried out to fix these conditions somewhat more definitely. The results of this work will be given in a paper soon to be published on *Equilibria Between Carbon, Hydrogen, and Iron Oxide*, by J. R. Cain and Leon Adler.

This paper shows that, in order to obtain the maximum yield of water when carbon, hydrogen, and oxide of iron are heated together, i. e., the conditions in the determination of oxygen in steel by the Ledebur method, it is necessary to pass the hydrogen at a rate of not less than 60 cc per minute. Under such conditions not less than 75 to 80 per cent of the oxygen present as iron oxide and oxides of manganese above  $\text{MnO}$  is obtained as water. At slow rates of passage of the hydrogen, diminishing amounts of water are obtained. At 5 cc per minute, for instance, only 22.5 per cent of the oxygen was given off as water. The balance was liberated as  $\text{CO}$  and  $\text{CO}_2$ .

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<sup>16</sup> Undoubtedly,  $\text{Cu}_2\text{O}$  should be included here also.

Reference should be made here to the attempts that have been made by others to determine the oxygen escaping as carbon monoxide along with the hydrogen that passes the phosphorus pentoxide tube during Ledebur oxygen determinations. A method sometimes used was to pass these gases over heated iodine pentoxide with the object of oxidizing the carbon monoxide and determining its amount either by measuring the equivalent carbon dioxide or iodine formed during the reaction. Such methods we find to be subject to large errors, for the iodine pentoxide not only oxidizes the carbon monoxide that may be present, but it also oxidizes certain hydrocarbon gases that are always formed by interaction of the hydrogen and the carbon in the steel. Such hydrocarbon gases are the result of secondary reactions between steel and hydrogen, and do not correspond to any gases present in the steel originally. These may, however, cause large errors in the determination of carbon monoxide by the iodine pentoxide method.

A method is being studied at this Bureau for correctly determining the carbon monoxide present as such in steels or generated by reaction of oxides and the carbon present in the steel upon heating it. This work will be described in a subsequent paper. The determination of the carbon monoxide present in steel and its differentiation from that generated by the action of carbon or carbides and heat on the other oxides present are subjects of considerable importance to metallurgists and will be discussed fully in this subsequent paper.

## VI. DETAILS OF METHOD USED FOR DETERMINING OXYGEN

Twenty to thirty grams of sample cut under oil, washed with benzol, dried, and preserved in a desiccator, all as described on pages 18 to 25, are weighed and immediately transferred to the quartz boat, which is kept in a desiccator when not in use. The boat is inserted into the cold combustion tube from end *K* (Fig. 3). The cap is replaced at *O*, the weighed phosphorus pentoxide tubes connected, and the passage of hydrogen through the combustion tube at not less than 3.6 liters per hour begun by opening cock *H* (Fig. 1). Previous to this the generator and apparatus up to cock *L* should have been freed from air as shown by the test described on page 14. As soon as absence of oxygen is thus indicated, cock *L* is opened, the catalyzer is heated to working temperature, and the hydrogen is passed for an hour. The heating of

the furnace is then begun. This heating should be pushed quite rapidly by cutting out most of the resistance in series with the furnace. The passage of hydrogen is continued at the same rate and the temperature is held at 1000° for an hour. At the end of this period the action is over. Cocks *K* and *L* on the combustion tube and the cocks on the U tube are then closed, the hydrogen current by-passed or stopped, and the U tube detached from the furnace and immediately weighed. This weight may be recorded for information, if desired, but the weight after one-half hour's standing in the balance case is the one to be used. A counterpoise is employed, as already stated. The percentage of oxygen in the sample is calculated from the observed weights after deducting the blank obtained as already directed. The furnace may be cooled for the next determination by opening the hinged portions, the current being left on all the time.

Table 9 shows how closely results by this method will check when samples of uniform size of chip are used. These are Bureau of Standards analyzed samples, in which all particles are very uniform in size, as is well known. The only purpose in inserting this table is to show how closely duplicates by the Ledebur method, as we use it, can agree, namely, within 0.002 per cent oxygen. The actual percentages given in the table are erroneous, because of surface oxidation and too coarse chips.

TABLE 9.—Oxygen Results Using Bureau of Standards Analyzed Steel Samples.

No. 1, Bessemer 0.8, per cent oxygen found	No. 2, Bessemer 0.4 (10B), per cent oxygen found	No. 3, Bessemer 0.1 (8A), per cent oxygen found
0.012	0.025	0.031
.011	.026	.030
.011	.025	.030
.011	.....	.031
.010	.....	.029
.012	.....	.....
.010	.....	.....
.012	.....	.....
Av. 0.011	.025	.030
<sup>a</sup> 0.001	<sup>a</sup> 0.001	<sup>a</sup> 0.001

<sup>a</sup> Greatest variation from average.

Nos. 1, 2, and 3, in Table 9, correspond to Nos. 23, 10b, and 8a of Table 10, respectively. Samples in Table 10 were prepared from the original bars used in making the corresponding Bureau of Standards analyzed samples. The procedure in making chips from

these bars was that described on pages 20 to 24. The averages in Table 10 represent the true Ledebur oxygen content of these samples within the probable experimental error of the method, which, as stated, is 0.002 per cent oxygen.

TABLE 10.—Authors' Determination of Ledebur Oxygen Content of Steels and Pig Iron

[The open-hearth Bessemer and special steel samples are milled from the bars used for making Bureau of Standards standardized samples.]

Kind of steel	Bureau of Standards No. —	Carbon	Oxygen
		Per cent	Per cent
A. Acid open-hearth.....	34	0.84	0.010
	21A	.62	.012
	20A	.39	.021
	19A	.20	.023
	18	.10	.015
B. Basic open-hearth.....	14A	.81	.006
	13A	.58	.016
	12A	.36	.012
	11A	.22	.014
	15A	.11	.018
C. Acid Bessemer.....	23	.80	.014
	22	.59	.020
	10b	.38	.014
	9a	.25	.014
	8a	.08	.021
D. Special steels.....	a 31	.....	.011
	b 32	.....	.005
	c 33	.....	.011
	d 30	.....	.010
E. Successive ingots of a duplex process steel, i. e., Bessemer open-hearth			0.016
			.014
			.014
			.014
F. Crucible steel.....			.009
G. Electric furnace steels—1.....			.010
	2.....		.007
	3.....		.006
H. Johnson pig iron: <sup>e</sup>			
Coarse portion.....			.014
			.013
			.014
Fine portion.....			.110
			.116
			.122

<sup>a</sup> Chrome tungsten.

<sup>b</sup> Chrome nickel.

<sup>c</sup> Nickel.

<sup>d</sup> Chrome vanadium.

<sup>e</sup> Upon washing with benzene after milling under oil, as described on page 21, there was a separation of the milled sample into two layers. These layers were separated by decantation; the upper carried the fine portions of the samples (about 10 per cent by weight). The material in suspension in each case was separated by filtration and dried as described. The oxygen is evidently much segregated in the fine portions of these irons.

## GENERAL CONCLUSIONS

From our investigations it is evident that the Ledebur method for determining oxygen in steel and iron is subject to many errors not hitherto fully recognized, and that it is very difficult to avoid such errors and to obtain correct determinations by this method. In fact, the precautions required are so great that the method can hardly be regarded as practicable for use as a control method in steel works even if it yielded information of value for control, which is doubtful, as will be shown.

Even when correct Ledebur determinations are made, the only information thus obtained is the content of oxides, existing as such, of iron, manganese (above  $MnO$ ), and of copper, nickel, and tungsten, if steel ever contains unreduced oxides of the latter three metals, which seems unlikely. The Ledebur method as ordinarily practiced gives little or no information about the oxides of carbon present in steel, and there are good reasons for believing that the oxygen so combined is of great importance.

An inspection of the results in Table 10 shows that there are no characteristic features in respect to Ledebur oxygen content among all the classes of material we have examined. The results to be communicated in a later paper giving Ledebur oxygen determinations on steels deoxidized with ferrosilicon, ferrotitanium, aluminum, ferromanganese, and with a combination of ferrosilicon and ferromanganese, show no connection between Ledebur oxygen determinations and methods of deoxidation. Our own work and Pickard's show that the Ledebur method does not determine any oxygen left as manganous oxide, and it could not therefore determine any residual manganous silicate left in the steel as a result of deoxidation with manganese. The work of Kassel<sup>17</sup> shows that only the ferric iron of iron silicate slags is reduced under the conditions of the Ledebur method. Silicate slags containing ferric oxide are not at all likely to be present in deoxidized steels, the iron in these silicates being present in the ferrous form only. Hence the Ledebur method fails even to determine the oxide of iron present as impurity in steel if there is enough silica present in the bath to combine with it, as is nearly always the case.

From this discussion it appears then that: (a) The Ledebur method requires extraordinary precautions to obtain reliable

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<sup>17</sup> Beiträge zur Kenntniss der Reduktion von Eisenschlacken durch Kohlenoxyd und Wasserstoff, Dissertation, Berlin; 1906.

results. The errors we have described undoubtedly affect in greater or less degree nearly all results by this method that have been described in the literature, and if these are approximately correct, it is because of compensating errors; (b) the Ledebur method as described herein determines with certainty only oxide of iron, oxides of manganese above  $MnO$ , and the oxides of nickel, copper and tungsten, if the latter three ever exist in steel. In turn, such oxides are determined correctly only in case they exist in the metal uncombined as silicates, which probably seldom happens; (c) Ledebur oxygen determinations show no distinguishing features for acid Bessemer, basic or acid open-hearth, duplex, electric furnace, or crucible steels; (d) Ledebur oxygen determinations show no differences in steels deoxidized with a variety of deoxidizers.

In view of these facts we believe that the method is of little practical value, and that it must be superseded by others which are more positive and more specific in the information they yield.

## VII. SUMMARY

1. The forms in which oxygen may occur in steel and the extent to which the Ledebur method determines these are discussed.

2. Sources of error in manipulation and use of the Ledebur apparatus are described with suggestions for minimizing or eliminating such errors.

3. The suitability of various kinds of combustion tubes, special hydrogen generators, boats, and weighing tubes is considered.

4. A new type of electric furnace suitable for Ledebur determinations is shown.

5. Errors from faulty sampling of metal, too large chips, discarding fine portions of sample, and cutting in air are described and a method is given for cutting chips under oil so as to prevent large errors from surface oxidation.

6. A method of carrying out the Ledebur procedure is described with a view to eliminating most of the errors described.

7. Results by this method are given for Bessemer, open-hearth, duplex (Bessemer basic open-hearth), electric furnace, and crucible steels and for special pig iron—all of American manufacture.

8. The specific application of the Ledebur method and its limited practical use are discussed.

WASHINGTON, August 23, 1918.

