

gunners who laid the test shells were clad in white duck working suits, yet the intrinsic luminosity of the phosphide flame was so slight that no useful result was obtained. Quite recently, however, according to reports, this result has been successfully accomplished and we find in calcium carbide, mixed with calcium phosphide, a material which, when thrown to a distance, will, when alighting in water, produce a self-igniting flame which has a high intrinsic illuminating power.

But the economic use to which this material has been longest put and even to-day, probably, the chief use to which it is put, is as an attachment to life-saving emergency buoys which are carried aboard passenger vessels in locations from which they may be readily thrown at the call of "Man Overboard," for though the flame given by the phosphide is dim yet it is often sufficient to enable the person struggling in the water to locate the buoy. This application is described in great detail in *De l'application de phosphure de calcium a l'appareil éclairant des bouées de sauvetage*,<sup>1</sup> and it therefore will not be enlarged upon here.

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### THE TEMPERATURE OF THE LEAD BUTTON IN CUPELLATION.

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Excellent work with the assay furnace was done by early investigators. They had no means of ascertaining exact temperatures, and hence in their writings they attempt to describe the desired temperatures by the appearance of the objects to the eye, using such color terms as would most nearly apply to the degree of heat under consideration. They recognized the importance of employing proper muffle temperatures in cupellation, as is indicated by the following careful description of the same given by an early text-book on assaying:<sup>2</sup> "When the interior of the muffle is reddish white the matters to be cupelled may be introduced. When the cupels are filled, the furnace is closed, either by the door or by pieces of lighted fuel, so that the fused metals may become of the same temperature as the muffle. When this point has been gained, air is allowed to pass into the furnace; the metallic bath is then in the state

termed 'uncovered;' that is, it presents a convex surface, very smooth, and without slag. When the air comes in contact with it, it becomes very lustrous, and is covered with luminous and iridescent patches, which move on the surface, and are thrown toward the sides. These spots are occasioned by the fused oxide of lead which is continually forming, and which, covering the bath with a very thin coating of variable thickness, presents the phenomenon of colored rings.

"As silver is sensibly volatile, it is essential, in order that the smallest possible quantity be lost, to make the cupellation at as low a temperature as may be. On the other hand, the heat ought to be sufficiently great, so that the litharge may be well fused and absorbed by the cupel.

"Experience has proved that the heat is too great when the cupels are whitish, and the metallic matter they contain can scarcely be seen, and when the fume is scarcely visible and rises rapidly to the arch of the muffle. On the contrary, the heat is not strong enough when the smoke is thick and heavy, falling in the muffle, and when the litharge can be seen not liquid enough to be absorbed, forming lumps and scales about the assay. When the degree of heat is suitable the cupel is red, and the fused metal very luminous and clear."

Modern texts are less elaborate in their descriptions, yet they lay especial stress on the importance of maintaining proper temperatures in the assay muffle.

The modern pyrometer, for accurately measuring high temperatures, has recently come to fill a long-felt want in many metallurgical operations. Since the need of employing definite temperatures in assaying is generally recognized, one would expect that the pyrometer would be employed more commonly in the muffle, and greater accuracy observed in stating degrees of temperature. It is gratifying to see some recent magazine articles and texts on assaying employing exact figures for representing temperatures required for the various operations in the furnace.

It is difficult to reconcile some explanations of cupellation phenomena, based on pyrometer readings, with certain well established facts. The lack of sufficient exact data may account for some apparent discrepancies, as the following instance will show. One very recent manual of assaying<sup>1</sup> in describing the process of cupellation says: "Little flakes of PbO form on the surface of the

<sup>1</sup> *Mémoires Militaires et Scientifiques*, 1878, XXXII.

<sup>2</sup> John Mitchell: "Manual of Practical Assaying," 2nd edition, p. 368-370 (1868).

<sup>1</sup> C. H. Fulton: "Manual of Fire Assaying," 1907, pages 70, 71.

molten lead and slide down the convex surface of the button, and are absorbed by the porous mass of the cupel. If the temperature of the cupellation is between 700 and 750° C. as it should be, this litharge is solid, as litharge melts at 906° C." The same author says further that the actual temperature of cupellation has never been determined, and that a determination of the temperature of the cupelling lead will, in his opinion, very much modify the present theory.

If it is necessary as stated by Mitchell to have the driving lead button constantly hot enough to keep the litharge in a molten condition, in order that the oxide shall be absorbed by the cupel, then the temperature of 700 to 750° C. as used by Fulton cannot be high enough, if applied to the button, because litharge freezes at 906° C.

the minimum temperature of a cupelling button, that the series of experiments herein reported were undertaken. The instrument used in the experiments was the Le Chatelier thermo-electric pyrometer, illustrated in Fig. 1. It consists of a platinum wire and a 90% platinum 10% rhodium wire twisted or soldered together, forming a thermo-electric couple, the loose ends of the wires being attached by means of copper leads to a galvanometer of high resistance. The cool ends of the wires were kept at a known temperature by being immersed in water along with a thermometer. The twisted junction of the wires was readily placed in any position in the muffle. In order to calibrate the instrument the deflections and cold junction temperatures were taken with the twisted junction at certain known temperatures. A curve was

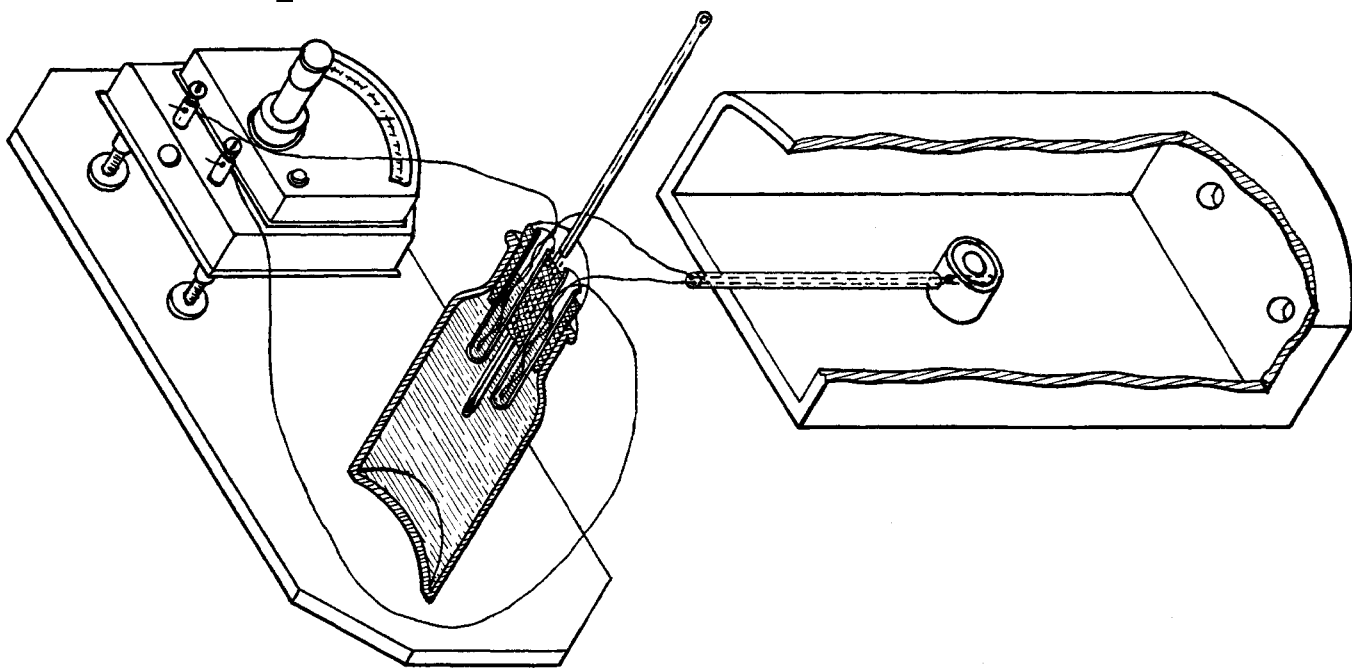


Fig. 1.

Since it is necessary to have a draught of air through the muffle in order that oxygen may be supplied to the cupelling button and since the air is cool as it enters the muffle, the temperature of the air above the button is considerably lower than that of the muffle itself or of the cupel interior, and very much lower than that of the cupelling metal. In previous magazine articles and textbook descriptions the recorded temperatures are apparently those of the surrounding atmosphere rather than the lead button, and very little information is on record concerning the temperature of the driving button.

It was with the object in view of determining

then plotted, showing the relationship between deflection and temperature. From such a curve any deflection of the galvanometer was interpreted in degrees Centigrade.

When the bare pyrometer wires were brought in direct contact with the driving lead they were immediately alloyed and fused. To prevent this destruction of the wires when employed with molten lead the couple was protected at the hot junction by a thin coating (see Fig. 2) of fire-clay. This coating was made on the spot from moistened raw material. It was made thin so that it would offer but little interference with the surface oxidation of the lead button. The temperature of the heat-

ing button was determined by placing the protected couple well within the molten lead, then reading the galvanometer and the cold junction thermometer, and interpolating on the calibration curve to find the degrees Centigrade.

The minimum temperature of the lead button itself requisite for starting cupellation was investigated by introducing buttons into cupels placed at varying distances from the front of the muffle and hence at varying temperatures. Pyrometer readings of the heating metal and the cupel interior were carefully taken in each instance.

Before driving commenced it was found that the temperature of the molten metal rose to  $900^{\circ}\text{C}$ . or above—approximately to that of melting litharge. If the heat conducted from the cupel or radiated from the muffle was not sufficient to raise the temperature to that of melting litharge the button froze and would not “uncover.”

In order to confirm the temperature readings of the cupelling metal the degree of heat of the interior of the cupel was determined by boring a small hole into the dry cupel with a one-eighth inch drill bit, and inserting the junction of the pyrometer wires well within the cupel. Holes were drilled to points beyond the centers of the cupels, and were made at different levels in the different cupels, from directly underneath the bottom of the cup-shaped depression, to the bottom of the cupel directly above the supporting muffle. The method of getting the temperature of the cupel interior is illustrated in Fig. 2.

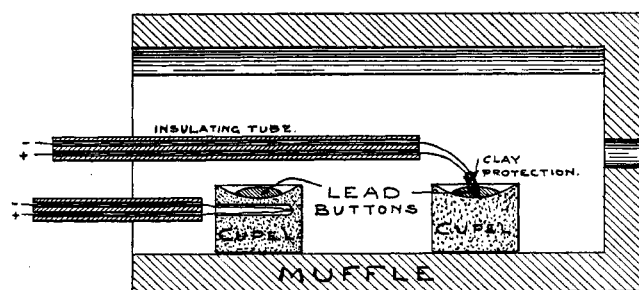


Fig. 2.

The temperature of the interior of the cupel was readily ascertained by the method previously described. In every case in which the cupel had been properly pre-heated beforehand, as is done in ordinary practice, the temperature directly under the button, although lowering as the lead melted, rose to  $900^{\circ}\text{C}$ . or above before cupellation commenced. Below this point and nearer the muffle the temperature was usually a few degrees

higher when the button opened. The melting metal had taken its heat from the upper layers, cooling these more than those near the bottom.

The temperature within the cupel and near the molten lead remained at  $906^{\circ}\text{C}$ . or above so long as the button continued to drive. If the button froze the temperature of the interior rapidly lowered, showing that its heat had been, in great part, derived from the heat of combustion of the driving lead. Upon freezing, the temperature of the button rapidly declined because its heat of combustion had been cut off.

If the interior of the cupel was well below  $906^{\circ}\text{C}$ . when the button was introduced and the cupel and contents then pushed back into the muffle, the button began to drive when the heat radiated from the arched roof of the muffle gave the litharge coating of the lead a temperature of  $906^{\circ}\text{C}$ . The bare couple could be safely placed in contact with the litharge in the above instance. The button rapidly heated to a much higher temperature if left in this position as cupellation proceeded. An intensity of heat resulting from the above conditions is not safe to use, owing to the excessive losses in silver and gold. Good practice would require that the cupel and contents be drawn forward to a cooler part of the muffle.

The temperature favorable for the formation and retention of “feathers” of litharge was determined by placing the bare couple among the crystals as they formed around the button. The temperature of the forming crystals in every instance was below  $906^{\circ}\text{C}$ . as measured near the driving lead. So long as the button continued to drive, the cooler the surrounding air and cupel surface, the more favorable was the temperature for the formation of the litharge crystals. After the cupellation was finished these crystals could be heated to  $850$  to  $890^{\circ}\text{C}$ . for many minutes without showing any tendency to fuse as indicated by their sharp edges, and without volatilizing to any considerable extent. If their temperature was raised to the melting point of litharge they immediately fused and were absorbed by the bone ash cupel.

The results of these experiments seem to establish the following facts:

When once the lead commences to oxidize rapidly and the molten litharge escapes into the cupel, the temperature of the button immediately rises owing to the heat of combustion of the oxidizing lead, and the heat from this source is sufficient

to keep the button driving, *i. e.*, to keep the litharge molten and thus in a condition to run down the sides of the button and in most part to be absorbed by the cupel—even though the cupel and contents are drawn forward to a cooler position. With a gentle draught through the muffle the temperature one-quarter inch above and near the front of the cupel may be maintained as stated by one text,<sup>1</sup> as low as 625–650° C. and cupellation continued, although the danger of freezing is very much lessened if the temperature is kept between 650° and 750°. So long as the heat of combustion of the driving button is able to maintain the temperature of the lead at that of melting litharge the cupellation proceeds. If the cupel is brought so near the mouth of the muffle that the transference of heat from the button is sufficiently rapid to overcome the heating effect of the combustion of the lead, the button cools; and when its temperature goes below the freezing point of molten litharge, it freezes, *i. e.*, solid litharge covers the molten lead and cupellation ceases.

If the surrounding air is kept well below the temperature of melting litharge, the surface of the cupel around the driving button becomes cooled below that temperature, and the molten lead oxide as it runs off the convex surface of the lead, solidifies, and crystals of litharge, or "feathers" form. These thin crystals volatilize slowly after forming, but do not disappear as a rule unless the temperature of the cupel surface is raised above 906° C. when they melt and are partly absorbed by the bone ash of the cupel.

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### A NICKEL CRUCIBLE FOR THE DETERMINATION OF CARBON IN STEEL.

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The high price of platinum crucibles for carbon determinations led the writer to seek some substitute to supplement the work of the Shimer crucible in regular use in his laboratory. Nickel naturally suggested itself for this purpose on account of its inexpensiveness, its high melting point and its resistance to oxidation. Crucibles of this material have been used for the past year for the determination of carbon in steel and the results, obtained both by direct combustion of

the steel and by solution in potassium copper chloride, have been so satisfactory that it seemed advisable to publish them together with a description of the apparatus.

At the beginning, a word should be said in regard to the conditions under which such crucibles can be used to advantage. A conservative estimate of the life of these crucibles is about thirty to fifty determinations when the solution method is used. On account of the low cost of these crucibles they can be used to advantage in those analytical laboratories where the number of carbon determinations performed is limited and the high initial cost of platinum precludes its use, especially in college laboratories where a single crucible may serve the needs of an entire class. They may also find a place as supplementary crucibles in steel laboratories where carbon determinations are a matter of daily routine. Since such crucibles are used up in time, it is necessary to make them as simple as possible and to provide for a separate water jacket not directly attached to the crucible.

The principle of a water-cooled stopper for platinum crucibles to be used in the determination of carbon in steel was first published by P. W. Shimer<sup>1</sup> and several forms are at present on the market. Although the present paper is intended solely to show that satisfactory results can be obtained with a nickel crucible, nevertheless the writer feels justified in giving a somewhat detailed description of the cooling apparatus as the design is particularly adapted to the simple form of nickel crucible employed.

The apparatus is shown in Fig. 1 and 2. Fig. 1 is a top view and Fig. 2 is a vertical section through the dotted line *x y*. It consists of three parts; the nickel crucible *A*, the cover *C* and the water jacket *B*. The nickel crucible is 1 7/8 inches deep, 1 9/16 inches in diameter at the mouth and is provided with a flange about 9/16 inch wide. These crucibles are now supplied to us in one piece, although we have used ordinary nickel crucibles to which a brass rim was soldered with silver solder. The area of the bottom was made comparatively large so that all the carbon might be in contact with the bottom of the crucible, even though the asbestos pad was made slightly large as sometimes happens. When this occurs with the platinum crucible, in which the

<sup>1</sup> Richard W. Lodge: "Notes on Assaying" (1905), page 60.

<sup>1</sup> "Carbon Combustion in a Platinum Crucible," *J. Am. Chem. Soc.*, 21, 7 (1899).