

In the two cases where data are available, the equation gives results which are probably as accurate as the data themselves.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]  
**OBSERVATIONS ON THE RARE EARTHS. XIV. THE PREPARATION AND PROPERTIES OF METALLIC LANTHANUM**

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One phase of the various researches on the rare earths carried on in this Laboratory is represented in a systematic study of the metallurgy and properties of the rare-earth metals. Very little is known of most of these metals and many of them, particularly those of the yttrium group, have never yet been isolated.

Lanthanum has been prepared in some quantity and studied by Muthmann and Weiss.<sup>2</sup> Most of the present accepted properties of the metal are those given by these workers. We have prepared lanthanum metal by the electrolysis of the chloride and have redetermined several of its properties. Some 3 kg. of pure lanthanum trioxide which showed no absorption bands of the other earths was obtained by a fractionation of the double magnesium nitrates and double ammonium nitrates and served as our starting material. A filtered solution of the chloride derived from this material was evaporated slowly in porcelain by direct flame until the thick sirupy liquid solidified to a crystalline mass when poured upon a cold surface. By exercising care in the extent of the evaporation no basic salt was formed. This solidified mass was then ground up and dried for several days at 85°. It was found that at this temperature basic salt was not formed and most of the water of crystallization was removed. Final dehydration was then easily and quickly carried out in an atmosphere of dry hydrogen chloride. The temperature was first kept at approximately 125° for 2 or 3 hours and then brought up to 300° for final dehydration.

### The Electrolysis

**The Cell.**—It was necessary to have the cell sufficiently small to conserve material and at the same time large enough to afford good current efficiency. After repeated trials the cell finally selected was that of a slightly tapering shape 8 cm. deep and of an average diameter of 5 cm. A cylindrical graphite anode 2.5 cm. in diameter was found to give best results with this type of cell. The cell, of course, was the cathode and

<sup>1</sup> Part of this paper was presented by R. G. Stevens to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Master of Science.

<sup>2</sup> Muthmann and Weiss, *Ann.*, **331**, 1 (1904).

was surrounded by an external, electrical heating element. All runs made in electrolytic cells of smaller dimensions than that given above resulted either in complete failures or very low current efficiency. The use of graphite cells also resulted in the formation of quantities of lanthanum carbide whether metal was obtained or not.

For best results a current of 40–50 amperes at a pressure of 7–8 volts was used. The bath was in all cases composed of anhydrous lanthanum trichloride with various amounts of sodium chloride and potassium fluoride added from time to time in order to maintain proper fluidity. In the earlier successful runs cells other than graphite were used with the hope of largely eliminating the formation of carbide.

TABLE I  
ELECTROLYSES

Run	Nature of Cell	Cathode	Electrolyte			Current Efficiency %	La obtained G.
			NaCl <sub>3</sub> G.	NaCl G.	KF G.		
1	wrought iron	cell	...	..	..	..	9.1
2	special iron	tungsten	150	35	30	6	12.2
3	graphite	cell	335	40	50	10	21.4
4	graphite	cell	365	20	30	27	68.4
5	graphite	cell	...	very little		18	46.5

The dimensions of the cell in Run 1 were those of the graphite cell. The lanthanum contained 15% of iron. To eliminate this contamination, in Run 2 an insulated tungsten rod electrode 1 cm. in diameter was used that projected for 2 cm. through the bottom of the cell. The lanthanum obtained with this cell contained only 0.77% of iron and no tungsten. In Run 4 a current of 50 amperes at 7–8 volts was used. Run 5 indicates that for best efficiency the bath should contain from 12 to 15% of sodium and potassium salts.

The lanthanum metal obtained from the electrolysis as carried out in graphite cells, after being washed with water so as to remove all adhering salt and carbide, was remelted in a graphite crucible under a flux of pure calcium chloride. The metal thus obtained was free from all other metals and gave no odor of carbide decomposition with water. In the subsequent determination of the properties this purified lanthanum was used.

### Properties

Lanthanum metal appears tin-white when freshly filed. On exposure to even dry air the metal very quickly tarnishes and becomes covered with a steel-blue film. After some hours this film is replaced by a coating of grayish-white oxide. It was practically impossible to retain the polish of a sample long enough to allow a photograph to be made. The metal is not ductile and is only slightly malleable.

**Melting Point.**—The melting point was determined by the cooling-curve method, using a portable potentiometer, a platinum-platinum rhodium couple and a small graphite crucible. The couple was protected by a specially prepared alundum tube. The pyrometer was carefully

standardized against the melting points of pure antimony and pure silver. A flux of calcium chloride was used to prevent the oxidation of the molten lanthanum. The lanthanum was found to melt very sharply at  $826^{\circ}$ . The present accepted value is  $810.^2$

**Specific Gravity.**—A 10g. sample of lanthanum suspended by a very fine aluminum wire was weighed first in air and then in absolute alcohol of known density. All weighings were made at  $15^{\circ}$ . The specific gravity was found to be 6.1598. Undoubtedly if the metal had been fused in a high vacuum and thus freed from dissolved gases a higher specific gravity would have been found. This property is being further investigated.

**Hardness.**—The Brinnell hardness test was applied using the 500 kg. weight. The average of several readings was found to be 37.

**Heat of Combustion.**<sup>3</sup>—The heat of combustion was determined in the Parr oxygen bomb colorimeter. Considerable difficulty was experienced in obtaining a capsule which would not react with the metal when oxidation took place. A simple metallic capsule was out of the question and an alundum capsule formed with the hot lanthanum trioxide a fusible product, presumably an aluminate. Finally, the regular metal capsule was lined with a heavy layer of lanthanum trioxide upon which the lanthanum metal had no effect. By this method the heat of combustion was found to be 1645 cal. per g.

**Kindling Temperature.**—In determining the kindling temperature it was fully realized that the method used gave only approximate results, since the state of division of the metal has considerable effect upon the kindling temperature. Lanthanum filings was used. An electrically heated muffle furnace was slowly brought up to heat. At every few degrees rise a few milligrams of the filings was placed inside. As the temperature of the furnace reached  $440^{\circ}$  the metal began to catch fire within about 10 seconds. At  $450^{\circ}$  the metal caught fire almost immediately;  $445^{\circ}$  was chosen as the approximate kindling temperature.

**Pyrophoric Properties.**—The metal is not pyrophoric in the ordinary sense of the word. No sparks are given off when the metal is filed, or sawed with a hack saw. "Mischmetal" gives off a violent shower of sparks when filed or sawed. Lanthanum gives off sparks only when violently struck a glancing blow so as to cause considerable friction.

**Iron Alloys.**—Lanthanum alloyed with 15% of iron shows a marked increase in hardness but is not pyrophoric when scratched with a file.

A 30% alloy with iron shows considerable increase in hardness and is more resistant to tarnishing than the pure metal. No increase in pyrophoric properties was indicated.

This lack of pyrophoric properties of both the pure metal and the two

<sup>3</sup> The determinations of the heat of combustion were carried out by J. E. Moose of the Industrial Division of this Laboratory.

iron alloys is no doubt closely connected with the high kindling temperature of the pure metal. The marked pyrophoric properties of cerium and its alloys is similarly, no doubt, due to the low (130°) kindling temperature of that metal.

### Summary

1. Metallic lanthanum was prepared by the electrolysis of the fused chloride with various amounts of potassium fluoride and sodium chloride.

2. The metal prepared by the use of a tungsten cathode did not contain tungsten. Metal prepared in iron cells was always contaminated with iron.

3. The metal is easily corroded in even dry air. Some of its physical constants are as follows: m. p., 826°;  $d^{15}$  (absolute alcohol), 6.1598; Brinnell hardness (500 kg. weight), 37; heat of combustion, 1645 cal. per g.; kindling temperature, 445°. The metal is not pyrophoric. Its alloys with iron are harder than the pure metal, and are not pyrophoric.

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## VAPOR PRESSURE OF COPPER OXIDE AND OF COPPER

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In his research on the subject of negative catalysis, Titoff<sup>1</sup> showed that copper in extremely small amounts causes a very great increase in the velocity with which a solution of sodium sulfite is oxidized to sulfate in the presence of dissolved oxygen, the reaction being  $2\text{Na}_2\text{SO}_3 + \text{O}_2 = 2\text{Na}_2\text{SO}_4$ . The velocity of this reaction responds in such a sensitive manner to the presence of the merest trace of copper that when a clean strip of copper is dipped into water for about a minute, the copper which is thus dissolved produces a measurable difference in the velocity constant of the reaction. In fact, Titoff found that the addition of enough copper sulfate to the sodium sulfite system to give a  $10^{-9}$  *M* solution of copper ions made a considerable change in the velocity constant.

The present paper is the account of an attempt which we have made to apply this sensitive method of measuring concentrations of copper to the determination of the vapor pressure of copper oxide and also of copper itself, at much lower temperatures than any hitherto reported in the literature. The method is so extremely sensitive that it is easily open to error, and we cannot claim much more for our figures than that they give a qualitative idea of the vapor pressure at the respective temperatures. In view, however, of the scarcity of data in this field, the approximate results which we have obtained are of considerable interest.

<sup>1</sup> Titoff, *Z. physik. Chem.*, **45**, 641 (1903).