[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# The Rare Earth Metals and their Compounds. I. The Binary System Hexahydrated Lanthanum and Magnesium Nitrates

BY LAURENCE L. QUILL AND RICHARD F. ROBEY

Although the reality of the existence of the rare earth double nitrates is supported by a multitude of early accumulated evidence, some doubt has been cast by the more recent work of di Capua.[1] In an endeavor to clarify the question a series of investigations on binary and ternary systems containing salts of the rare earth elements has been undertaken. The first results of these investigations, consisting of the thermal analysis of the system hexahydrated lanthanum and magnesium nitrates, are herein reported.

## Experimental

The magnesium salt was prepared from Baker and Adamson "C. P. Reagent" magnesium nitrate employing the procedure of Ewing and others.[2] The lanthanum was originally purchased as a "pure" oxide from the Maywood Chemical Co. This oxide was mixed with pure magnesium oxide in the ratio 1 mole to 3.1 moles, dissolved in nitric acid, and fractionally crystallized in a series of a constant number of fractions for at least fifty times. A middle fraction of the series finally was chosen as the purest for the intended purpose. The magnesium was removed by repeated precipitation of the lanthanum oxalate in acid solution, washing, ignition, solution. Ultimately the nitrate was crystallized from the nitric acid solution, twice from water, and dried over 55% sulfuric acid in a desiccator. A 20-cm. layer of a sirupy solution of the nitrate showed no absorption spectrum of the didymium elements. The arc emission spectrum gave no indication of the presence of any of the rare earth elements other than lanthanum.

TABLE I

CRYSTALLIZATION TEMPERATURES: THE SYSTEM LANTHANUM AND MAGNESIUM NITRATE HEXAHYDRATE

| $La(NO_3)_3{:}6H_2O$ wt., % | | Temp., °C. |
|---|---|---|
| 0.0 | | 89.7 |
| 5.0 | | 88.5 |
| ... | (Eutectic I) | 88.0 |
| 10.0 | | 91.0 |
| 20.0 | | 101.7 |
| 30.0 | | 107.7 |
| 40.0 | | 111.5 |
| 50.0 | | 113.2 |
| 60.0 | | 110.8 |
| 67.2 | | 110.6 |
| 70.0 | | 107.8 |
| 78.0 | | 101.6 |
| 90.0 | | 76.5 |
| 95.0 | (Eutectic II) | 64.7 |
| 100.0 | | 66.5 |

The experimental method was that used by other investigators in similar systems.[2] Briefly it consisted of heating the mixtures in Pyrex glass tubes inserted in a well-stirred oil-bath to a temperature somewhat above their melting points. The constantly stirred mixtures were then permitted to cool, the rate of cooling being determined by means of a thermometer. The thermometer was comparatively calibrated with a Bureau of Standards certified instrument. The temperature difference between the mixtures and the bath was always kept as small as possible.

**Results.**—The data of Table I have been derived from time-differential temperature cooling curves of the various mixtures. Slight losses of water were noted, especially among the higher melting mixtures on repeated determination.

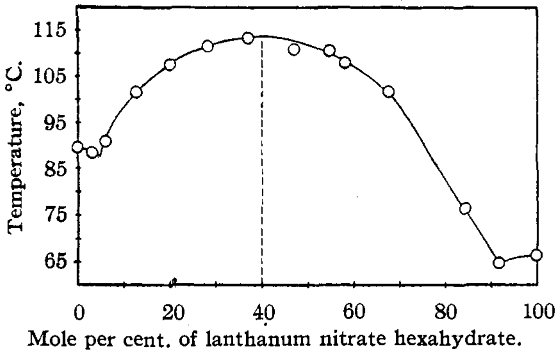

Fig. 1.—Liquidus of the system hexahydrated lanthanum and magnesium nitrates.

The observed temperature points have been plotted in Fig. 1 against the mole percentage composition. The melting point of the magnesium nitrate (89.7°) agrees well with that already recorded in the literature (89.9°);[2] the melting point of the lanthanum nitrate (66.5°) is slightly higher than that for the *beta* form (65.4°), as reported by Friend.[3] The type of the liquidus curve confirms the formation of a compound by these nitrates with the ratio $2La(NO_3)_3{:}3Mg(NO_3)_2$. A comprehensive study of the ternary system rare earth metals-magnesium nitrates-water is being conducted at the present time.

COLUMBUS, OHIO RECEIVED APRIL 12, 1937

---

(1) C. di Capua, *Gazz. chim. ital.*, **59**, 164-169 (1929).

(2) W. W. Ewing, J. D. Brandner, C. B. Slichter and W. K. Griesinger, THIS JOURNAL, **55**, 4822-4824 (1933).

(3) J. N. Friend, *J. Chem. Soc.*, **824** (1935).