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INTERACTION OF METALLIC LANTHANUM WITH THE MELT OF ITS TRICHLORIDE AND THE EQUILIBRIUM CONSTANT OF THE REACTION

$$2\mathrm{LaCl}_3(\ell) + \mathrm{La}(\ell) \rightleftarrows 3\mathrm{LaCl}_2(\ell)$$

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We undertook the present work in order to study the nature of the interaction of lanthanum with the melt of its trichloride by an electrochemical method, which makes it possible to proceed directly to the thermodynamic characterization of the reaction. Lanthanum trichloride was prepared by dissolving an oxide containing more than 99.9% La_2O_3 in chemically pure hydrochloric acid. A 1-1.5-fold amount of ammonium chloride was added to the solution, it was evaporated, and the residue of salts was carefully heated until fumes of NH_4Cl appeared; the heating was then continued under a reduced pressure of about 10^{-3} mm Hg. To remove the remains of ammonium chloride, the melt was kept for 1-2 hours under vacuum, cooled in an atmosphere of pure argon; the salt was stored before the experiments in hermetically sealed vessels. Analysis showed that the lanthanum trichloride obtained in this way contained less than 1.5% oxychloride. The metal used by us contained 98.66% La; the remainder was Ce, Nd, Pr.

Experiments to determine the solubility of metallic lanthanum in the melt of its trichloride were carried out in small molybdenum crucibles, into which 2 g of salt and about 3 g of metal were placed (molar ratio $\mathrm{La} : \mathrm{LaCl}_3 > 2$). This was done in order to ensure establishment of equilibrium between the metallic and salt phases in a relatively short time (3-6 hours). The crucibles with their contents were heated in quartz test tubes under an atmosphere of pure argon and held for a specified time at a given temperature, which was maintained automatically constant within $\pm 1^\circ$. It was measured with a chromel-alumel thermocouple pressed against the wall of the crucible. In one series of experiments the test tube was rapidly cooled by immersion in water without separating the salt from the unreacted residue of metal (it solidified at the bottom in the form of a continuous globule); in another, before cooling, the salt melt was poured off from the metal into an alundum crucible located at the bottom of the test tube, without disturbing the inert atmosphere.

Table 1

Temp., °C	Holding time, h	La content, %	Cl content, %
864	3	64.66	35.22
900	4	64.37	35.56
900	3	62.70	36.22
900		67.72	32.25
963	4	62.71	36.97
963	6	63.19	35.86
963	3	65.25	35.39
1013	4	65.29	–
1013	6	64.78	–
1063	6	63.71	35.04

For chemical analysis, the entire salt was taken, after carefully separating it from the metal globule. The results of analyses of products obtained at different temperatures and holding times are given in Table 1. As can be seen, under the conditions of our experiments the reaction between lanthanum trichloride and the metal is practically completed in 3 hours, and the composition of its product depends little on the temperature. In the investigated interval 864—1063°, within the limits of possible errors of determination, it is close to $LaCl_{2.14}$.

Analysis of the solidified metal globule showed that it contained 0.46% Cl. In contrast to the initial material, the metal globule after holding in the salt possessed a clearly expressed coarse-crystalline structure and considerable brittleness. It should be noted that we observed melting of the metal in experiments at 850°. Apparently, this is due to the fact that lanthanum chloride partially dissolves in the liquid metal, and the solidified metal globule

is a product of decomposition of this solution. Since we were interested only in the nature of the liquid salt phase, we measured the oxidation-reduction potentials of solutions of lanthanum in a melt of its trichloride at various concentrations up to saturation with lanthanum. The measurements were reduced to determining the temperature dependence of the emf of concentration cells:

$$\mathrm{La}(\ell)\,|\,\text{melt } \mathrm{LaCl_3},\ \text{saturated with La}\,\|\,\text{melt } \mathrm{LaCl_3} + x\mathrm{La}\,|\,\mathrm{Mo}$$

at different ratios of lanthanum and trichloride in the right-hand half-cell and at their equilibrium ratios in the left-hand one.

Fig. 1. Dependence of the emf on temperature for various compositions of the electrolyte obtained by adding lanthanum to $LaCl_3$ (in mole %):
1 –0.35, 2 –0.70, 3 –1.39, 4 –2.74, 5 –5.34, 6 –10.1, 7 –23.39

The cell is simple in construction. It is a hermetically sealed quartz test tube, the gas space of which was filled with pure argon. It contained two crucibles,

Figure 1 graph: emf vs. temperature for electrolyte compositions obtained by adding lanthanum to $LaCl_3$

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one inside the other. Into the inner crucible, made of beryllium oxide, 10 g of trichloride and a weighed portion of metal carefully cleaned of surface oxide films were charged in each experiment. In the outer alumina crucible were placed trichloride and metallic lanthanum, the latter being taken in considerable excess compared with the amount required to reduce the trichloride to the dichloride. The inner beryllium oxide crucible was sufficiently porous to serve as a diaphragm. The indicator electrode, accepting the oxidation-reduction potential of the $LaCl_3$—La system, was a molybdenum wire. The current lead to the lanthanum electrode was also molybdenum. The temperature was measured with a chromel—alumel thermocouple. It could be maintained constant at a specified value within $±$1°. The emf of the cell became established 4–6 h after the beginning of the experiments; after that, changes in emf rapidly followed changes in temperature. For each composition of the mixtures studied, the emf was measured at 4–5 temperatures with a high-resistance potentiometer with a null-instrument sensitivity of $1.5 \cdot 10^{-9}$ A/div.

Figure 1 graphically presents the results of emf measurements for eight mixtures of different composition. For each composition, within the possible errors of measurement, a linear dependence of emf on temperature is observed, which can be represented in the form of the following empirical equations:

$$\mathcal{E} = -0.039 + 5.8 \cdot 10^{-4} T \text{ V}; \tag{1}$$

$$\mathcal{E} = -0.041 + 5.1 \cdot 10^{-4} T \text{ V}; \tag{2}$$

$$\mathcal{E} = -0.043 + 4.6 \cdot 10^{-4} T \text{ V}; \tag{3}$$

$$\mathcal{E} = -0.042 + 3.9 \cdot 10^{-4} T \text{ V}; \tag{4}$$

$$\mathcal{E} = -0.038 + 3.3 \cdot 10^{-4} T \text{ V}; \tag{5}$$

$$\mathcal{E} = -0.043 + 2.6 \cdot 10^{-4} T \text{ V}; \tag{6}$$

$$\mathcal{E} = -0.047 + 2.0 \cdot 10^{-4} T \text{ V}; \tag{7}$$

Fig. 2. EMF isotherms.

Figure 2: Fig. 2. EMF isotherms.

$$\mathcal{E} = -0.048 + 1.2 \cdot 10^{-4} T \text{ V}. \tag{8}$$

The behavior of the galvanic cell studied is typical of molten salt electrolytes. This permits the assumption that dissolution of lanthanum in the trichloride is accompanied by reduction of the latter to subchlorides: $LaCl_2$ or LaCl. To decide which of them is actually formed, emf isotherms (Fig. 2) were constructed for 880, 930, and 980° with respect to the logarithm of the ratio of the mole-fraction concentrations of lanthanum tri- and dichloride in the melt. The experimental points fall quite satisfactorily on straight lines corresponding to empirical

equations:

$$\mathcal{E}_{880} = 0.174 + 0.229 \lg \frac{[LaCl_3]}{[LaCl_2]}; \qquad \mathcal{E}_{930} = 0.184 + 0.239 \lg \frac{[LaCl_3]}{[LaCl_2]};$$

$$\mathcal{E}_{980} = 0.193 + 0.249 \lg \frac{[LaCl_3]}{[LaCl_2]}.$$

They reach the composition axis when metallic lanthanum appears in equilibrium with the salt phase in the half-cell with the molybdenum electrode. Therefore, further addition of metal did not change the emf, which remained equal to zero. The prelogarithmic coefficients of the emf isotherms coincide in value with $2.3RT/F$ at the corresponding temperatures. This indicates that the melts studied behave as mixtures of lanthanum tri- and dichloride, close to ideal over the entire composition range from pure $LaCl_3$ to the mixture $LaCl_3 + LaCl_2$, in equilibrium with the metal, in which the dichloride predominates.

At the indifferent molybdenum electrode of our cell, the one-electron reaction proceeds

$$La^{3+}_{(melt)} + e \rightleftarrows La^{2+}_{(melt)}.$$

The emf of the cell $La_{(\ell)}$ | melt $LaCl_2 + LaCl_3$ ‖ melt $x\,LaCl_2 + LaCl_3$ | Mo is equal to

$$\mathcal{E} = \mathcal{E}^0 + 1.984 \cdot 10^{-4} T \lg \frac{[LaCl_3]}{[LaCl_2]},$$

Fig. 2. EMF isotherms.

where [$LaCl_3$] and [$LaCl_2$] are the mole-fraction concentrations of lanthanum tri- and dichloride in the half-cell with the molybdenum electrode, specified in the experiment, and

$$\mathcal{E}^0 = -1.984 \cdot 10^{-4} T \lg \frac{[\mathrm{LaCl_3}]_{\mathrm{eq}}}{[\mathrm{LaCl_2}]_{\mathrm{eq}}},$$

where $[\mathrm{LaCl_3}]_{\mathrm{eq}}$ and $[\mathrm{LaCl_2}]_{\mathrm{eq}}$ are the concentrations of the corresponding lanthanum chlorides in the molten mixture that is in equilibrium with metallic lanthanum in the other half-cell. In the experiment we find a linear dependence of the emf on temperature, which in general form can be represented as $\mathcal{E} = a + bT$. Equating these two expressions to each other, we obtain

$$\mathcal{E}^0 = a + \left(b - 1.984 \cdot 10^{-4} \lg \frac{[\mathrm{LaCl_3}]}{[\mathrm{LaCl_2}]} T \right);$$

obviously,

$$\lg \frac{[\mathrm{LaCl_3}]_{\mathrm{eq}}}{[\mathrm{LaCl_2}]_{\mathrm{eq}}} = \left(\lg \frac{[\mathrm{LaCl_3}]}{[\mathrm{LaCl_2}]} - \frac{10}{1.984} b \right) - \frac{10^4 a}{1.984 T}.$$

This equation contains the experimentally determined coefficients a and b, included in the empirical equations (1)–(8) for the emf of the cell for the corresponding concentrations [$LaCl_3$] and [$LaCl_2$]. Taking the mean value $a = -0.043$, we obtain the expression for the temperature dependence:

$$\mathcal{E} = -0.043 + 1.88 \cdot 10^{-4} T \text{ V},$$

and for the ratio of the mole-fraction concentrations of lanthanum tri- and dichloride in melts in equilibrium with the metal:

$$\lg \frac{[\mathrm{LaCl_3}]_{\mathrm{eq}}}{[\mathrm{LaCl_2}]_{\mathrm{eq}}} = -0.94933 + \frac{214.84}{T}.$$

The composition of the mixture of $LaCl_2$ and $LaCl_3$ in equilibrium with the metal at 850-1050°, calculated from this equation, corresponds to the empirical formula $LaCl_{2\cdot14}$, i.e., is in complete agreement with direct analytical determinations.

Knowing how the equilibrium concentrations of $LaCl_2$ and $LaCl_3$ vary with temperature, it is easy to find the equation for the equilibrium constant of the reaction
$2\mathrm{LaCl_3}(\ell) - \mathrm{La}(\ell) \rightleftarrows 3\mathrm{LaCl_2}(\ell)$:

Fig. 3. Melting diagram of the La + $LaCl_3$ system

Figure 3: Fig. 3. Melting diagram of the La + $LaCl_3$ system

$$\lg K = \lg \frac{[LaCl_2]^3_{eq}}{[LaCl_3]^2_{eq}} = 1.8656 - \frac{471.54}{T}.$$

It follows directly from this that the change in isobaric potential for this reaction is

$$\Delta Z = -4.575\, T \lg K :$$

$$\Delta z = 2160 - 8.53\, T \text{ cal.}$$

As can be seen, it proceeds with absorption of heat ($\Delta H = 2.16$ kcal) and an increase in entropy ($\Delta S = 8.53$ cal/deg). With increasing temperature, the equilibrium of this reaction shifts toward formation of the dichloride, while at temperatures close to the melting of the salt mixture, liquid lanthanum dichloride cannot exist in the free state; it partially disproportionates into metal and trichloride. On solidification of mixtures of lanthanum tri- and dichlorides, the equilibrium of the disproportionation reaction $3LaCl_2$ (melt)

$$\underset{\text{melting}}{\overset{\text{solidification}}{\rightleftarrows}} 2LaCl_3(s) + La(s)$$

is shifted still more completely toward decomposition of this salt. Taking into account the heats and entropies of melting of lanthanum trichloride and the metal [2], for this reaction $\Delta Z = -25300 + 28.83\, T$ cal. Within the limits of experimental error, ΔZ is close to zero at the solidification temperature of $LaCl_2$ + $LaCl_3$ melts.

Fig. 3. Melting diagram of the La + $LaCl_3$ system

To verify this assumption, we studied the melting diagram of the La–$LaCl_3$ system in the concentration range from pure trichloride to the mixture $LaCl_2$ + $LaCl_3$ in equilibrium with the metallic phase. The melting points were determined from heating curves using a differential thermocouple. Salt melts of specified compositions were prepared by melting, in molybdenum crucibles, the corresponding weighed portions of trichloride and metal under an atmosphere of pure argon. The thermocouples were protected from the action of the melt by thin molybdenum sheaths.

The results of the measurements are presented in Fig. 3. In the range 0–9 mol.% La, the liquidus decreases almost linearly from 852° (the melting temperature of pure $LaCl_3$) to 830°, and the trichloride crystallizes. When the temperature reaches 827 ± 2°, the entire melt, like a eutectic, solidifies; moreover, the dichloride does not separate as a solid independent phase, but decomposes into lanthanum and trichloride. The metal is formed as an extremely fine dispersion, uniformly distributed throughout the mass of trichloride.

Our diagram is close to that obtained by Keneshea and Cubicciotti [1] from thermal-analysis points in the range of compositions that we investigated. However, the liquidus line constructed by them on the basis of chemical analyses loses physical meaning in the light of our work.

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References

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2. O. Kubaschewski, E. Evans, *Thermochemistry in Metallurgy*, Moscow, 1954.

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