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Abstract

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DECOMPOSITION VOLTAGE AND THERMODYNAMICS OF THE REACTION OF FORMATION FROM THE ELEMENTS OF LIQUID LANTHANUM DI- AND TRICHLORIDE

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The information available in the literature on the thermodynamics of lanthanum chlorides is limited to the trichloride, and only in the solid state. As for the dichloride, at present there is not even a common opinion on the fact of its existence, let alone on the properties of this compound. In our preceding work ([1]) it was shown that when metallic lanthanum is dissolved in a melt of the trichloride, the dichloride is formed, but complete reduction does not occur. The molten mixture of salts in equilibrium with the metal contains about 86 mole % $LaCl_2$ and 14 mole % $LaCl_3$ in the interval 860–1060°. With increasing temperature, the equilibrium of the reduction reaction shifts toward the formation of the dichloride, but this shift is insignificant. Thus, liquid dichloride does not exist in the free state. It cannot exist in the solid state either, since upon solidification of molten mixtures $LaCl_3 + LaCl_2$ the equilibrium of the disproportionation reaction of the dichloride into solid trichloride and lanthanum shifts toward formation of the latter.

Nevertheless, from electrochemical studies on the system La–$LaCl_3$ it is possible to give a thermodynamic characterization of this unstable lanthanum compound, as well as of the trichloride in the liquid state. Over the entire range of compositions the mixtures $LaCl_3$–$LaCl_2$ behave as ideal. This circumstance makes it possible to find the decomposition voltages of the pure liquid lanthanum di- and trichlorides by measuring the e.m.f. of the galvanic cell:

$$\mathrm{La_{(l)}} \,|\, \text{melt } \mathrm{LaCl_2 + LaCl_3} \,\|\, \text{melt } \mathrm{NaCl - KCl} \,|\, \mathrm{Cl_2, C}$$

at various temperatures.

Indeed, the potential of the lanthanum electrode measured relative to the chlorine electrode in an equilibrium mixture of its chlorides is equal to:

$$E_{\mathrm{La}} = E^0_{\mathrm{La/La^{2+}}} + 0.992 \times 10^{-4} T \lg[\mathrm{La^{2+}}] = E^0_{\mathrm{La/La^{3+}}} + 0.661 \times 10^{-4} T \lg[\mathrm{La^{3+}}],$$

where $E^0_{\mathrm{La/La^{2+}}}$ and $E^0_{\mathrm{La/La^{3+}}}$ are numerically equal and opposite in sign to the

decomposition voltages, respectively, of pure dichloride ($[La^{2+}] = 1$ and trichloride ($[LaCl_3] = 1$), while $[La^{2+}]$ and $[La^{3+}]$ are the mole-fraction concentrations of divalent and trivalent lanthanum in the mixture of chlorides, in equilibrium with respect to the metal.

For any temperature they may be calculated from the equation:

$$\lg \frac{[LaCl_3]_{eq}}{[LaCl_2]_{eq}} = -0.94933 + \frac{214.84}{T} \quad (1)$$

since $[La^{2+}] + [La^{3+}] = 1$. Substituting their values into the equalities for the electrode potential of lanthanum and measuring the latter relative to the chlorine comparison electrode, we obtain the desired expressions for $E^0_{La/La^{2+}}$ and $E^0_{La/La^{3+}}$.

The measurements were carried out with a cell whose design is shown schematically in Fig. 1. The initial lanthanum trichloride, which was prepared in the same way as described in the preceding work ([1]), melted at $850 \pm 2°$, which testified to its purity (according to the latest data ([4]) the m.p.

$LaCl_3 = 852°$). Since the salt mixture containing lanthanum dichloride strongly interacts with quartz, the electrolyte was placed in an alumina crucible, the walls of which had previously been treated at the experimental temperature with a mixture of $LaCl_3$ + La. During the treatment the evolution of aluminum was observed. Evidently the reaction was:

$$Al_2O_{3(s)} + 6LaCl_{2(melt)} = 2Al_{(l)} + 4LaCl_{3(melt)} + La_2O_{3(s)}.$$

The lanthanum oxide formed covered the walls of the crucible rather densely and protected them from further action of the melt. If it did continue to some extent during the measurements, then the $LaCl_3$ passing into the melt could not noticeably disturb the equilibrium, since it was freely reduced by the metal (the surface and mass of the metallic lanthanum electrode were sufficiently large). In the wall of the crucible there was a small opening, closed with an asbestos diaphragm, through which electrical contact with the electrolyte was made (the NaCl + KCl melt) in an outer crucible, into which an encapsulated chlorine electrode was immersed. The crucibles were placed in a hermetically sealed quartz tube filled with carefully purified argon. The liquid lanthanum, which served as the second electrode of the cell, was in a molybdenum cup standing on the bottom of the inner crucible with the molten equilibrium mixture $LaCl_2$ + $LaCl_3$.

A chromel–alumel thermocouple was immersed in the NaCl–KCl salt melt in the outer crucible. The cell was heated in a silite furnace in a massive metal block, which made it possible to maintain the temperature at a prescribed value constant within $±$1°.

Fig. 1. Cell. 1—quartz tube, 2—chlorine electrode, 3—alumina crucible, 4—molybdenum cup with lanthanum, 5—alumina crucible, 6—thermocouple

Figure 1: Fig. 1. Cell. 1—quartz tube, 2—chlorine electrode, 3—alumina crucible, 4—molybdenum cup with lanthanum, 5—alumina crucible, 6—thermocouple

The emf of the cell (the difference in potentials between the chlorine and lanthanum electrodes) was measured with a high-resistance potentiometer with a null instrument of $1.5 \cdot 10^{-9}$ A/div. It became established 4-5 hours after the start of the experiments, when the initial lanthanum trichloride in the inner crucible had been reduced by the metal to the equilibrium mixture $LaCl_2$ + $LaCl_3$. Thereafter, measurements of the emf rapidly followed changes in temperature (usually within 15-20 min). In one experiment the measurements were carried out at 3-4 temperatures.

Fig. 1. Cell. *1*—quartz tube, *2*—chlorine electrode, *3*—alumina crucible, *4*—molybdenum cup with lanthanum, *5*—alumina crucible, *6*—thermocouple.

The measurement results are presented graphically in Fig. 2. The experimental points fall quite satisfactorily on a straight line corresponding to the empirical equation: $\mathcal{E}_{\text{meas}} = 3.484 - 8.47 \cdot 10^{-4}T$ V, found by the method of least squares. In the measured emf, along with the desired electrochemical potential difference, there enters a thermoe.m.f. opposite in sign to it between the molybdenum and carbon current leads, and correspondingly to the lanthanum and chlorine electrodes of the cell, $\mathcal{E}_t = -0.008 + 0.17 \cdot 10^{-4}T$ V (3): $\mathcal{E}_{\text{meas}} = \mathcal{E} - \mathcal{E}_t$. Excluding it, we obtain the equation for the temperature dependence of the potential of the lanthanum electrode relative to the chlorine reference electrode ($E_{\text{La}} = -\mathcal{E}$):

$$E_{\text{La}} = -3.476 + 8.30 \cdot 10^{-4}T \text{ V}.$$

Knowing the equilibrium concentrations of $LaCl_2$ and $LaCl_3$ and the potential of the lanthanum electrode, one can calculate the values of $E^{\circ}_{\text{La/La}^{2+}}$ and $E^{\circ}_{\text{La/La}^{3+}}$ at the corresponding temperatures.

The results of the calculation are given in Table 1 and plotted in Fig. 3 as a function of absolute temperature. They lie on straight lines, the equations of which give us the required temperature dependences:

$$\mathcal{E}^{\circ}_{\text{La/La}^{2+}} = -3.469 + 8.3 \cdot 10^{-4}T_{\text{v}},$$

$$\mathcal{E}^{\circ}_{\text{La/La}^{3+}} = -3.494 + 9.0 \cdot 10^{-4}T_{\text{v}}$$

relative to the chlorine reference electrode. Taken with the opposite sign,

Table 1

Fig. 2. Dependence of the emf on temperature

Figure 2: Fig. 2. Dependence of the emf on temperature

Fig. 3. Temperature dependence of the standard electrode potentials of lanthanum

Figure 3: Fig. 3. Temperature dependence of the standard electrode potentials of lanthanum

T, °K	E_{La}	$[\mathrm{La}^{2+}]_{\mathrm{eq}}$	$E^{\circ}_{\mathrm{La/La^{2+}}}$	$(\mathrm{La}^{3+})_{\mathrm{eq}}$	$E^{\circ}_{\mathrm{La/La^{3+}}}$
1150	−2.522	0.85266	−2.514	0.14734	−2.459
1170	−2.505	0.85361	−2.497	0.14539	−2.441
1190	−2.488	0.85448	−2.480	0.14552	−2.422
1210	−2.472	0.85529	−2.464	0.14471	−2.405
1230	−2.455	0.85617	−2.447	0.14383	−2.387
1250	−2.439	0.85697	−2.431	0.14303	−2.369

they give the decomposition voltages of the corresponding pure liquid chlorides:

$$\mathcal{E}_{\text{decomp. LaCl}_2(\ell)} = 3.469 - 8.3 \cdot 10^{-4} T_{\text{v}},$$

$$\mathcal{E}_{\text{decomp. LaCl}_3(\ell)} = 3.494 - 9.0 \cdot 10^{-4} T_{\text{v}}.$$

The decomposition voltage of a pure molten salt is a direct measure of the change in isobaric potential in the reaction of its formation from the elements. For the reaction

$$\mathrm{La}_{(\ell)} + \frac{3}{2}\mathrm{Cl}_{2(\mathrm{g})} = \mathrm{LaCl}_{3(\ell)}$$

$$\Delta Z = -69186\mathcal{E}_{\text{decomp. LaCl}_3(\ell)} = -241700 + 62.3T \text{ cal}.$$

Consequently, the heat effect and entropy of this reaction are:

$$\Delta H = -241.7 \text{ kcal} \quad \text{and} \quad \Delta S = -62.3 \text{ cal/deg}.$$

According to the literature data, for lanthanum trichloride the heat of formation is −255.91 kcal/mol ([2]), the standard entropy is 34.5 cal/deg mol ([3]),

Fig. 2. Dependence of the emf on temperature

Fig. 3. Temperature dependence of the standard electrode potentials of lanthanum

the heat of fusion is 9.0 kcal/mol ([5]), and the melting temperature is 852° ([5]); while for metallic lanthanum the standard entropy is 13.7 cal/g-atom · deg ([3]), the heat of fusion is 2400 cal/g-atom, and the melting temperature is 920° ([4]). On the basis of these data, and neglecting the temperature dependence of the heat effect and entropy of the reaction

$$\mathrm{La}_{(\ell)} + \frac{3}{2}\mathrm{Cl}_{2(\mathrm{g})} = \mathrm{LaCl}_{3(\ell)},$$

we obtain:

$$\Delta Z_{\mathrm{calc}} = -249300 + 53.2T \text{ cal}.$$

Comparing the calculated value with that found by us, we see that under the conditions of our experiments the heat effect of the reaction is found to be smaller by approximately

by 8 kcal, and the entropy by more than 10 cal/deg. This discrepancy, along with possible errors of measurement and the assumption adopted in the calculations that the heat effect and entropy of the reaction remain unchanged, may also be due to the fact that the thermodynamic quantities measured by us refer not to the pure metal, but to a metallic phase saturated with lanthanum chloride. If it is denoted conventionally by $\mathrm{La}^{*}_{(\ell)}$, then the interaction of metallic lanthanum with chlorine may be represented as two successive reactions

$$\mathrm{La}_{(\ell)} \xrightarrow{\mathrm{Cl}_2} \mathrm{La}^{*}_{(\ell)} \xrightarrow{\mathrm{Cl}_2} \mathrm{LaCl}_{3(\ell)}.$$

The change in the isobaric potential in the first reaction is evidently equal to $\Delta Z^{*} = \Delta Z_{\mathrm{calc}} - \Delta Z = -7600 - 9.1\,T$ cal. According to the relation obtained, with increasing temperature the solubility of the salt in the metallic phase should increase, which is consistent with observations on the solubility of molten salts in liquid metals.

For the reaction $\mathrm{La}_{(\ell)} + \mathrm{Cl}_{2(g)} = \mathrm{LaCl}_{2(\ell)}$, $\Delta Z = -46124\,\mathcal{E}_{\mathrm{decomp\ LaCl}_{2(\ell)}} = -160000 + 38.3\,T$ cal. Thus, the heat effect and entropy of this reaction are equal to:

$$\Delta H = -160.0 \text{ kcal} \quad \text{and} \quad \Delta S = -37.3 \text{ cal/deg}.$$

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CITED LITERATURE

[1] M. V. Smirnov, P. M. Usov, T. F. Khazemova, DAN, **151**, No. 3 (1963).
[2] F. H. Spedding, J. P. Flynn, J. Am. Chem. Soc., **76**, No. 6, 1474 (1954).
[3] V. Latimer, *Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, IL, 1954.
[4] *Rare-Earth Metals*, collected articles, IL, 1957.
[5] Shimazaki Eichi, Niwa Kichizo, Zs. anorg. u. allgem. Chem., **314**, No. 1-2, 21 (1962).

Note: Figure translations are in progress. See original paper for figures.