# Lanthanum–Lanthanum Trichloride Phase Diagram

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PHASE EQUILIBRIUM studies in the Ce-$CeCl_3$ system recently reported by Mellors and Senderoff (*15*) indicated that the solubility of cerium in $CeCl_3$ is 9 mole % between 774° and 950° C. and the solubility of $CeCl_3$ in cerium is not greater than 0.2 mole % at 950°. The salt-rich data are consistent with e.m.f. measurements made by the same authors (*17*). Cubicciotti (*5*) found a much higher solubility (33 mole %) of cerium in $CeCl_3$ between 775° and 850° C. Druding and Corbett (*8*) examined the Pr-$PrCl_3$, Pr-$PrI_3$, Nd-$NdCl_3$, and Nd-$NdI_3$ systems and found appreciable solubility of the metals in their salts. This solubility behavior in the rare earth–metal salt systems is analogous to the solubility behavior observed in other metal salt systems—e.g., the alkali-alkali halides (*2*), alkaline earth–alkaline earth halides (*6, 16*), bismuth-bismuth halides (*9, 13, 21, 22*), Cd-$CdCl_2$ (*1, 10*), and Ni-$NiCl_2$ (*12*). To determine the solubility relationships in the La-$LaCl_3$ system three kinds of measurements were made: thermal analysis of samples of known composition, sampling of the liquid salt phase in equilibrium with excess metal, and quenching followed by analysis of the quenched material.

## EXPERIMENTAL

**Materials.** The $LaCl_3$ was prepared from $La_2O_3$ (99.99%, from Lindsay Chemical Co.). The oxide was dissolved in aqueous HCl and the hydrated chloride was obtained by evaporation of the water. This material was then dehydrated in a stream of dry HCl, the temperature being gradually raised to 450° C. over a period of several days (*11*). The dehydrated chloride was then distilled under vacuum in a quartz bulb at about 1150° C.

Chlorine was determined gravimetrically as AgCl and lanthanum by converting the salt to nitrate and igniting to $La_2O_3$, which was weighed. Analysis of one of the $LaCl_3$ preparations, which is typical of the results obtained with all of the prepared material, gave La 56.67%, Cl 43.27%; theoretical for $LaCl_3$: La 56.63%, Cl 43.37%. By thermal analysis the melting point of the pure salt was 859° ± 2° C. Literature values are 852° C. (*3*) and 862° C. (*7*).

The lanthanum metal was obtained from Research Chemicals, Lunex Corp., and Lindsay Chemical Division. Most of the material used was from Lindsay with a purity designation of 99.9% (based on rare earth content). Analysis furnished by the supplier showed 0.05% Fe, 0.01 to 0.1% Al, 0.1% $O_2$, 0.1% Er, and traces of tantalum, zirconium, and copper. The metal was washed with acetone and mechanically cleaned of its oxide film. In the first few experiments this operation was done in air; in later runs a helium-filled dry box was used. The freezing point of lanthanum was found to be 927° ± 5° C. compared to a literature value of 920° ± 5° C. (*18*).

**Thermal Analysis.** For carrying out the thermal analysis an apparatus (Figure 1) was arranged so that to a large sample of $LaCl_3$ or lanthanum several successive additions of lanthanum or $LaCl_3$ could be made without opening the system to the atmosphere. A quartz furnace tube 2 inches in o.d. and 18 inches long was placed vertically in a furnace. The bottom end of this tube was closed and the top end was provided with a water-cooled standard-taper joint. A borosilicate glass tube was attached to the quartz tube at the joint, and the glass tube was provided with one side arm for evacuating and filling with argon, another large side arm through which samples could be introduced, and a Wilson seal at the top. A steel tube, $\frac{1}{2}$-inch o.d., passed through the Wilson seal into the furnace tube. Attached to the bottom of the steel tube was a steel basket which held the tantalum crucible containing the sample. The thermocouple well was a tantalum tube $\frac{1}{8}$-inch i.d. and 12 inches long, attached to a stainless steel tube which in turn extended out of the furnace through the $\frac{1}{2}$-inch steel tube.

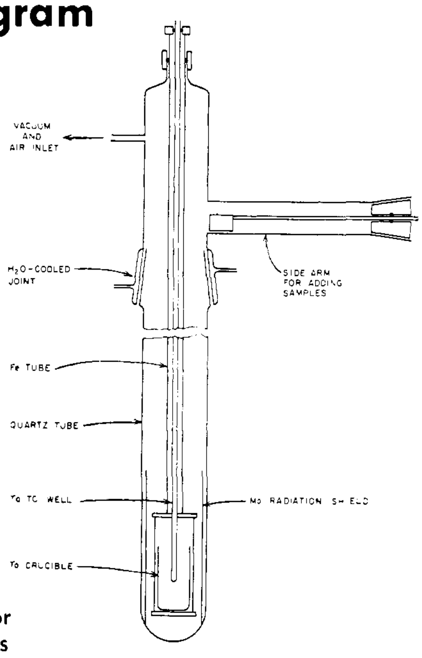


Figure 1. Apparatus for thermal analysis

The Pt-Pt:Rh thermocouple was contained in a thin porcelain protection tube closed at the bottom, which fitted snugly inside the thermocouple well. The thermocouple itself could be exposed to air at all times, while the tantalum–stainless steel well was exposed to argon.

Heating was accomplished by a 16-inch Marshall furnace with the temperature controlled by a Celectray controller. The temperature gradient over the length of the sample was 2° to 3° at 900° C. A molybdenum radiation shield surrounded the crucible.

Samples were melted in tantalum crucibles, 1 to $1\frac{1}{4}$ inches in o.d. and $2\frac{1}{2}$ inches deep. The "high purity" argon in which the samples were melted was passed through a trap cooled with dry ice–acetone.

Cooling curves were taken by feeding the thermocouple output to a Brown recorder with a 1-mv. span, with part of the output of the thermocouple balanced out by a counterpotential supplied by a portable potentiometer.

In carrying out an experiment the crucible containing pure $LaCl_3$ or lanthanum was lowered into the furnace and cooling curves were taken until reproducible results were obtained. The crucible was then raised to the upper part of the apparatus next to the large side arm which contained several weighed pieces of lanthanum or $LaCl_3$. One of these samples was added to the crucible by means of a scoop attached to a movable shaft working through an O-ring seal, the crucible was lowered into the furnace, and heating and cooling curves were again taken. This procedure was repeated with successive addition of salt or metal to the solution. Several such series were carried out starting with 40 to 100 grams of pure $LaCl_3$ or lanthanum. All heating and cooling were carried out under argon at a pressure of 5 to 10 cm. of Hg above atmospheric. Before cooling, the samples were kept at a high temperature (950° to 1000° C.) for 2 hours or longer, with occasional stirring. Cooling rates were generally 2° to 4° per minute.

**Sampling.** The apparatus used for equilibrating and sampling is shown in Figure 2. In carrying out the experiment 24 grams of lanthanum metal and 152 grams of $LaCl_3$ were added to the 2 × 2 inch tantalum crucible in a helium-filled dry box. The crucible containing the salt and metal was quickly transferred to the quartz furnace tube (Figure 2) and the system was immediately evacuated. After heating to about 500° C. under vacuum, argon was added and heating was continued to the highest temperature used. The sample was maintained at temperature for 1.5 to 2 hours to reach equilibrium. The sampling rod was lowered until the small tantalum sampling cup was positioned just above the surface of the melt and held there for 10 to 15 minutes to reach temperature equilibrium. A sample of the upper (salt-rich) phase was removed by dipping the cup into the melt; the level of the liquid metal phase was calculated to be well below the top of the sampling cup when the cup was resting on the bottom of the crucible. The sampling cup was raised to the upper part of the furnace tube and withdrawn, after cooling, into the chamber, *C*. Stopcocks *A* and *B* (25-mm. bore) were closed, and the upper assembly (stopcock *A* and chamber *C* containing the sample) was disconnected from the system and transferred to the dry box. The sampling cup was removed from the assembly, and its outside surfaces were cleaned mechanically. The cup and sample were transferred to a weighing bottle, removed from the dry box, and weighed. The sample was then dissolved in dilute $HNO_3$ and analyzed for La and Cl.

For removal of another sample a clean tantalum sampling cup was attached to the sampling rod and positioned in chamber *C*. The upper assembly (*A* and *C*) was then connected to stopcock *B*. Stopcock *A* was opened and chamber *C* evacuated and filled with argon. Stopcock *B* was opened and the sample cup inserted into the system for a sample at a lower temperature. The several samples collected in this way weighed between 2.2 and 2.9 grams.

The temperature was controlled by means of a Leeds & Northrup Speedomax H controller. Temperatures were measured with a Pt-Pt:Rh thermocouple positioned just beneath the tantalum crucible. Previous temperature checks with a similar arrangement indicated the melt temperature was probably within $\pm 2°$ of the values reported in Table I.

**Quenching.** In two experiments after thermal analysis the sample was equilibrated at a temperature high enough for two liquid phases to coexist and then was quenched by lifting the crucible out of the furnace into the cold part of the apparatus. The salt phase was dissolved in water and the metal phase was dissolved in dilute acid. Analysis of the separated phases helped to establish the limits of the miscibility gap.

## RESULTS

The results are summarized in Figure 3.

**Thermal Analysis.** Of three pure metal samples studied, one showed a thermal halt corresponding to the $\beta$-$\gamma$ transition at 869° C., while the other two showed halts at 848° and 827° C. For all solutions with these samples the high temperature arrests (914° C. and above) and the arrests in the vicinity of 826° were in good agreement. Furthermore, the addition of $LaCl_3$ lowered the $\beta$-$\gamma$ transition temperature approximately the same amount in each metal sample. The reason for the difference in temperatures for the $\beta$-$\gamma$ point is not understood. Since the halt at 869° C. is in good agreement with literature values of 868° (*18*), 866° (*19*), and 864° C. (*20*), the results from the sample showing this transition temperature were plotted and the results from the other two were omitted from the figure.

The thermal halts occurring below 826° for metal-rich samples all showed a fairly large degree of supercooling. Because of the small amount of salt phase present and the rapid removal by the solid mass of metal of any heat evolved by the salt, these temperatures are undoubtedly too low and probably all belong to the eutectic shown at 826°. These points were definitely associated with the salt phase and not with the solid metal, as was shown by positioning the thermocouple in the upper liquid phase; in this case the halts associated with the metal transitions were indistinct while the low temperature (826°) halt became more pronounced, although still showing some supercooling.

Two small apparent thermal arrests occurred at approximately 775° and 763° C. and were not always seen. The transitions involved cannot be determined from these data.

**Sampling.** The weights of La and Cl found in seven different samples, together with the material balances, are shown in Table I along with the temperature and mole per cent of La in $LaCl_3$ based on the La and Cl found. Although the error in the analytical results is only about $\pm 0.2\%$, the error in the reported solubilities, based on the over-all procedure, is estimated to be about 1%. Since the original mixture of La and $LaCl_3$ contained 22 mole % La, the fact that the amount of La in the samples was between 9 and 12% indicates that all the La did not dissolve—i.e., the system consisted of two phases. Equilibrium of the La between the two phases was tested with samples 3 and 4 (Table I). After sample 3 was taken, the melt was allowed to cool to room temperature (overnight). The system was

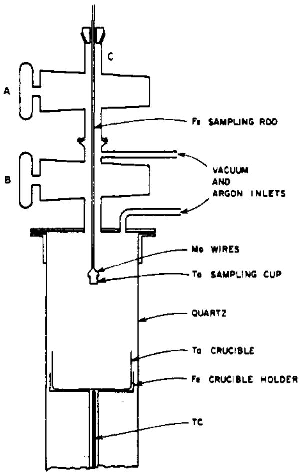
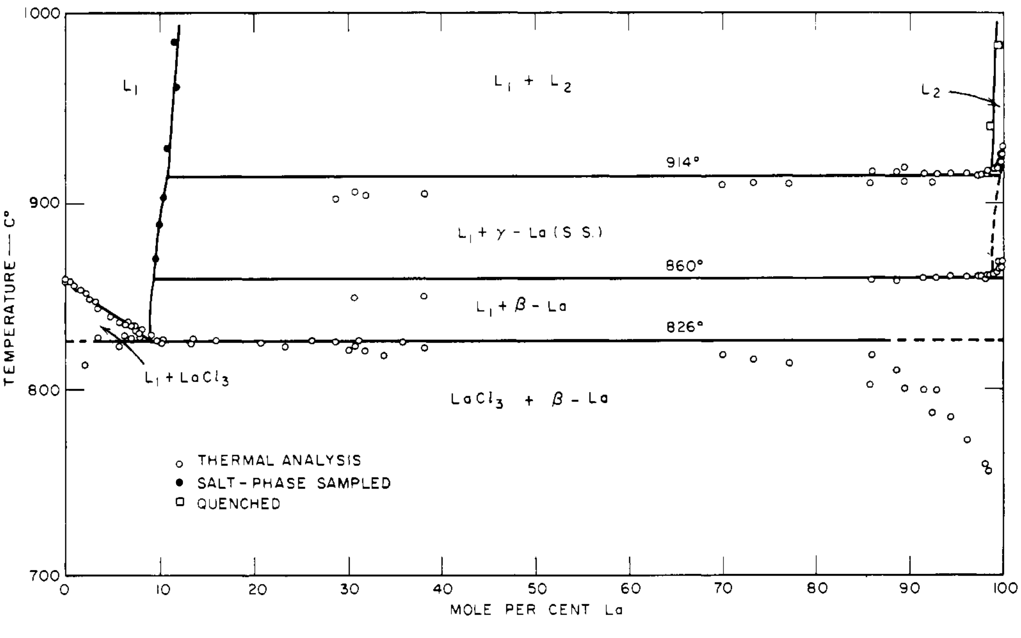


Figure 2. Apparatus for solubility measurements

Figure 3. The La-$LaCl_3$ ⟶ phase diagram



then heated to the same temperature and, after equilibrating, sample 4 was removed. The close agreement of the results for these two samples indicates that equilibrium was obtained in the first 1.5 hours of heating.

After the last sample was removed, the remainder of the salt-metal mixture was weighed and analyzed. The material balance on this material was 100.12%. The good material balances on this sample and on the solubility samples suggest that very little oxide was present and the solubilities shown in Table I are not due in any large part to a lanthanum oxide impurity.

**Quenching.** Analysis of the salt phase in the two quenching experiments indicated a La solubility somewhat higher than that found in the sampling experiments. This was probably due to dissolution of some of the metal phase during recovery of the salt. The metal phase analyses, however, should be fairly reliable (Figure 3). The material balances on the two quenched samples—i.e., total weight of La plus Cl found in both phases compared to the original total weight—were 99.97 and 100.10%.

## DISCUSSION

The eutectic halt at 826° was seen in mixtures from about 4 mole % La to better than 90 mole % La; it is concluded that no solid lower-valent lanthanum chlorides exist in this system, at least down to 775°. The thermal effects seen at 775° C. may be related to the decomposition of a lower chloride; however, there is no support for this. Brewer and others (*4*) have pointed out that divalent La and Ce chlorides are probably unstable in the solid state because of disproportionation. The lack of existence of a stable solid divalent chloride has been shown to be the case for Ce-CeCl$_3$ (*5, 15*) and apparently is also verified here for La-LaCl$_3$. Praseodymium also does not have a stable solid divalent chloride, whereas neodymium does (*8*).

Whether a lower-valent La species exists in the liquid solution cannot be decided from the present data. Druding and Corbett (*8*) suggest that a reduced form of Pr is present in the liquid Pr-PrCl$_3$ system, and Senderoff and Mellors (*17*) have concluded from electromotive force measurements on Ce-CeCl$_3$ that a reduced Ce species exists in the liquid. If the solubility of the metal in their salts is related to the tendency toward formation of lower-valent chlorides, one might expect the solubility to increase in the order $\mathrm{La} \leqq \mathrm{Ce} < \mathrm{Pr} < \mathrm{Nd}$, the order of the stabilities of the divalent chlorides (*4*). The solubilities of these elements in their chlorides are compared in Table II at 920°, where all the systems presumably consist of two liquid phases. Evidently there is a tendency toward the expected trend, although the La solubility might have been predicted to be somewhat smaller than Ce. When compared at eutectic temperatures, La and Ce have the same solubility (9 mole %) whereas Pr is now more soluble (17%) than Nd (15%).

The activity coefficient of LaCl$_3$ in the La-LaCl$_3$ solutions cannot be calculated with any degree of certainty, since a reliable value for the heat of fusion is not known. Although the heat of fusion of La metal is known (*18*), a cryoscopic number for LaCl$_3$ dissolved in La cannot be calculated because of the presence of an unknown degree of solid solution. The existence of a solid solution in the La-rich mixtures is indicated by the lowering of the $\beta$-$\gamma$ transition temperature on the addition of LaCl$_3$ to La. A similar effect has been reported for the Sr-Sr halides (*6*). Mellors and Senderoff (*15*) have indicated that in the Ce-CeCl$_3$ system the transition observed at 725° corresponds to a metal-rich eutectic. Their tentative diagram for the metal-rich side indicates that the melting point of Ce is lowered 80° by the addition of less than 1% CeCl$_3$. For an ideal solution the f.p. lowering of 1% undissociated CeCl$_3$ in Ce calculated from the heat of fusion of 2.2 kcal. (*18*) is only 12°. For dissociation into three particles [cf. BiCl$_3$ in Bi (*14*)] the decrease would be 36°. The transition observed in the Ce-CeCl$_3$ system at 725° is about 5° lower than the high temperature solid-solid transition in pure Ce (*19*). The break in the Ce-CeCl$_3$ system at 725° is probably actually associated with this solid phase transformation, analogous to the solid transformation halts seen in the La-LaCl$_3$ system.

Table I. Results of Solubility Measurements in the La-LaCl$_3$ System

| Sample | Weight, Grams La | Weight, Grams Cl | Material Balance, % | La in LaCl$_3$, Mole % | Temp., ° C. |
|---|---|---|---|---|---|
| 1 | 1.7254 | 1.1674 | 100.06 | 11.6 | 985 |
| 2 | 1.3564 | 0.9164 | 100.11 | 11.8 | 961 |
| 3 | 1.3475 | 0.9203 | 100.21 | 10.8 | 929 |
| 4 | 1.5658 | 1.0699 | 100.09 | 10.8 | 929 |
| 5 | 1.6533 | 1.1340 | 100.00 | 10.4 | 903 |
| 6 | 1.6636 | 1.1467 | 100.11 | 10.0 | 889 |
| 7 | 1.7512 | 1.2133 | 100.06 | 9.5 | 871 |

Table II. Solubilities of Rare Earth Metals in Their Chlorides at 920° C.

| System | Mole % Metal | Reference |
|---|---|---|
| La-LaCl$_3$ | 11 | This work |
| Ce-CeCl$_3$ | 9 | (2) |
| Pr-PrCl$_3$ | 20 | (5) |
| Nd-NdCl$_3$ | 31 | (5) |

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