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Partition of lanthanum and neodymium metals and chloride salts between molten cadmium and molten LiCl–KCl eutectic

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Abstract

The distribution of lanthanum and neodymium between a molten cadmium pool and molten LiCl–KCl eutectic was measured over the temperature range 753–788 K. Lanthanum and neodymium metals in amounts more than sufficient to form a saturated solution were added to cadmium, then progressively oxidized to salt-soluble trichlorides by additions of cadmium chloride. In the early stages of oxidation a solid metal phase existed; it can be described as a solid solution of $LaCd_{11}$ and $NdCd_{11}$. A regular solution solubility parameter of -1990 ± 390 ($\pm 2\sigma$) was derived for the solid solution. In the later stages of oxidation only an unsaturated solution of lanthanum and neodymium in cadmium existed. Lanthanum was slightly more easily oxidized than neodymium; a separation factor of 2.5 ± 1.1 was measured.

1. Introduction

Partition of the chemical constituents of spent metallic nuclear fuel between a metal phase (either solid or cadmium solution) and molten LiCl–KCl eutectic salt is the chemical basis for the pyrochemical reprocessing of fuel in the Integral Fast Reactor (IFR) concept [1–3]. In the IFR process successive batches of spent metal fuel from the reactor are immersed in a molten salt phase at 773 K in an electrorefining apparatus. The fuel is partially oxidized with cadmium chloride to convert all the alkali and alkaline earth metals and most of the lanthanide metals into their chlorides. Initially, an actinide chloride concentration of about 2 mol.% in the salt is established by oxidation of fuel. Subsequently, actinides are purified by electrotransport from the spent fuel to removable cathodes. Radioactive lanthanide fission products accumulate in the salt; they are periodically removed by chemical reduction into cadmium. Noble metals (*i.e.* those metals that are less electropositive than uranium) are not oxidized and are removed in a separate step. Both electrotransport and reduction result in a cadmium solution of lanthanides and actinides in contact with molten salt. Differences among the lanthanides and actinides in partition between cadmium and salt are of fundamental importance because they control product and waste stream compositions.

The relative partition of uranium and plutonium can be predicted from existing data [4–8] by the methods outlined below. Compared with uranium, plutonium is more easily oxidized from cadmium solution into the salt phase. It is desirable to achieve a predictive capability for partition of the rare earth elements that is at least as accurate as that for uranium and plutonium; most, but not all, of the necessary data are available in the literature. The work described here was undertaken as the first step; we measured the quantity of greatest practical interest (the separation factor) directly for the La–Nd pair. Our results can be used to check on the consistency of calculations based on calorimetric and electrochemical activity measurements and they identify a significant phenomenon that might otherwise have been overlooked, namely solid state interactions.

2. Theory

The distribution of a pair of metallic elements between cadmium and molten salt phases is described by

$$y(\mathrm{MCl}_x)+x(\mathrm{M}'_{(\mathrm{Cd})}) \longleftrightarrow y(\mathrm{M}_{(\mathrm{Cd})})+x(\mathrm{M}'\mathrm{Cl}_y)$$

where M and M′ are metallic elements and x and y are the respective oxidation states of their stable chlorides; x or y is 3 for lanthanum and neodymium. A reaction of this kind can be written to determine the distribution of each of the possible metal pairs between the salt and metal phases, but significant concentrations of both metals will be found in both phases only if the metal chlorides have similar free energies of formation.

The standard free-energy change (ΔG°) in this reaction is

$$\Delta G^\circ = x\Delta G_f^\circ(\mathrm{M}'\mathrm{Cl}_y) - y\Delta G_f^\circ(\mathrm{MCl}_x) \tag{1}$$

where ΔG_f° means the free energy of formation from the pure elements in their standard states. The standard states used throughout this paper for all species, including solutes, are pure crystalline solids or, above the melting points of the pure materials, pure liquid. The equilibrium constant K_{eq} for the reaction is calculated from the standard free-energy change:

$$K_{\mathrm{eq}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \tag{2}$$

Free-energy changes for most compounds of interest have been evaluated and tabulated [7, 8], so the corresponding equilibrium constants are known. Concentrations of the metals and their chlorides can be determined from the equilibrium constant combined with the activity coefficients of metal and chloride species. For this class of reactions the equilibrium constant expression is

$$K_{\mathrm{eq}} = \frac{(a_{\mathrm{M}})^y (a_{\mathrm{M}'\mathrm{Cl}_y})^x}{(a_{\mathrm{M}'})^x (a_{\mathrm{MCl}_x})^y} = \frac{(X_{\mathrm{M}})^y (X_{\mathrm{M}'\mathrm{Cl}_y})^x}{(X_{\mathrm{M}'})^x (X_{\mathrm{MCl}_x})^y} \, \frac{(\gamma_{\mathrm{M}})^y (\gamma_{\mathrm{M}'\mathrm{Cl}_y})^x}{(\gamma_{\mathrm{M}'})^x (\gamma_{\mathrm{MCl}_x})^y} \tag{3}$$

Here a signifies activity, X indicates mole fraction and γ means activity coefficient. The expression

$$\mathrm{SF} = \frac{(X_{\mathrm{M}})^y (X_{\mathrm{M'Cl}_y})^x}{(X_{\mathrm{M'}})^x (X_{\mathrm{MCl}_x})^y} \tag{4}$$

is the separation factor; it describes the relative distribution of the two metals between the phases. Unlike the equilibrium constant, the separation factor is not necessarily constant over wide composition ranges. Because the equilibrium constant does not change (at any temperature), the separation factor can also be constant if and only if the product of the activity coefficients (the second term of eqn. (3)) is constant. The activity coefficients are frequently not known. Because the rare earth chloride concentrations in the work reported here and in pyrochemical processing are on the order of only a few mole per cent and the salt phases are almost certainly not saturated with rare earths [9, 10], we assume that the condition of constant activity coefficient products obtains approximately in dilute solution, *i.e.* we assume that Henry's law applies.

Lanthanum and neodymium concentrations in cadmium are also low: all measured concentrations of lanthanum and neodymium are less than 0.26 wt.% (0.32 at.%) and 1.8 wt.% (2.3 at.%) respectively, although the saturation solubilities at 788 K are 0.6 wt.% and 2.6 wt.% [11] in the binary rare earth–cadmium solutions. In the absence of activity coefficient data as a function of temperature, we assume Henry's law for the metal solutes in cadmium as well and therefore take the metal activity to vary linearly between zero and its activity in the precipitating phase (MCd_{11} for lanthanum and neodymium) as its concentration varies from zero to saturation.

The relationship of the solute metal activity (in the saturated solution) to intermetallic activity (in the precipitating phase) is determined by

$$\mathrm{M}_{(\mathrm{Cd})} + x\mathrm{Cd} \longleftrightarrow \mathrm{MCd}_x$$

and given by

$$\frac{a_{\mathrm{M}}(a_{\mathrm{Cd}})^x}{a_{\mathrm{MCd}_x}} = \exp\left(\frac{\Delta G_{\mathrm{f}}^\circ}{RT}\right) \tag{5}$$

where $\Delta G_{\mathrm{f}}^\circ$ is the free energy of formation of the intermetallic compound.

When $\Delta G_{\mathrm{f}}^\circ$ and the solubility of the metal in cadmium are known, one can use eqn. (5) together with Raoult's law to determine the activity coefficient of the solute metal in saturated cadmium solution. A value of $\Delta G_{\mathrm{f}}^\circ$ has been published for LaCd_{11} [12] but not for NdCd_{11}; the absolute activity coefficients and activities relative to the pure metal are thus known for LaCd_{11} but not for NdCd_{11}.

In mixtures of more than one rare earth and cadmium, solid solutions of the rare earth–cadmium intermetallic compounds can form at saturation, especially where, as here, the crystal structures of the intermetallic compounds are identical [12] and the unit cell dimensions are similar. We propose that such solid solutions formed in this work. Activities of each intermetallic compound in the solid solution were derived from the concentration of the corresponding solute metal in the saturated (ternary) cadmium solution by simultaneous solution of eqn. (5) for the saturated binary rare earth–cadmium mixture and the saturated ternary mixture under the assumption that the activity of the intermetallic compound is unity in the binary case. This gives

$$a_{\mathrm{MCd}_x}=\frac{a_{\mathrm{M(t)}}(a_{\mathrm{Cd(t)}})^x}{a_{\mathrm{M(b)}}(a_{\mathrm{Cd(b)}})^x} \tag{6}$$

Here (t) signifies the ternary mixture and (b) the binary mixture. Under Henry's law for the solutes and Raoult's law for the cadmium, eqn. (6) reduces to

$$a_{\mathrm{MCd}_x}=\frac{X_{\mathrm{M(t)}}(1-X_{\mathrm{M(t)}}-X_{\mathrm{M'(t)}})^x}{X_{\mathrm{M(b)}}(1-X_{\mathrm{M(b)}})^x} \tag{7}$$

The solid solutions of the intermetallic compounds can be treated as regular solutions by applying

$$RT\ln\gamma_{\mathrm{MCd}_{11}}=A(X_{\mathrm{M'Cd}_{11}})^2 \tag{8}$$

Here A is the regular solution parameter. The activities of the intermetallic compounds are used in eqn. (8) to give an expression in A and X_{M} for each intermetallic compound. Equating the two expressions for A, we get

$$\frac{\ln\left(\dfrac{a_{\mathrm{MCd}_{11}}}{X_{\mathrm{MCd}_{11}}}\right)}{(1-X_{\mathrm{MCd}_{11}})^2}=\frac{\ln\left(\dfrac{a_{\mathrm{M'Cd}_{11}}}{1-X_{\mathrm{MCd}_{11}}}\right)}{(X_{\mathrm{MCd}_{11}})^2} \tag{9}$$

Numerical solution of eqn. (9) and entry of the resultant X_{M} in eqn. (8) gives the solubility parameter A.

3. Experimental details

3.1. Apparatus

The salt and cadmium phases were held in a tantalum crucible, which was in turn held in a heavy iron block covered with a massive iron lid (Fig. 1). The lid was penetrated by three holes. One hole admitted the salt-sampling tube. A tantalum shield tube used to prevent salt contamination of the metal sampling tube fitted closely in a second hole in the lid and extended down into the cadmium. A tantalum stirrer passed through a third hole which was in the center of the lid. All the holes were closed with long removable plugs when they were not in use.

The iron block and lid were located in a well in the floor of a glovebox that had a continuously purified helium atmosphere; water and oxygen levels were typically less then 2 ppm by volume. The well was heated from outside with a lower furnace powered by a proportional controller and a small upper furnace controlled by a variable autotransformer. The space

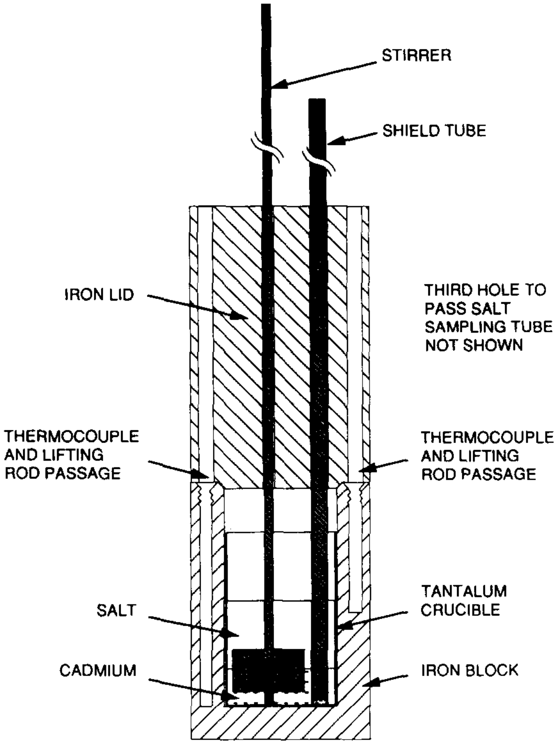

Fig. 1. Apparatus for sampling cadmium and salt phases.

above the block and lid, 30 cm high, was filled with LAVA A[r] and iron disks of thickness 1.27 cm to decrease the temperature gradients. The axial temperature gradient in the space occupied by the melts, 6 cm high, was less than 0.1 K cm^{-1}.

Temperatures were measured with sheathed, ungrounded, type K thermocouples in the wall of the iron block or in the hollow shank of the tantalum stirrer; the temperatures thus measured were identical. Each type K thermocouple was calibrated by comparison to a standard type S thermocouple traceable to NIST freezing point references. The measured temperatures were accurate to less than 1 K and the reproducibility of temperature measurement between thermocouples was better than 0.5 K. The temperature drift rate within the sample zone was approximately 0.1 K h^{-1}.

Sample masses ranged from 0.5 to 4 g and averaged 2.4 g. Masses were measured to better than 0.0001 g on a Sartorius Model R160D balance. Tantalum sampling tubes (6 mm outer diameter) were used; one end of each sampling tube was swaged onto a cylindrical fritted tantalum filter (length 0.64 cm; medium porosity, less than 50 μm pore size) obtained from the Tantalum Pellet Company. A long stainless steel tube was press fitted at room temperature into the opposite end of the sampling tube. The stainless steel tube was connected via a flexible hose and a valve to an evacuable steel ballast bulb having a volume of 1 L.

3.2. Reagents

LiCl–KCl eutectic salt (58 mol.% LiCl, stated to contain less than 50 ppm water, sealed in glass ampoules) was obtained from APL Engineered Materials. $CdCl_2$ (stated purity 99.999%) was obtained from AESAR, as were lanthanum and neodymium (stated purity 99.99%, metal basis, vacuum-remelted reaction grade, lump form, in sealed glass ampoules) and cadmium shot (stated purity 99.9999%).

3.3. Procedure

Cadmium (506.746 g), lanthanum (2.0826 g) and neodymium (10.0047 g) were loaded into the tantalum crucible. The crucible was placed in the iron block and the block-and-lid assembly was lowered into the well and heated to melt the cadmium. The salt shield tube was inserted until it touched the bottom of the crucible, then the furnace was cooled to freeze the cadmium. LiCl–KCl salt (202.6558 g) was added in two batches, with melting between batches to avoid overflowing the crucible.

The entire apparatus was assembled and heated to 773 K for 20 h before the first set of samples was taken. The salt was frozen and cadmium chloride was added to the system between each set of samples by pouring through a funnel and a long tube that rested on the salt surface. The salt and metal were stirred at 20 rev min^{-1} for 20 h after each temperature change or oxidant addition to allow equilibrium to be established. Five oxidant additions (18 pairs of samples) were made. Sampling temperatures of 753, 773 and 788 K were selected in random order and one salt and one metal sample were taken at each temperature. The temperature of the apparatus was limited to 788 K to avoid excessive cadmium vaporization.

Sampling was begun by evacuating the ballast bulb to about 70 kPa. A weighed sampling tube was inserted through the salt shield to a location just above the cadmium, preheated for 5 min, then inserted into the cadmium for 30 min. Next, the connecting valve was opened for 1 or 2 s to draw up the metal sample. The sampling tube was withdrawn from the apparatus, reweighed and filed clean of external contamination. The filter and the opposite end of the tube were cut away with a tubing cutter and the remaining section containing the sample was weighed and submitted for analysis. The empty tube sections were weighed after analysis to determine the sample mass. Sampling of the salt was similar, except that evacuation of the sample tube was not normally necessary and care was taken to avoid inserting the sample tube into the cadmium.

3.4. Chemical analysis

Both salt and metal samples were dissolved in dilute nitric acid and analyzed for potassium, lithium, lanthanum, neodymium and cadmium. The cadmium content was determined by titration using ethylenediaminetetraactetic acid; the content of the other elements was determined by atomic emission spectroscopy using an inductively coupled plasma source (ICP-AES). The ICP-AES method was calibrated against standards traceable to

NIST for each element. At the 95% confidence level the precision of all analytical techniques for substances present in concentrations greater than 0.1% was given as ± 5%; for those whose concentrations were in the range 0.01%–0.1% the precision was ± 10%; and for those whose concentrations were in the range 0.001%–0.01% the precision was ± 20%. The average mass balance in all the samples was 99.8% ± 0.3%. Chloride was obtained by difference. The maximum error in material balance was 2.0%. The lanthanum and neodymium results were corrected for possible cross-contamination by using potassium as a tracer for salt contamination of metal samples and cadmium to measure metal in the salt; we assume that all tracer came from phase admixture. The relative correction was defined as the absolute value of [100 × (measured value − corrected value)/measured value]. Since the largest relative correction was 0.70% and the average relative correction for all rare earth analyses was 0.043%, only the corrected lanthanum and neodymium analyses are reported in Table 1.

4. Results and discussion

No correlation was found between metal or salt concentrations and the order in which temperatures were changed. The lanthanum and neodymium concentrations from all sample pairs are presented in Table 1, along with separation factors and solid solution solubility parameters calculated from pairs 1–9. Since the oxidizing ability of LiCl is enhanced by the low value (about 2×10^{-3}) [13] of the lithium activity coefficient in cadmium, the rare earths were oxidized to a small extent by LiCl. Thus neodymium and lanthanum were oxidized into the salt phase even before $CdCl_2$ addition. The lithium concentration in the cadmium was 0.006 wt.% in metal samples 1–3 and fell to undetectable levels after sufficient $CdCl_2$ had been added to consume all the solid phase; potassium in cadmium was usually below detection limits and was only measurable when there was minor salt contamination.

The presence of a solid phase was inferred from the cadmium phase solute concentrations in the first nine metal samples (at three temperatures and three states of oxidation, see Figs. 2 and 3). In these samples only there was a clear-cut temperature dependence of both neodymium and lanthanum concentrations, as would be expected in the presence of a solid. Also, the lanthanum concentration in cadmium actually increased when $CdCl_2$ was added to the system and rare earth metal was oxidized. In metal samples 13–18 the temperature dependence disappeared and the lanthanum concentration decreased with $CdCl_2$ addition, as expected for an unsaturated solution. It is not clear whether the cadmium solution in samples 10–12 was saturated or not.

Although the present work was intended to measure the separation factors and no assessment of the homogeneity of the solids was made, we can formally describe the solid as though it were a solid solution of $LaCd_{11}$ and $NdCd_{11}$. Other descriptions may be possible. Measured lanthanum and neo-

TABLE 1

Solute concentrations, solubility parameters and separation factors in the La–Cd–Nd system

Sample no.	Temperature (K)	Grammes of $CdCl_2$ (cumulative)	Weight per cent of metal				*A*	SF
			La in salt	La in Cd	Nd in salt	Nd in Cd		
1	753	0.000	0.0010	0.0531	0.0017	0.9110	−1802	10.16
2	773	0.000	0.0022	0.0972	0.0070	1.3470	−1195	4.37
3	788	0.000	0.0045	0.1460	0.0148	1.6600	−2311	3.46
4	788	1.162	0.0590	0.1520	0.1740	1.7000	−1513	3.79
5	752	1.162	0.0476	0.0568	0.1730	0.8830	−1959	4.28
6	773	1.162	0.0506	0.1160	0.1930	1.1900	−2080	2.69
7	773	3.492	0.1140	0.1250	0.7660	1.0800	−2974	1.29
8	789	3.492	0.1620	0.2089	0.7490	1.3097	−2646	1.36
9	753	3.492	0.1660	0.0610	0.7660	0.8808	−1426	3.13
10	773	11.621	0.3030	0.1330	2.4500	0.8920		0.83
11	754	11.621	0.3980	0.1258	2.6200	0.6248		0.75
12	788	11.621	0.4970	0.2579	2.6500	0.8773		0.64
13	753	15.548	0.6440	0.0760	3.3100	0.3920		1.00
14	788	15.548	0.7540	0.1455	3.5000	0.4116		0.61
15	773	15.548	0.8950	0.0642	3.4900	0.3840		1.53
16	773	18.779	0.9900	0.0107	4.1800	0.0760		1.68
17	753	18.779	1.0150	0.0054	4.3000	0.0414		1.81
18	789	18.779	1.0270	0.0038	4.3200	0.0284		1.78

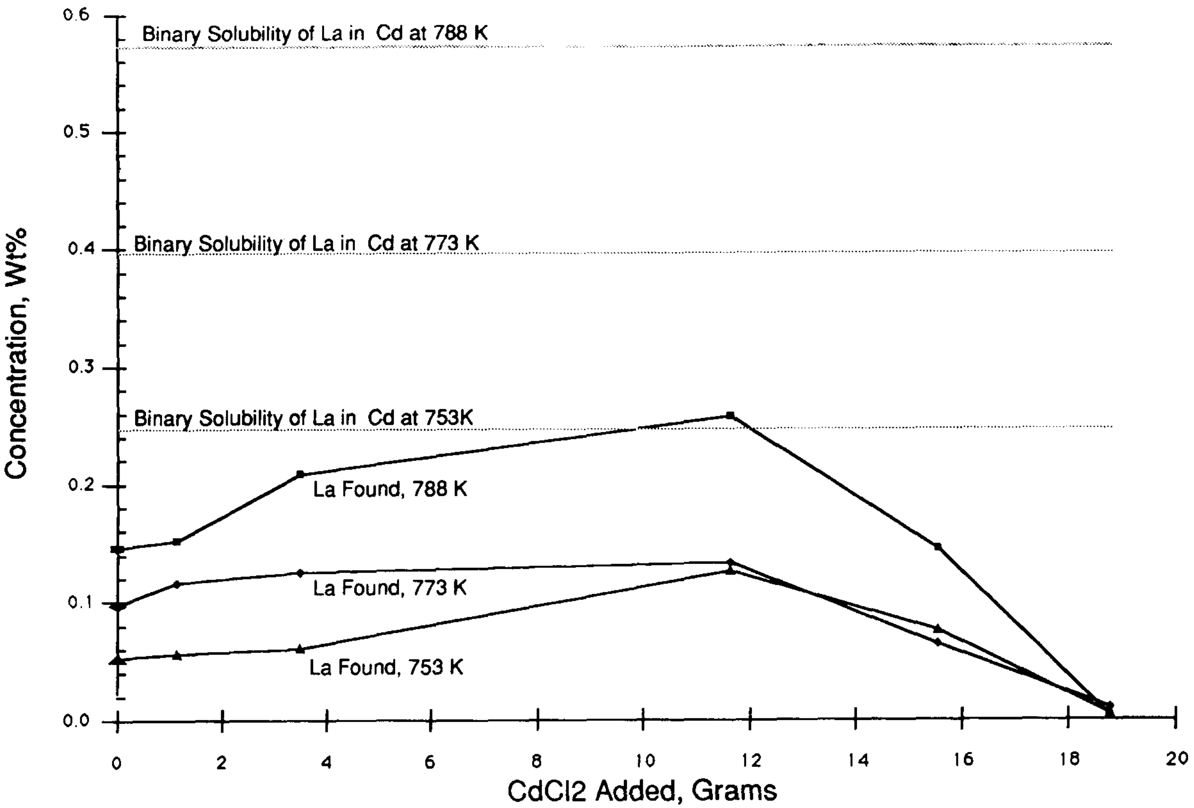

Fig. 2. Concentration of lanthanum in cadmium at 753, 773 and 788 K as a function of amount oxidized.

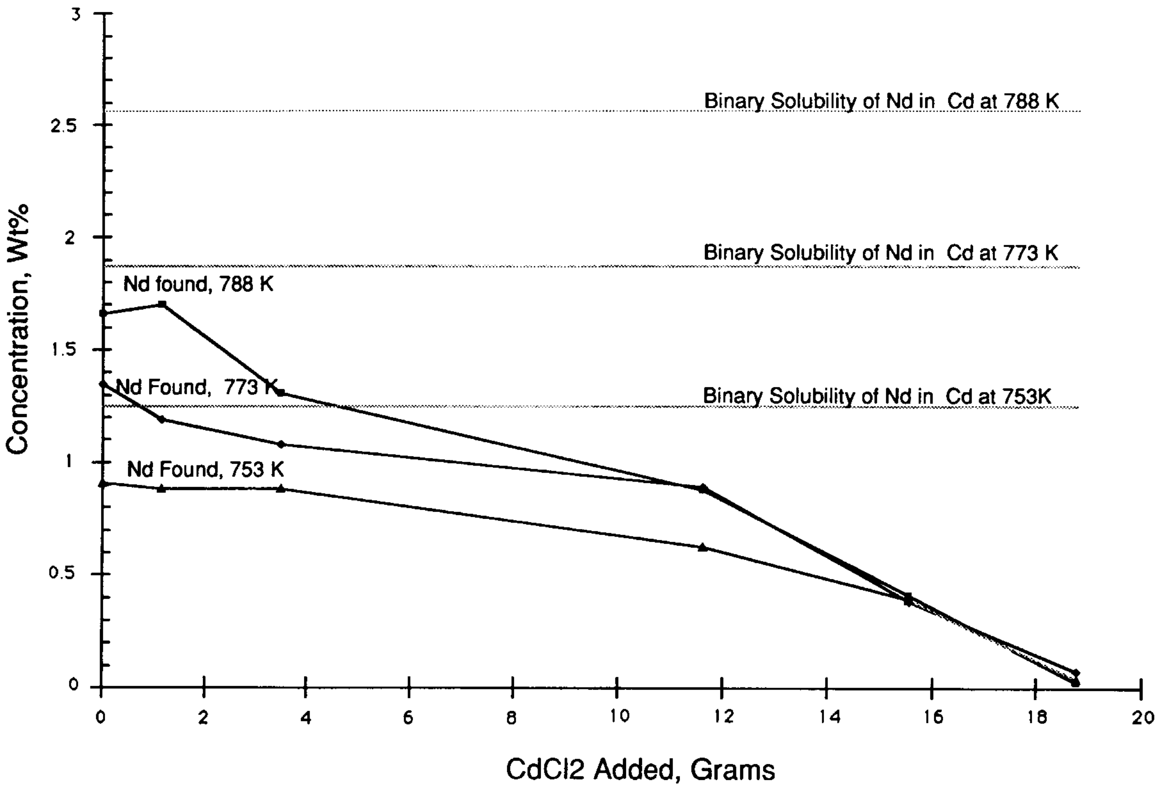

Fig. 3. Concentration of neodymium in cadmium at 753, 773 and 788 K as a function of amount oxidized.

dymium concentrations in the liquid cadmium phase were lower than the saturation values measured in the binary rare earth–cadmium systems by Johnson *et al.* [11], presumably because the intermetallics have lowered activities in solid solution and the metal activities in solution are related to the intermetallic activities by eqn. (5). There was more than four times as much neodymium as lanthanum in the system at the beginning; apparently there was also more neodymium than lanthanum in the solid phase. Accordingly, on $CdCl_2$ addition more neodymium than lanthanum was oxidized when $CdCl_2$ was added, even though lanthanum is slightly more easily oxidized than neodymium. This caused an increase in the fraction of $LaCd_{11}$ in the solid, and hence in its activity, and a corresponding increase in the lanthanum concentration in the cadmium. Figure 4 shows the increase in lanthanum concentration in cadmium with progressive oxidation of lanthanum and neodymium. The $NdCd_{11}$ activity in the solid and the neodymium concentration in the cadmium decreased concurrently.

For metal samples in the group 1–9 the concentrations of lanthanum and neodymium divided by the saturation solubilities measured by Johnson *et al.* [11] ranged from 0.22 to 0.37 and from 0.52 to 0.73 respectively. The corresponding values of intermetallic compound activities in the solid ranged from 0.20 to 0.34 for $LaCd_{11}$ and from 0.57 to 0.75 for $NdCd_{11}$. The calculated mole fractions of $NdCd_{11}$ fell in the interval from 0.60 to 0.76. The solubility parameter A ranged from 1430 to 2980, with an average value of A for all nine points of -1990 ± 390 ($\pm 2\sigma$).

For each metal sample the concentration of lanthanum and neodymium in cadmium solution was back calculated from the average A and the mole fraction of $NdCd_{11}$ in that sample. These back-calculated concentrations were compared with the experimental values. The absolute value of the relative difference between the experimental and calculated values was |(calculated − experimental)/experimental|. The average of the 18 relative differences was 0.076; the largest relative difference was 0.147.

The average separation factor was 2.5 ± 1.1 ($\pm 2\sigma$), with a range from 0.6 to 10.2. Thus lanthanum favored the salt phase relative to neodymium to a small extent. There was no detectable trend of the separation factor with temperature.

5. Conclusions

At equilibrium a larger fraction of lanthanum is oxidized than neodymium. A separation factor of 2.5 was derived; this value can be used for calculations of the distributions of these elements between cadmium and molten LiCl–KCl. In those cases where the concentration of lanthanum or neodymium in cadmium approaches its solubility, the presence of solid intermetallic solutions and attendant reduction in solubility should be anticipated. In this work the solubility of lanthanum in cadmium was decreased relative to the binary system values by factors ranging from 2.7 to 4.6. The solubility of neodymium,

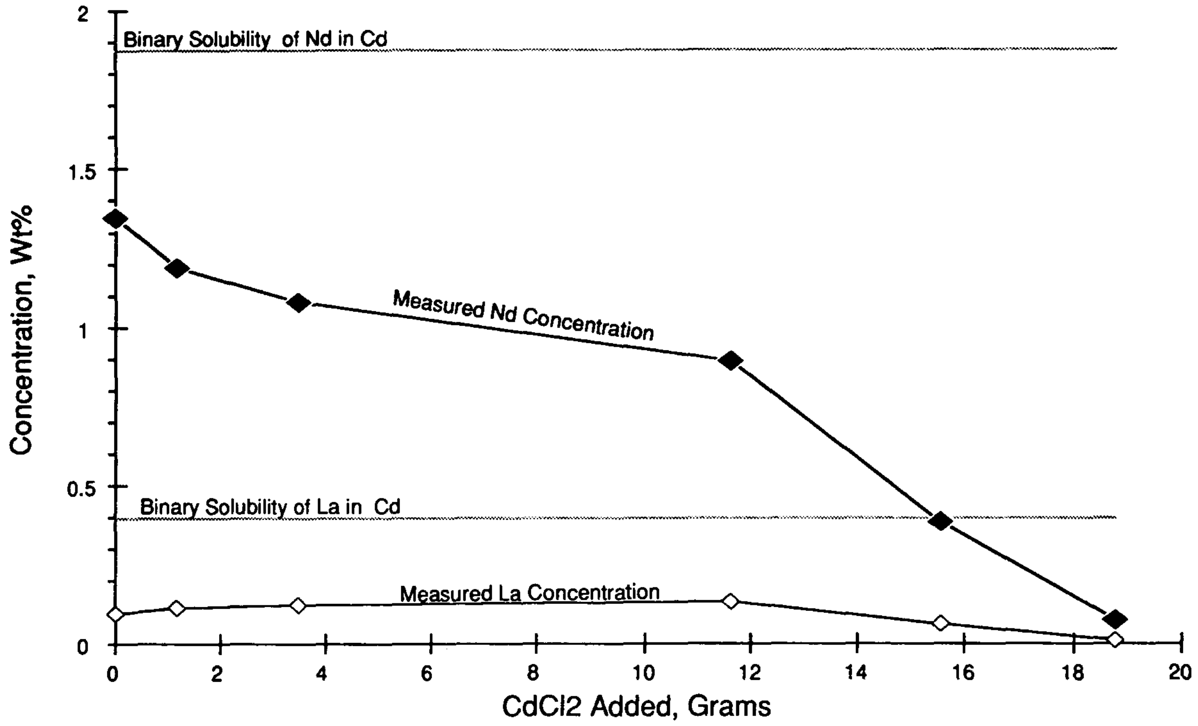

Fig. 4. Concentration of lanthanum and neodymium in cadmium at 773 K as a function of amount oxidized.

which was present in much larger quantity, was decreased by factors ranging from 1.4 to 2.0. We believe that a solid metal phase was present in samples 1–9 and that it can be formally described as a solid solution of $LaCd_{11}$ and $NdCd_{11}$. For calculations of solid composition a regular solution parameter A of -1990 is recommended.

Acknowledgments

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