ABSTRACT

The enthalpies of phase transitions as well as the heat capacities of LaCl₃, CeCl₃, PrCl₃, NdCl₃, GdCl₃ and DyCl₃ were measured previously. Their mixtures with alkali metal chlorides were also examined and enthalpy of mixing determined. These MCl-LnCl₃ systems characterize by one or several compounds. The M₃LnCl₆ compounds in particular exist in most systems, with various stability ranges, and often undergo phase transition at high temperature, prior to melting. The related enthalpy changes were determined for those compounds where M = K, Rb, Cs and Ln = La, Ce, Pr, Nd and for K₂LaCl₅. The present work focussed on the solid and liquid K₃LnCl₆ and Rb₃LnCl₆ compounds (Ln = La, Ce, Pr, Nd), and heat capacities were measured. Since no Cp data were available so far in literature, these values were checked for consistency in calculating the formation enthalpy of the liquid phase.

INTRODUCTION

Although rare earth halide melts and their mixtures with alkali halides are used in a number of high temperature processes (1-3), it should be stressed that available thermodynamic data are scarce and heterogeneous, mostly because of experimental difficulties. Indeed, the well-known difficult features of high temperature experimentation are complicated here by the extreme reactivity of the lanthanide halides which sometimes makes questionable sample purity and, hence, data reliability. Our purpose is to propose a route to access the thermodynamic features of the MCl-LnCl₃ mixtures (M = alkali metal and Ln = lanthanide) from available data and significant investigations to be conducted.

Pyrochemical processes, which are being investigated intensively for nuclear applications, require reliable databases to be established (4-6). A number of investigations have been performed recently on the MCl-LnCl₃ melts. Several multi-instrumental techniques were used complementarily to characterize the macroscopic and microscopic behavior of these mixtures (7-23).
THERMOCHEMICAL DATA

Most MCl-LnCl₃ systems exhibit phase diagrams characterized by stoichiometric compounds, the formation of which and the domain of existence vary depending on the nature of the alkali metal and of the lanthanide. This can be exemplified with the KCl-PrCl₃ phase diagram (24) reported in Fig. 1.

![Equilibrium phase diagram of the KCl-PrCl₃ system](image)

Figure 1. Equilibrium phase diagram of the KCl-PrCl₃ system

The congruently melting K₃PrCl₆ does not exist at room temperature and forms peritectically from K₂PrCl₅ according to the reaction:

\[ \text{KCl} + \text{K₂PrCl₅} \rightarrow \text{K₃PrCl₆} \]

The thermochemical cycle given in Figure 2 describes the synthesis of liquid K₃LnCl₆ from KCl and LnCl₃. The left branch of this flow chart corresponds to the direct synthesis, while the right branch involves an intermediate stage, when K₃LnCl₆ forms from KCl and K₂LnCl₅.
Figure 2. Thermochemical cycle for the formation of liquid K₃LnCl₆.

The thermodynamic data involved in this cycle are:
- molar heat capacity in the solid and liquid state,
- molar enthalpy of (transition and) fusion,
- molar enthalpy of formation in the solid and liquid state,
- temperature of transition and of fusion.

The data available so far were the molar heat capacities and enthalpies of phase transitions relative to the pure components MCl (25-26) and LnCl₃, as determined from our previous investigations (9, 27). We also measured the enthalpies of phase transitions and of fusion of the M₃LnCl₆ and M₂LnCl₅ compounds (8). The molar enthalpies of formation of the solid potassium compounds at 298 K were determined by dissolution calorimetry by Blachnik (28, 29) while those relative to rubidium compounds were investigated by Seifert et al. by a similar technique (30-32). Finally, the enthalpy of formation of the liquid mixtures was measured by direct high temperature microcalorimetry (8, 9, 33, 34). From this inventory, it can be seen that heat capacities of solid and liquid compounds have to be determined in order to allow the calculation of the previous thermochemical cycle.

HEAT CAPACITY MEASUREMENTS.

The experimental procedure for Cp measurements with a differential scanning calorimeter SETARAM DSC 121, the method of lanthanide chloride synthesis and the preparation of samples have been described previously (1,2).

The LnCl₃ lanthanide chlorides were synthesized from oxides. Purification was processed by sublimation. Purity was checked by chemical analysis. Alkali chlorides were purified and treated by progressive heating up to fusion under a gaseous HCl atmosphere. Excess HCl was removed from the melt by flushing with argon.
All handling and preparations of experimental samples were carried out in a controlled purified argon atmosphere glove box.

Samples used for heat capacity measurements (300 - 500 mg masses) were sealed under a low pressure of argon in quartz cells (15 mm long and 7 mm diameter). These cells were placed in the DSC 121 calorimeter and measurements were carried out by the step method, each heating step of 5 K being followed by a 400 s isothermal delay. The apparatus was calibrated by the Joule effect, and some test experiments were carried out with NIST 720 α-alumina for secondary calibration, to monitor the Cp measurements.

The classical heat capacity polynomial equation

\[ \text{Cp} = a + b \ T + c \ T^2 + d/T \]  

was used to fit the experimental results.

Figure 3 reports as an example, the heat capacity dependence on temperature of K₃PrCl₆. The formation of the stoichiometric compound can be clearly seen at \( T = 768 \text{ K} \) while fusion occurs at \( T = 944 \text{ K} \), in excellent agreement with our previous DSC investigations (8).

![Figure 3. Molar heat capacity of K₃PrCl₆ against temperature.](image)

Figure 4, relative to Rb₃PrCl₆, shows that in the compounds which involve a heavier alkali metal like Rb, the \( \text{Cp} = f \ (T) \) plot exhibits a supplementary feature before melting due to a transition after the formation of this compound.
These new heat capacity data, obtained for all the K₃LnCl₆ (Table 1) and Rb₃LnCl₆ (Table 2) compounds (with Ln = La, Ce, Pr, Nd) were used with the other already available data on the KCl-LnCl₃ and RbCl – LnCl₃ systems.

Table 1. Heat capacity of K₂LnCl₅ and K₃LnCl₆ compounds: Regression coefficients and standard error of \( C_p \) (J mol\(^{-1}\) K\(^{-1}\)) = a + bT + cT\(^2\) + d/T

| compound       | temperature range/K | a         | b*10\(^{-2}\) | c*10\(^{-4}\) | d*10\(^{4}\) | S.E. |
|----------------|---------------------|-----------|--------------|--------------|--------------|------|
| \( K_2\text{LaCl}_5 \) (s) | 300 - 866           | 453.33    | -49.824      | 3.37         | -3.7506      | 1.63 |
| \( K_2\text{LaCl}_5 \) (l) | 915 - 945           | 290.0     |              |             |              | 2.52 |
| \( K\text{Cl}+ \) \( K_2\text{CeCl}_5 \) (s) | 300 - 805           | 306.52    | -11.105      | 0.95         | -0.5995      | 1.60 |
| \( K_3\text{CeCl}_6 \) (s) | 815 - 865           | 284.60    |              |             |              | 1.75 |
| \( K_3\text{CeCl}_6 \) (l) | 915 - 970           | 337.40    |              |             |              | 2.41 |
| \( K\text{Cl}+ \) \( K_2\text{PrCl}_5 \) (s) | 380 - 760           | 612.49    | -66.488      | 4.36         | -5.8489      | 1.03 |
| \( K_3\text{PrCl}_6 \) (s) | 780 - 930           | 262.19    | 3.998        | 5.8030       |              | 2.43 |
| \( K_3\text{PrCl}_6 \) (l) | 950 - 1100          | 278.30    |              |              |              | 4.26 |
| \( K\text{Cl}+ \) \( K_2\text{NdCl}_5 \) (s) | 300 - 715           | 363.84    | -20.699      | 1.63         | -2.1254      | 1.58 |
| \( K_3\text{NdCl}_6 \) (s) | 740 - 940           | 1346.61   | -261.78      | 15.98        |              | 2.70 |
| \( K_3\text{NdCl}_6 \) (l) | 985 - 1020          | 321.90    |              |              |              | 3.89 |
CONCLUSION

Beyond this enthalpy consistency of thermodynamic data sets, the next stage will be an optimization procedure involving all available thermodynamic data and phase diagrams.

Phase diagram assessment will check the new thermodynamic data obtained in the present work for consistency with those already existing. As already stressed for other lanthanide chloride melts like NaCl-EuCl₂ (35), the Thermo-Calc thermodynamic software used for optimization generally does not include assessed parameters on lanthanide halides in its built-in database. Thus these new experimental data determined here and in previous studies, will be implemented in the database. The optimization procedure will be run from a consistent data set but also using proper modeling hypotheses.

Hence these validated data could be used with confidence, in particular for the design of nuclear processes (3-6).

REFERENCES

1. R.A. Sharma and R.A. Roge, J. Am. Ceram. Soc. 75, 2484 (1992).
2. E.W. Dewing, G.M. Haarberg, S. Rolseth, L. Ronne, J. Thonstad, and N. Aalberg, Metal. and Mat. Trans. B 26B, 81-86 (1995).
3. Y.I. Chang, L.C. Walters, J.E. Battles, D.R. Pedersen, D.C. Wade, and M.J. Lineberry, ANL-IFR-125 (1990).
4. T. Ogawa, S. Yamagishi, A. Itoh, T. Mukayama, M. Handa and R.G. Haire, Proc. International Conference on Evaluation of Emerging Nuclear Fuel Dense Systems, France, 11-14 september, (1995).
5. T. Ogawa and M. Igarashi, J. High Temp. Material Processes, 2, 587 (1998).
6. CEA (Commissariat a l’Energie Atomique, France) PG DRRV/DIR/99-08, p.137 April (1999).
7. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, Thermochim. Acta 236, 51 (1994).
8. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, Thermochim. Acta 236, 59 (1994).
9. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, Thermochim. Acta 236, 67 (1994).
10. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, Thermochim. Acta 279, 1 (1996).
11. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, Thermochim. Acta 279, 11 (1996).
12. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, J. Alloys Comp. 204, 185 (1994).
13. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, J. Alloys Comp. 204, 189 (1994).
14. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, J. Alloys Comp. 204, 193 (1994).
15. M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, J. Alloys Comp. 279, 11 (1996).
16. M. Gaune-Escard, L. Rycerz and R. Takagi, J. Alloys Comp. 257, 134 (1997).
17. M. Gaune-Escard and L. Rycerz, Proc. VIIth Int. Symp. on Molten Salt Chemistry and Technology, Dresden, Germany, 24-29 August 1997, Molten Salt Forum, v. 5-6, 217 (1998).
18. K. Fukushima, T. Ikumi, J. Mochinaga, R. Takagi, M. Gaune-Escard and Y. Iwadate, J. Alloys Comp. 229, 274 (1995).
19. M. Sakurai, R. Takagi, A.K. Adya, M. Gaune-Escard. Z. Naturforsch. Part a : 53 a, 655 (1998).
Table 2. Heat capacity of Rb2LnCl5 and Rb3LnCl6 compounds: Regression coefficients and standard error of $C_p$ (J mol$^{-1}$ K$^{-1}$) = $a + bT + cT^2$.

| Compound             | Temperature range/K | a J mol$^{-1}$K$^{-1}$ | b J mol$^{-1}$K$^{-2}$ | $c \times 10^4$ J mol$^{-1}$K$^{-3}$ | S.E. J mol$^{-1}$K$^{-1}$ |
|----------------------|---------------------|-------------------------|-------------------------|--------------------------------------|--------------------------|
| RbCl+Rb$_2$LaCl$_5$  | 300-717             | 308.09                  | -0.16741                | 1.92                                 | 2.71                     |
| Rb$_3$LaCl$_6$       | 735-955             | 712.62                  | -1.0079                 | 6.13                                 | 3.63                     |
| RbCl+Rb$_2$CeCl$_5$  | 300-390             | 274.83                  | 0.01348                 | 2.54                                 |
| Rb$_3$CeCl$_6$-I     | 420-643             | 486.85                  | -0.74019                | 6.26                                 | 5.21                     |
| Rb$_3$CeCl$_6$-II    | 662-980             | 693.29                  | -0.99720                | 6.13                                 | 3.67                     |
| Rb$_3$CeCl$_6$       | 1016-1074           | 345.73                  | 2.43                    | 3.15                                 |
| RbCl+Rb$_2$PrCl$_5$  | 300-400             | 621.75                  | -2.12574                | 33.96                                | 2.99                     |
| Rb$_3$PrCl$_6$-I     | 405-654             | 472.63                  | -0.75499                | 7.43                                 | 1.93                     |
| Rb$_3$PrCl$_6$-II    | 664-1000            | 794.60                  | -1.22287                | 7.23                                 | 3.15                     |
| RbCl+Rb$_2$NdCl$_5$  | 300-380             | 360.46                  | -0.54373                | 8.77                                 | 1.51                     |
| Rb$_3$NdCl$_6$-I     | 400-660             | 391.21                  | -0.52122                | 5.53                                 | 1.40                     |
| Rb$_3$NdCl$_6$-II    | 675-1050            | 636.70                  | -0.79808                | 4.26                                 | 3.82                     |
|                     | 1060-1093           | 325.77                  | 3.05                    |                                      |

Table 3 reports the values of the enthalpy of formation of the liquid compounds computed from the thermochemical cycle.

Table 3. M$_3$LnCl$_6$ compounds: experimental and calculated enthalpies of formation $\Delta_{\text{form}}H_m$ in the liquid state.

| compound   | T/K  | $\Delta_{\text{form}}H_m$ / kJ·mol$^{-1}$ (experimental) | $\Delta_{\text{form}}H_m$ / kJ·mol$^{-1}$ (calculated) |
|------------|------|----------------------------------------------------------|--------------------------------------------------------|
| K$_3$CeCl$_6$ | 1118 | -55.7 (34)                                               | -56.9                                                 |
| K$_3$PrCl$_6$ | 1122 | -55.9 (8)                                                | -63.3                                                 |
| K$_3$NdCl$_6$ | 1065 | -55.2 (9)                                                | -62.2                                                 |
| Rb$_3$LaCl$_6$ | 1173 | -65.3 (33)                                               | -42.2                                                 |
| Rb$_3$CeCl$_6$ | 1118 | -68.2 (34)                                               | -70.8                                                 |
| Rb$_3$NdCl$_6$ | 1122 | -68.8 (9)                                                | -69.5                                                 |

The agreement with the experimental enthalpies measured previously by high temperature calorimetry, also reported in Table 3, is fairly good taking into account that these enthalpies of formation are about 4 orders of magnitude smaller than the enthalpy increments due to heat capacity and phase transitions.
20. A.K. Adya, R. Takagi, M. Gaune-Escard, Z. Naturforsch., 53a, 1037 (1998).
21. M. Gaune-Escard, L. Rycerz, High Temp. Material Processes, 2, 483 (1998).
22. R. Takagi, F. Hutchinson, P.A. Madden, A.K. Adya, M. Gaune-Escard. J. Physics : Cond. Matter. 11, 645 (1999).
23. L. Rycerz, M. Gaune-Escard. J. Thermal Analysis and Calorimetry, 56, 355 (1999).
24. H.J. Seifert, J. Sandrock and J. Uebach, Z. anorg. Allg. Chem. 555, 143 (1987).
25. S. Sternberg and I. Adorian, Revue Roumaine de Chimie. 18, 945 (1973).
26. L.B. Pankratz, Thermodynamic Properties of Halides, Bulletin 674, U. S. Dept. of Interior, Bureau of Mines, (1984).
27. M. Gaune-Escard, A. Bogacz, L. Rycerz, W. Szczepaniak. J. Alloys Compounds, 235, 176, (1996).
28. R. Blachnik and A. Schneider, Monatschewte für Chemie 1337 (1971)
29. R. Blachnik and D. Sele, Z. anorg. allg. Chem. 454, 90 (1979).
30. H.J. Seifert, H. Fink and G. Thiel, J. Less-Common Met. 110, 139 (1985).
31. H.J. Seifert, J. Sandrock and G. Thiel, J. Therm. Anal. 31, 1309 (1986).
32. H.J. Seifert, H. Fink and J. Uebach, J. Therm. Anal. 33, 625 (1988).
33. G.N. Papatheodorou and T. Østvold, J. Phys. Chem. 78, 181 (1974).
34. G.N. Papatheodorou and O.J. Kleppa, J. Phys. Chem. 78, 178 (1974).
35. M. Gaune-Escard, F. da Silva, L. Rycerz, R. Takagi, Y. Iwadate, A. Adya. ECS Meeting Abstracts, vol. MA 98-1, 1102 (1998).