Determination and Assessment of Thermodynamic Data for the Earth Alkali Metal Alanates $Mg(AlH_4)_2$, $Ca(AlH_4)_2$ and $Sr(AlH_4)_2$

Franziska Habermann, Anneliese Wirth, Konrad Burkmann, Bianca Störr, Jürgen Seidel, Klaus Bohmhammel, Roman Gumeniuk, Florian Mertens

Technische Universität Bergakademie Freiberg, Institut für Physikalische Chemie,
Leipziger Str. 29, 09599 Freiberg, Germany

The suitability of complex hydrides such as alanates for solid-state hydrogen storage applications, especially regarding the transition to a renewable energy-based economy, is being widely discussed. Although the alanates of the earth alkali metals Mg, Ca and Sr were already investigated to some extent in that regard, hardly any reliable thermodynamic data exists [1].

For instance, until now no heat capacity functions and absolute entropies have been reported. In order to measure the heat capacity functions of $Mg(AlH_4)_2$, $Ca(AlH_4)_2$ and $Sr(AlH_4)_2$ in the temperature range from 2 K to 360 K, the alanates had first to be synthesised as they are not commercially available. Since the synthesis of the pure compounds proved to be challenging because of their metastability, mixtures of the composition $M(AlH_4)_2 + 2\ M'Cl$ (M = Mg, Ca, Sr; M' = Li, Na) were used instead. Those mixtures were prepared by ball milling via metathesis reactions. The heat capacities of the alanates themselves were then obtained by subtracting the ones of the by-product from those measured.

Heat capacity measurements from 2 K to 298 K were carried out on a Physical Property Measurement System (PPMS, Quantum Design, USA). The measurement was performed using the heat capacity option based on a relaxation technique. By means of a DSC-111 (SETARAM) the heat capacity between 283 K and 360 K was measured employing a C_p-by-step technique.

The absolute entropies of the alanates were derived from the respective measured heat capacity functions.

While theoretically computed enthalpies of formation have been reported for $Mg(AlH_4)_2$ [2] and $Ca(AlH_4)_2$ [3], no value exists for $Sr(AlH_4)_2$. $Mg(AlH_4)_2$ is the only one of the three alanates for which a enthalpy of formation was derived from the dehydrogenation enthalpy in the literature [4]. Nevertheless, as the heat capacity function of $Mg(AlH_4)_2$ was not known then, the temperature dependence of the enthalpy of formation could not have been taken into account and therefore the published value has to be regarded as an estimate. To assess the values reported in the literature and to determine one for $Sr(AlH_4)_2$, we computed the enthalpies of formation of the earth alkali metal alanates using their heat capacity functions and dehydrogenation enthalpies obtained by integrating the corresponding heat effects determined by DSC measurements.

References

[1] K. Suárez-Alcántara, J. R. Tena-Garcia, R. Guerrero-Ortiz, *Materials* **2019**, *12*, 2724-2787.

[2] a) M. Palumbo, F. J. Torres, J. R. Ares, C. Pisani, J. F. Fernandez, M. Baricco, *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2007**, *31*, 457; b) O. M. Løvvik, P. N. Molin, *Phys. Rev. B* **2005**, *72*, 1; c) O. M. Loevvik, P. N. Molin, *AIP Conf. Proc.* **2006**, *837*, 85-90; d) Y.-l. Wang, S. Liu, L.-j. Rong, Y.-m. Wang, *Journal of physics. Condensed matter: an Institute of Physics journal* **2010**, *22*, 175502; e) M. Fichtner, J. Engel, O. Fuhr, A. Gloess, O. Rubner, R. Ahlrichs, *Inorg. Chem.* **2003**, *42*, 7060; f) Z.F. Hou, *J. Power Sources* **2006**, *159*, 111; g) M. J. van Setten, G. A. de Wijs, V. A. Popa, G. Brocks, *Phys. Rev. B* **2005**, *72*, 1; h) J. F. Herbst, *J. Alloys Compd.* **2002**, *337*, 99.

[3] a) O. M. Loevvik, *Phys. Rev. B* **2005**, *71*, 144111; b) A. Klaveness, P. Vajeeston, P. Ravindran, H. Fjellvåg, A. Kjekshus, *J. Alloys Compd.* **2007**, *433*, 225; c) C. Weidenthaler, T. J. Frankcombe, M. Felderhoff, *Inorg. Chem.* **2006**, *45*, 3849.
[4] C. Claudy, B. Bonnetot, J. M. Letoffe, *J. Therm. Anal.* **1979**, 119.