THERMODYNAMIC DIFFERENCE RULES APPLIED TO COMPLEX HYDRIDES

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Over the last decade dozens of new hydride structures have been synthesised based on complex anions including $[BH_4]^-$, $[B_{12}H_{12}]^{2-}$, $[AlH_4]^-$, $[AlH_6]^{3-}$, $[NH_2]^-$, $[NH]^{2-}$ and $[FeH_6]^{4-}$. Many of these new structures are comprised of combinations of cations, complex hydride anions and halide anions. In addition, a large number of complex hydride metal ammines have also been synthesised. The prediction of the decomposition pathway of these complex hydrides requires knowledge of their thermodynamic properties. This can be achieved using Density Functional Theory (DFT), but DFT has a number of limitations: functionals that are suitable for hydrides must first be chosen, the calculations are performed at 0 K and approximations need to be made to obtain estimates of the enthalpies and entropies at room temperature and above. Lastly, it cannot easily be applied if the crystal structures of reaction products are unknown or amorphous. The thermodynamics for complex hydrides can be estimated using the Thermodynamics by Difference Rules (TDR) [1] and Volume Based Thermodynamics (VBT) method[2]. The TDR and VBT methods achieve this by relating the unknown thermodynamic properties of a new complex hydride to the experimental thermodynamic properties of a related phase. The TDR and VBT methods are most accurate if the crystal structure or density of the new complex hydride is known, but they can also be applied to amorphous compounds and compounds where only the chemical formula might be known. Thermodynamic quantities such as enthalpy of formation, entropy and heat capacity can be readily estimated and used to predict the reaction pathways of new complex hydrides. Preliminary calculations from the TDR and VBT methods will be presented and compared with both experimental and DFT data, where available.

References

1. Jenkins, H. D. B.; Glasser, L., Thermodynamic Difference Rules: A Prescription for Their Application and Usage to Approximate Thermodynamic Data. *Journal of Chemical and Engineering Data* **2010,** *55*, 4231-4238.
2. Glasser, L.; Jenkins, H. D. B., Volume-Based Thermodynamics: A Prescription for Its Application and Usage in Approximation and Prediction of Thermodynamic Data. *Journal of Chemical and Engineering Data* **2011,** *56*, 874-880.

Drew Sheppard received his Ph.D. degree in 2009. He was a founding member of the Hydrogen Storage Research Group at Curtin University, Australia. In 2011 he was awarded a prestigious Australian Post-Doctoral Industry Fellowship and in 2013 he was awarded a Curtin University Early Career Research Fellowship. His main expertise is in the solid-state synthesis and thermodynamic characterisation of metal hydrides with his research focussed on unconventional hydrogen storage materials.