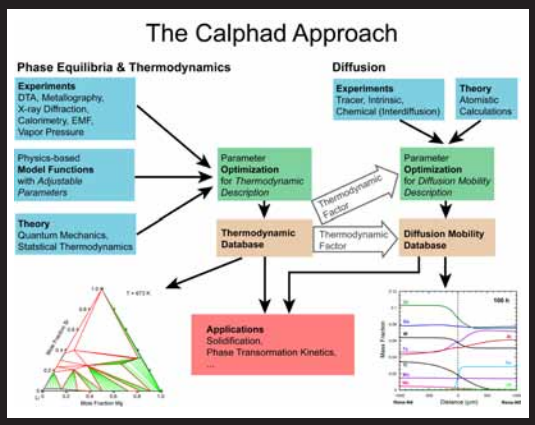
# Thermodynamic & Kinetic Data for Sustainable Energy

## Objective

This project will establish thermodynamic and diffusion mobility databases for use in the development of new sustainable energy sources, such as high efficiency turbines, hydrogen storage materials, and photovoltaics. The approach and database formats employed will allow efficient mining of the wealth of data provided.




## Impact and Customers

- Higher efficiency energy sources will require the development of new materials. Thermodynamic and diffusion mobility databases provide the data needed to accelerate materials discovery and development.
- NIST thermodynamic and diffusion databases have enabled companies such as CompuTherm, QuesTek, and Thermo-Calc AB to develop a variety of new software tools. The NIST-Ni mobility database is enabling GE and NASA to design improved superalloys.
- The NIST-Metal Hydride thermodynamic database for hydrogen storage materials enables the Department of Energy's Metal Hydride Center of Excellence (MHCoE) partners to evaluate promising storage materials.
- The NIST Diffusion Workgroup includes members from GE, HelioVolt, Thermo-Calc AB, CompuTherm, QuesTek, NASA, SGTE, University of Central Florida, Northwestern University, Pennsylvania State University, Ohio State University, University of Michigan and George Mason University.

*Turbine Blade*
*image: Michael Cervenka, Rolls-Royce Plc*

## Approach

Knowledge of the thermodynamic, phase equilibria and diffusion properties of potential novel materials can greatly accelerate their development. However, the data needed for new, multicomponent materials are often not available. The Calphad (Calculation of Phase Diagrams) approach allows the development of thermodynamic and diffusion mobility databases, enabling the extrapolation of higher systems from binary and ternary systems. Phase equilibria calculations using the thermodynamic databases determine the phases present and their compositions, as well as enthalpy contents, temperature and concentration dependence of phase boundaries, and enable the coupling of microscopic and macroscopic models.

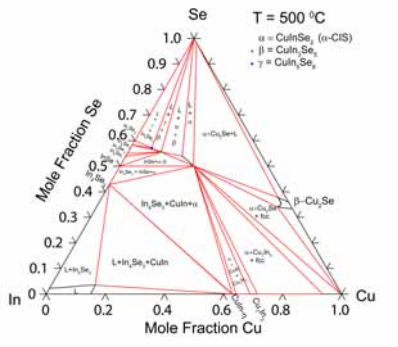
Going beyond equilibrium properties, these methods can also be applied to the dynamics of materials. Diffusion rates can be expressed as a product of a thermodynamic factor and diffusion mobility. Diffusion mobility functions are optimized with the Calphad method using a variety of diffusion data and a given thermodynamic description. These diffusion mobility databases have become crucial in numerical diffusion process simulations for multicomponent alloys where composition and temperature dependent diffusion coefficient matrices are needed at each point in the material.

METALS

# Accomplishments

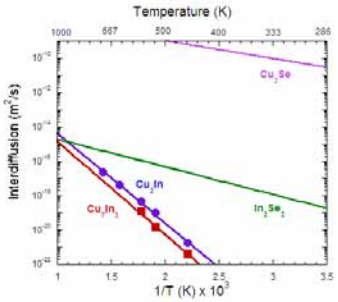
Currently NIST is focused on extending the CALPHAD methodology beyond traditional metallic systems as it works to develop improved thermodynamic and diffusion mobility descriptions for photovoltaic and hydrogen storage materials.

Working in conjunction with researchers at the University of Florida, thermodynamic and diffusion mobility descriptions for the Cu-In-Ga-Se system are being developed. This system is critical in the processing of the $\alpha$-Cu(In,Ga)$Se_2$ (CIGS) photovoltaic absorber material. Advantages of the CIGS-based photovoltaic cells include high efficiency (19.9%), the possibility of direct band gap engineering, high optical absorption coefficient, high radiation resistance, high reliability, and use on flexible substrates. Production costs, however, prevent CIGS from being widely used. To reduce the processing cost requires reducing the current processing times from an average of 30 minutes to less than 3 minutes.




*Isothermal section of Cu-In-Se diagram*

NIST is developing a diffusion mobility database for the Cu-In-Ga-Se system to use with thermodynamic descriptions to enable modeling of a variety of different processing routes. The mobility descriptions are optimized using available measured diffusion coefficients and composition profiles from the literature, and growth rate constants measured during in-situ high temperature x-ray diffraction studies by U. Florida and Oakridge National Laboratory. The calculated ternary Cu-In-Se isothermal section at 500 °C shows its complexity, and demonstrates the need for diffusion simulations to investigate the numerous possible processing routes to form the $\alpha$–CIS phase. Initial comparisons of measured and calculated interdiffusion coefficients for some of the binary intermetallic compounds in the system are shown in the figure below.

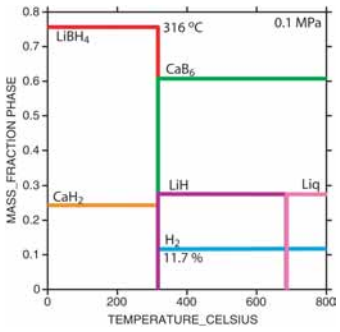



*Binary interdiffusion coefficients in the Cu-In-Se system*

To support materials development efforts in hydrogen storage for the Hydrogen Economy, NIST has developed a thermodynamic database for CALPHAD modeling from the available literature, which includes the elements Li, Mg, Ca, B, Si, and H, and their respective phases.

The CALPHAD approach incorporates experimental data and first principles calculation results into an overall temperature-pressure-composition framework for metal-hydrogen systems with three or more components. Data and functions have been compiled into a consistent database describing the multi-component systems. Missing quantities have been identified, and descriptions are being developed in collaboration with MHCoE partners. The Neumann-Kopp rule for the prediction of heat capacities was modified for more accurate predictions for compounds with anion complexes. This database has been used to calculate the reaction paths in multi-component hydrogen systems. These results are the basis for the evaluation of the suitability of a series of promising light weight hydride mixtures, such as 6$LiBH_4$ + $CaH_2$ or x$LiBH_4$ + $MgH_2$, that have the potential for a favorable hydrogenation/dehydrogenation temperature (for a given pressure) and storage capacities suitable for automotive applications.

While extending the CALPHAD methodology to specific materials systems of interest, NIST is also working to establish a set of reference self-diffusion mobilities to enable more efficient construction of multicomponent diffusion mobility databases in the future. Just as the lattice stabilities for the free energy parameters describing the thermodynamics must be self-consistent within a multicompoent system, so must the pure element self-diffusion mobility coefficients. That is, the values defining the self-diffusion of fcc Ni in the assessed Ni-Al system should be same as those used in the assessed Ni-Cu system. This effort is being initiated in the spring of 2009 with a meeting of selected international experts in diffusion mobility modeling, first principles calculation methods as applied to diffusion, and experimental methods.




*Reaction path for 6$LiBH_4$ + $CaH_2$*

# Learn More

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# Publications

Schmid Fetzer R, Andersson D, Chevalier PY, Eleno L, Fabrichnaya O, Kattner UR, Sundman B, Wang C, Watson A, Zabdyr L and Zinkevich M *Assessment Techniques, Database Design and Software Facilities for Thermodynamics and Diffusion: Group Report from the Ringberg Workshop on Thermodynamic Modeling and First Principles Calculations* CALPHAD, 31: 38 (2007)

Campbell CE *Assessment of the Diffusion Mobilities in the γ′ and B2 Phases in the Ni-Al-Cr System* Acta Mater., 56:4277 (2008)

Moon KW, Kattner UR and Handwerker CA *The Effect of Bi Contamination on the Solidification Behavior of Sn-Pb Solders* J. Electron. Mater., 36:676 (2007)

Kattner UR and Campbell CE *Modeling of Thermodynamics and Diffusion in Multicomponent Systems* Mater. Sci. Tech., In Press (2009)