Calculation of phase equilibria from critically assessed thermodynamic data

Alan Dinsdale
Hampton Thermodynamics, UK
Outline

• Critically assessed thermodynamic data
  o Demonstrate how closely they are linked to phase diagrams
  o What are critically assessed data?

• How thermodynamic data are modelled
  o Temperature
  o Composition
  o Pressure

• Final thoughts
Why calculate phase diagrams?

• Provides way to rationalise different but related sets of experimental properties
• ..... and to extrapolate thermodynamic data from small systems into higher order systems in such a way that they allow prediction of multicomponent phase equilibria
• Now software and data are sufficiently robust for
  o Prediction of the microstructure and properties of materials
  o monitoring and controlling industrial plant
  o choosing materials used in everyday household appliances
  o understanding the way in which materials behave in various environments
Principles of Phase Equilibrium Calculations

G(T,P,x) Model For Each Phase

Experimental Data

Develop Parameters For SMALL Systems To Reproduce Experimental Data

MTDATA

Database

Predictions For LARGE Systems

Problem Solved

Validation

Industrial Problem

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In a nutshell
Model Gibbs energy over a range of temperatures and compositions
.... in order to calculate the phase diagram
What are critically assessed data?
What do we mean by critically assessed data?

- Enthalpies of mixing of liquid Cu-Fe alloys
- Large scatter in experimental values
- Which data best represent reality?
- .. and are these data consistent
- with ...
.... with the experimental phase diagram
...... and measured activity data
What is the aim of a critical assessment?

- To generate a set of reliable data or diagrams which are self-consistent and represent all the available experimental and *ab initio* data
- Involves a critical analysis of the experimental and *ab initio* data
- ... followed by a computer-based optimisation process to reduce the experimental and *ab initio* data into a small number of model parameters
- ... using a rigorous theoretical basis underlying thermodynamics
Critical analysis of experimental data

• Experimental and *ab initio* data: Search and analysis
• Search through standard compilations eg Hultgren, Massalski
• Use a database of references to the literature eg ThermDoc
• Carry out a full literature search
• Which properties
  • Phase diagram information
    o Liquidus / solidus temperatures
    o Solubilities
  • Thermodynamic information
    o Enthalpies of mixing
    o Vapour pressure data
    o Emf data
    o Heat capacities
    o Enthalpies of transformation
• Ab-initio calculations
ThermDoc

- Collection of references compiled by SGTE
- Searchable by system name
- Coverage is general but incomplete
- Free access

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- Comprehensive search of literature for all systems covered
- Analysis of information by team of experts
- Not free
Obtaining model parameters

- Aim is to determine set of coefficients which gives best agreement with experimental data
  - ... by least-squares fitting of the thermodynamic functions to selected set of experimental and \textit{ab-initio} data
- It is usually carried out with the assistance of a computer
  - ... using optimisation software
    - MTDATA optimisation module
    - PARROT (inside ThermoCalc)
    - LUKAS program BINGSS
    - CHEMOPT
Calculated enthalpies of mixing for liquid Fe-Cu alloys
Calculated Fe-Cu phase diagram
Calculated activities for Fe-Cu liquid alloys

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Variation of Gibbs energy of phases at fixed temperature
How to model thermodynamic data

need to understand how $G$ changes with $T$, $P$ and $x$
Variation of Gibbs energy of phases at fixed temperature

Difference in Gibbs energy between fcc and liquid Fe

Difference in Gibbs energy between fcc and bcc Cu

fcc phase is reference for both elements

Change in Gibbs energy with composition is complex

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### §GTE Pure Element Transformation Data

Compiled by A.T. Dinsdale  
Division of Materials Metrology  
National Physical Laboratory  
Teddington, Middlesex, UK

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<th>$\Delta$S(298), J/mol K</th>
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Heat capacity of Sn for different phases

The diagram shows the heat capacity of Sn as a function of temperature. Key points include:

- **BCT_A5**
- **DIAMOND**
- **L I Q U I D**

Notable temperatures:

- **T_{trs}**
- **T_{fus} = 505.078 K**

Temperature range: 200 K to 1600 K

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Enthalpy of Sn relative to 298.15 K
Entropy of phases of Sn

**Graph:**
- **Y-axis:** Entropy / J mol⁻¹ K⁻¹
- **X-axis:** Temperature / K
- **Key Phases:**
  - **DIAMOND_A4**
  - **BCT_A5**
  - **LIQUID**

**Legend:**
- **Sn:** Diagram indicating phase transitions and entropy changes at different temperatures.
Gibbs energy of phases of Sn relative to BCT
Mathematical description of Gibbs energy variation with temperature

• Heat capacity generally represented by 1 or more expressions of the form:
  \[ C_p = a + b \, T + c \, T^2 + d \, T^{-2} \]
  (generally obtained from experiment)
• With enthalpy of formation and entropies at 298.15 K (or transition enthalpies and entropies) this leads to expressions for the Gibbs energy of the form:
  \[ G = A + B \, T + C \, T \ln(T) + D \, T^2 + E \, T^3 + F \, T^{-1} \]
  (relative to some defined reference state)
Magnetic materials

• Magnetism has a big influence on the heat capacity and therefore on the Gibbs energy

Heat capacity of bcc Fe

Gibbs energy of liquid and bcc phases of Fe relative to fcc
Effect of pressure

\[ G = H - TS + PV \]
Effect of composition on Gibbs energy

- Basic approach is to use a simple theory to model what we measure and then
- Fit any discrepancies (excess Gibbs energy) to a power series expression

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Simplest theory – ideal mixing

- Assumes that the components (elements) mix randomly without giving off or absorbing any heat and with no net volume change
- The mixing does result in a change in the entropy and therefore the Gibbs energy

\[ G_{\text{ideal}} = R \ T \ [x_{\text{Fe}} \ ln(x_{\text{Fe}}) + x_{\text{Cu}} \ ln(x_{\text{Cu}})] \]
Real materials – excess Gibbs energy

• In most cases mixing between components (elements) is accompanied by a significant heat effect which may be simple or complex
• The deviation from ideal behaviour may also vary with temperature leading to an “excess entropy of mixing”
Overall Gibbs energy of mixing

- $G(\text{excess})$
- $G(\text{ref Fe})$
- $G(\text{total})$
- $G(\text{ideal})$
- $G(\text{ref Cu})$

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Gibbs energy of binary solutions

\[ G = x_{Fe} G_{Fe} + x_{Cu} G_{Cu} \]

\[ + R \, T \left[ x_{Fe} \ln(x_{Fe}) + x_{Cu} \ln(x_{Cu}) \right] \]

\[ + x_{Cu} x_{Fe} \left[ a + b \, (x_{Cu}-x_{Fe}) + c \, (x_{Cu}-x_{Fe})^2 \right. \]

\[ \left. + d \, (x_{Cu}-x_{Fe})^3 + \ldots \right] \]

where \( a, b, c, d \ldots \) could be temperature dependent

(in practice for Fe-Cu we may need only one or possibly two parameters)
Use of binary data to calculate ternary phase diagrams
From binary to multicomponent

• Multicomponent Gibbs energy given by
  \[ G = \sum x_i G_i + R T \sum x_i \ln(x_i) + G_{\text{excess}} \]

Various models used to extrapolate excess Gibbs energy into ternary and higher order systems from data for binary systems. Extra ternary terms may be used if required.
Compound phases

• Stoichiometric phases: variation of Gibbs energy with $T$ similar to that for phases of elements
• Many important compound phases are stable over ranges of homogeneity. Crystal structure tell us about the sublattices and the preferred occupancy.
  eg: sigma, mu, gamma brass
• Use compound energy formalism to allow mixing on different sites
  Laves phases: $(\text{Cu},\text{Mg})_2 (\text{Cu},\text{Mg})_1$
  Interstitial solution of carbon: $(\text{Cr},\text{Fe})_1 (\text{C},\text{Va})_1$
  Spinels: $(\text{Fe}^{2+},\text{Fe}^{3+})_1 (\text{Fe}^{2+},\text{Fe}^{3+})_2 (\text{O}^2-)_4$
Gibbs energy using compound energy formalism eg \((\text{Cu},\text{Mg})_2 (\text{Cu},\text{Mg})_1\)

- Gibbs energy again has 3 contributions
- Pure compounds with element from each sublattice
  \(\text{Cu}:\text{Cu}, \text{Cu}:\text{Mg}, \text{Mg}:\text{Cu}, \text{Mg}:\text{Mg}\)
- Ideal mixing of elements on each sublattice
  \(\text{Cu}\) and \(\text{Mg}\) on first and on second sublattices
- Non-ideal interaction between the elements on each sublattice but with a specific element on the other sublattice
  \(\text{Cu},\text{Mg}:\text{Cu} \quad \text{Cu},\text{Mg}:\text{Mg} \quad \text{Cu}:\text{Cu},\text{Mg} \quad \text{Mg}:\text{Cu},\text{Mg}\)
Gas phase data

- Assume ideal mixing between gas phase species eg. H₂, H, O₂, O, O₃, H₂O, H₂O₂
- Gas phase entropy and heat capacity usually calculated from statistical mechanics
- Experimental vapour pressure data then used to determine enthalpies of formation
- Molecular constants could be determined in principle from spectroscopic information
- *Ab initio* quantum mechanics is used when no spectroscopic data are available
Zn<g> electronic energy level data

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Calculated $C_p\ Zn^{<g>}$
Zn vapour pressures
Data for $S_8$
Gibbs energy C-O(gas) system
Enthalpy C-O(gas) system
Associated solution model

• Some liquid phases also show very sharp and negative curves of Gibbs energy of mixing with composition
  o Cu-S, Ni-S, Fe-S
  o Cr-O, Si-O
  o CaO-SiO$_2$, MgO-SiO$_2$

• The thermodynamic properties of such systems may also be modelled in terms of the formation of mixing of “species” in the liquid
  o Cu, Cu$_2$S, S
  o CaO, Ca$_2$SiO$_4$, CaSiO$_3$, SiO$_2$

• In such cases the mixing will often be non-ideal
Oxide liquid modelled as non-ideal mixture of species
Gibbs energy of CaO-SiO$_2$ liquid at 2000 K
Enthalpy of CaO-SiO$_2$ liquid at 2000 K
Other models for liquid phases

• Ionic liquid model
  o Assumes the existence of separate sublattices for cations, and for anions + neutral species
    • $\text{Ca}^{2+}_p \text{O}^{2-}_q \text{SiO}_2, \text{SiO}_4^{4-}$
    • The ratio of the sites varies to maintain electroneutrality
    • Similar (sometimes exactly equivalent) to associated solution model
    • Used mainly by colleagues at Royal Institute of Technology in Stockholm

• Modified quasi-chemical model
  o Different basis for ideal entropy of mixing
    • Most other models assume ideal mixing between atoms and species. Interaction terms introduced to compensate for any non-ideality
    • Modified quasichemical model assumes a random distribution of bonds throughout the liquid (instead of species)
    • This leads to a very different ideal of entropy of mixing
    • ...... and complicated mathematical descriptions of thermodynamic functions
    • Used with success especially by group in Montreal
    • It is really the only successful model for complex molten salt systems

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Final thoughts

• Now possible to calculate phase equilibria for a wide range of materials
• They rely on good quality critically assessed data compiled into comprehensive databases
• These in turn rely on high quality experimental data and ab initio data where available
• A number of organisations are involved in developing databases
• Other sorts of properties can be modelled from a thermodynamic basis (eg. surface tension, viscosity)
Thank you for listening
Applications
Liquidus projection for solders
Isopleths: Mixing electrician’s solder with lead free solder
Plot of mass of phases with variation of temperature
Calculated heat capacity and volume change
Use of thermodynamic data to predict thermophysical properties
Calculation of surface tension: equilibrium between bulk and surface
Calculated viscosity

Viscosity of CaO-SiO$_2$ liquids

Viscosity of CaO-MgO-Al$_2$O$_3$-SiO$_2$ liquids

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Engineering toolkits
Virtual Measurement Systems

- Use MTDATA to calculate properties such as liquidus and solidus temperatures, enthalpy, heat capacity and density
- Develop and use thermodynamics as basis for modelling other thermophysical properties
- Simple interface - user is shielded from complexity of models
- Easy to export data to Excel and other software
### Amalgam Toolkit for compact fluorescent lamp design

- **Provide an easy to use tool for lamp design engineers**
- **Amalgam thermodynamic database + MTDATA api**
- **Automatic selection of elements and compositions for amalgams to optimise light output**
- **Light output calculations derived from calculated materials chemistry**

**Diagram: GE Amalgam Toolkit: Amalgam database for use by GE Lighting v4.2 - 26 January 2000**

**Amalgam Compositions**

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**Properties for unchanged amalgam**

- pHg (mm Hg) = 6.36
- Relative light output = 95.0%

**Properties for modified amalgam and lamp**

- Amalgam temperature = 95°C
- Limiting pHg (mm Hg) = 6.26
- Real pHg (mm Hg) = 6.26

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Relative Light Output results

Non cylindrical Genura type - *(56Bi+44In) + 1.3 mol % Hg

![Graph showing relative light output vs amalgam temperature for different Hg concentrations.](image)
Ab-initio techniques

- DFT can be used to supplement experimental thermodynamic measurements
  - Enthalpy differences between phases of pure elements
  - Enthalpies of formation of intermetallic phases for 0 K
  - Results are as good as experiment if crystal structure is well known and no magnetism involved

- Heat capacities of phases of elements and compounds at elevated temperatures – expensive calculations and not as good as experiment at the moment but could potentially be used to estimate entropies