Experimental Techniques

Andy Watson

The University of Leeds
Outline

• **Phase Diagram**
  - Phase Diagram - Dynamic
    • Liquidus & Solidus
      - Thermal Analysis
        - DTA
        - DSC
  - Phase Equilibria - static
    - XRD
    - EPMA
      » Diffusion couple studies

• **Thermodynamic Properties**
  - Enthalpies of formation, enthalpies of mixing, Cp
    • Calorimetry
  - Activities / partial Gibbs energies
    • Effusion
      – Knudsen cell
      – Torsion
    • EMF studies
Determination of Phase Diagrams
Thermal Analysis

![Diagram of phase diagram and thermal analysis]

**Figure:**

- **DTA** and **Heat Flux DSC**
- **Phase Diagram:**
  - Liquid
  - BCC_A2
  - BCC_A2 + NiV3
  - Ni2V + SIGMA
  - FCC_A1 + Ni3V
DTA Signal

[Graph showing DTA Signal for Cooling and Heating processes]
DTA of Al:Ni 50:50 (mass%)
Non-dynamic methods (X-ray analysis)

\[ n\lambda = 2d\sin\theta \]

Point where incident beam enters ($2\theta = 180^\circ$)

\[ 2\theta = 0^\circ \]
Scanning Electron Microscopy
a) 10 keV
b) 20 keV
c) 30 keV

Activation volume
Determination of thermodynamic properties
Background

- Calculating phase equilibria
  - *Using thermodynamics*
Background

• Calculating phase equilibria
  – Using thermodynamics
    • Need to have a correct description of thermodynamic properties
      – Temperature dependence of Gibbs energy
        » Calculations related to Heat changes
        » Solidification modelling
        » Thermophysical properties – modelling of surface tension
  – Not enough to have the phase diagram
What do we want to measure?

• Enthalpies of formation (reaction)
  – $\Delta_f H$, $\Delta_r H$
• Heat capacities
  – $C_p$
• Enthalpies of mixing (solution phases)
  – $\Delta H_{mix}$
• Enthalpies of transformation
  – $\Delta H_{tr}$
• Component activities in solutions
  – $a(m)$
• Vapour pressures
  – Partial pressures, total pressure.....
Isoperibol Calorimeter

$Ts = \text{constant}$

- **Surroundings**
  - Held at constant temperature

\[Q_T = W\Delta T\]
Isothermal Calorimetry

- $T_s = T_c = \text{constant}$
  - No temperature rise, temperature not measured
- Heat evolved melts solid
  - Measure amount of liquid produced
  - Calculate heat evolved from Heat of fusion

Ice calorimeter (Bunsen)
Adiabatic Calorimetry

- $T_s = T_c \neq \text{constant}$
  - No heat losses to the surrounding

- Measure the heat input to raise sample over a prescribed temperature range.
Adiabatic Calorimetry (Direct reaction)

- Determination of enthalpies of formation.
- Sample heated from ‘safe’ temperature to ‘final’ temperature
  - Safe = max. temperature where no alloying takes place
  - Final = min. temperature where complete alloying takes place within 30 mins

\[
\begin{align*}
    m_1 + m_2 & \rightarrow m_1 m_2 & \Delta H_1 \\
    T_s & \quad T_f \\

    m_1 + m_2 & \rightarrow m_1 + m_2 & \Delta H_2 \\
    T_s & \quad T_f \\

    \Delta f H (T_f) & = \Delta H_1 - \Delta H_2
\end{align*}
\]
Enthalpies of Formation of Cr-Ni alloys at 1265°C
Heat-flow calorimeters

- **Tian-Calvet**
  - Reaction vessel connected to surroundings by a series of thermocouple junctions
  - **Thermopile**

- Heat flow between reaction vessel and surroundings realised as an emf
  - **Seebeck effect**

  \[
  \varepsilon = \frac{dE}{d\theta} \quad \varepsilon = \text{thermoelectric power} \\
  E = \text{emf} \\
  \theta = \text{temperature} \\
  \]

For \( n \) thermocouples

\[
E = n\varepsilon (\theta_A - \theta_C)
\]

Total emf in relation to heat flux:

\[
E = \frac{\varepsilon \lambda}{C} \Phi
\]

Proportion of the heat flux conducted by a single thermocouple wire:

\[
\lambda \Phi_1 = C(\theta_A - \theta_C)
\]
Twin microcalorimeter

A: Main Heater
B: Top Heater
C: Heat Shield
D: Aluminium/nickel jacket
E: Calorimeter
F: Protection Tube
G: Radiation Shields
H: Dropping Tube

Kleppa (500/800°C)
SETARAM HT1500

Water-cooled vertical furnace

Thermopile

Calorimeter
Drop Calorimetry

- Sample is dropped into the calorimeter
  - From $T_1$,
    - Typically room temperature
  - To $T_2$
    - The calorimeter temperature

Electrical output from thermopile

\[ H(T_2) - H(T_1) \]
\[ H(T_2) - H(T_1) + \Delta H \]
Direct Reaction Calorimeter

Samples are synthesized directly in the calorimeter starting from a mixture of the finely powdered components.

High T drop calorimeter

Mass ≈ 1g
Ta crucible
Arc-welding under argon

Enthalpy of Formation by Direct Reaction Drop Calorimetry

First drop (reaction drop)

\[ Q_1 = \Delta H(cru, Tc-Tr) \]
\[ + x\Delta H(A, Tc-Tr) \]
\[ + y\Delta H(B, Tc-Tr) \]
\[ + z\Delta H(C, Tc-Tr) \]
\[ + \Delta_f H(A_xB_yC_z, T_c) \]

Second drop (reference drop)

\[ Q_2 = \Delta H(cru, Tc-Tr) \]
\[ + \Delta H(A_xB_yC_z, Tc-Tr) \]

\[ \Delta_f H^\circ (A_xB_yC_z, T_r) = Q_1 - Q_2 \]

4Au + 3In + 3Sn = Au_4In_3Sn_3

\[ Q_1 \]
300K \hspace{1cm} 653K

\[ \text{Au}_4\text{In}_3\text{Sn}_3 = \text{Au}_4\text{In}_3\text{Sn}_3 \]

\[ Q_2 \]
300K \hspace{1cm} 653K

\[ \text{Au}_4\text{In}_3\text{Sn}_3 : \Delta_f H^0 = -21.0 \pm 1.0 \text{ kJ/mol.at.} \]
Enthalpy of Formation by Metal Dissolution Drop Calorimetry

Samples are dissolved in an appropriate solvent
*moles solvent* → *moles solute*

Samples of the component elements
Samples of the compound of interest

\[
\begin{align*}
\text{Au} \ (T_1) + \text{Sn} \ (T_2) &= [\text{Au}]_{\text{Sn}} \ (T_2) \quad & Q_1 \\
\text{In} \ (T_1) + \text{Sn} \ (T_2) &= [\text{In}]_{\text{Sn}} \ (T_2) \quad & Q_2 \\
\text{Sn} \ (T_1) &= \text{Sn} \ (T_2) \quad & Q_3 \\
\text{Au}_4\text{In}_3\text{Sn}_3 \ (T_1) + \text{Sn} \ (T_2) &= [4\text{Au} + 3\text{In}]_{\text{Sn}} \ (T_2) \quad & Q_4
\end{align*}
\]

\[
4\text{Au} \ (T_1) + 3\text{In} \ (T_1) + 3\text{Sn} \ (T_1) = \text{Au}_4\text{In}_3\text{Sn}_3 \ (T_1)
\]

\[
\Delta_f H (\text{Au}_4\text{In}_3\text{Sn}_3) = 4Q_1 + 3Q_2 + 3Q_3 - Q_4
\]

\[
= -23.7 \text{ kJ/mol}
\]
Enthalpy of Mixing by Metal Dissolution Drop Calorimetry

Small solute samples added incrementally to liquid solvent

\[ x_1 \text{Au (cr, } T_1) + In_y Sn_z (\text{sol'n, } T_2) \rightarrow Au_{x_1} In_y Sn_z (\text{sol'n, } T_2) \quad Q_1 \]

\[ x_2 \text{Au (cr, } T_1) + Au_{x_1} In_y Sn_z (\text{sol'n, } T_2) \rightarrow Au_{x_1 + x_2} In_y Sn_z (\text{sol'n, } T_2) \quad Q_2 \]

\[ Q_i = x_i (H(\text{Au, cr, } T_2) - H(\text{Au, cr, } T_1)) + x_i \Delta H(\text{fus, Au, } T_2) + \Delta H_{r,i} \]

\[ h_i \approx \Delta H_{r,i} / x_i \]

\[ \Delta H_{\text{mix}} = \frac{(y + z) \Delta H_{m,B} \sum_i \Delta H_{r,i}}{y + z + \sum_i x_i} \]
Integral Enthalpies of Mixing of Au-In-Sn alloys

Thermogram
Determination of component activities in solutions
Determination of Component Activities

Change of pressure of 1 mole of A from $p^\circ$ to $p$

Vaporise 1 mole of A under equilibrium conditions

$\Delta G_1 = 0$

Condense 1 mole of A under equilibrium conditions

$\Delta G_3 = 0$

Transfer of 1 mole of A

$\Delta G_A = \Delta G_1 + \Delta G_2 + \Delta G_3$

$\Delta G_A = RT \ln \frac{P_A}{P_A^\circ}$

$\Delta G_A = RT \ln a_A$

Pure A

Alloy of A
Knudsen Effusion

**Tracer Method**

Samples made using radioactive Cr
Effusing species condenses in Mo tube and on target
Collected by dissolution in acid
Mass effused determined by radiochemical assay

\[ p = \frac{m}{tA} \sqrt{\frac{2\pi RT}{M}} = 0.02256 \frac{m}{tA} \sqrt{\frac{T}{M}} \]

\[ p = \text{pressure of effusing species} \]
\[ m = \text{mass of material effused} \]
\[ t = \text{effusion time} \]
\[ A = \text{cross-sectional area of effusion orifice} \]
\[ T = \text{temperature} \]
\[ M = \text{molecular mass of effusing species} \]

Kubaschewski & Heymer, Acta. Met., 1960, 8, 416
Knudsen Effusion + Mass Spectrometry

- Molecular beam from K cell ionised by beam of monoenergetic electrons
  - Ions produced per unit time is proportional to molecular beam flux
    - Related to pressure
    - Related to nature of effusing species
      - Charge/mass ratio

Time of Flight

- Pulsed accelerating potential
- Allows ions to be separated in group of constant ‘Time of Flight’
- Fast analysis of a number of ionic species

Magnetic Separation

- Constant accelerating potential
- Fixed magnetic field separates ions into groups of constant charge/mass ratio
- Continuous analysis – higher sensitivity
Knudsen Effusion + Mass Spectrometry
Knudsen Effusion + Mass Spectrometry

\[ p_i = \text{pressure of effusing species} \]
\[ S_i = \text{sensitivity of the mass spec.} \]
\[ I_i = \text{ionic intensity for species } I \]
\[ T = \text{Cell temperature} \]

\[ p_i S_i = I_i T \]

\[ S_i = A \sigma_i \gamma_i f_i \]

\( A = \text{geometrical factor of the coupling of the } K \text{ cell and the mass spec.} \)
\( \sigma_i = \text{ionisation cross-section} \)
\( \gamma_i = \text{detector yield} \)
\( f_i = \text{isotopic abundance} \)

\[ a = \frac{p}{p^0} = \frac{IT}{S} \frac{S^0}{I^0 T^0} = I \frac{A^0}{I^0} \frac{A}{A} \approx \frac{I}{I^0} \]
Dual Cell
EMF methods
EMF Methods

Pt <M, MO> | electrolyte | (O₂, 1 atm) Pt

\[ \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \]

M + O^{2-} \rightarrow MO + 2e^-

\[ \frac{1}{2}O_2 + <M> \rightarrow <MO> \]

\[-\Delta G^o = zFE^o\]
Electrolytes

• **Liquid**
  - Mixtures of molten salts
    • LiCl-KCl eutectic mixture
      - Lead-free solders
      - In-Sn, Sb-Sn....
    • LiCl-RbCl
      - Lu-Pb
    • KCl-LiCl-BaCl$_2$
      - Pb-Pd

• **Solid**
  - Current carried by ions
  - Halides, sulphides, chlorides
  - Caused by lattice defects
    • Doping with aliovalent ions -> vacancies
    • ZrO$_2$ based
      - CaO, MgO Y$_2$O$_3$
EMF studies of $a_{\text{In}}$ in Ag-Cu-In liquid alloys

Leszek Zabdyr, IMM/PAS, Krakow, Poland
(-) Kanthal, Re $\Box$ Ag-Cu-In, $\ln_2\text{O}_3(s)$ $\Box$ ZrO$_2$ - $\text{Y}_2\text{O}_3$ $\Box$ Ni(s), NiO(s) $\Box$ Pt(+)


(+) $3\text{NiO} \rightarrow 3\text{Ni} + 3/2 \text{O}_2$ - 6e
(-) $2\text{In} + 3/2 \text{O}_2 \rightarrow \text{In}_2\text{O}_3 + 6e$

$3\text{NiO} + 2\text{In} + 3/2\text{O}_2 \rightarrow 3\text{Ni} + 3/2\text{O}_2 + \text{In}_2\text{O}_3$

$\Delta G = -6FE = 3\mu^O_{\text{Ni}} + 3/2\mu^O_{\text{O}_2} + \mu^O_{\text{In}_2\text{O}_3} - 3\mu^O_{\text{NiO}} - (2\mu^O_{\text{In}} + 2RTlna_{\text{In}}) - 3/2\mu^O_{\text{O}_2}$


\[ \text{ln}a_{\text{In}} = \frac{-3\Delta G^o_{f,\text{NiO}} + \Delta G^o_{f,\text{In}_2\text{O}_3}}{2RT} + \frac{3EF}{RT} \]

where: $\Delta G^o_{f,\text{NiO}}$ and $\Delta G^o_{f,\text{In}_2\text{O}_3}$ - Gibbs energies of formation of nickel and indium oxides, respectively;

F - Faraday constant;
R – gas constant;
E – electromotive force;
In Activity in liquid Ag-Cu-In at 1273K

$X_{Cu}/X_{In} = 1$

$X_{Cu}/X_{In} = 1/3$

$X_{Cu}/X_{In} = 3$
Conclusions……

• Experiments are *still* important
• Range of techniques available
• Complementary to *ab initio* techniques for improved modelling
• *We need more experiments*
Thank you