

Experimental Methods for the Measurement of Thermodynamic Data and Recommendation about Future Capability at NPL

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Abstract

The types of data required for the thermodynamic modelling of multicomponent systems is described, and the reason why both phase equilibria measurements and thermodynamic properties such as enthalpy, heat capacities and heats of mixing are needed is explained.

The problems associated with conventional thermal analysis techniques when used for the determination of phase boundaries are highlighted. The technique of Smith thermal analysis (SMTA) is described and the reasons why it is better than conventional thermal analysis are discussed. The ways that the current use of SMTA at UMIST can be improved and extended are outlined.

Recommendations for future thermodynamic experimental capability at NPL are given. There is a need to get both phase boundary information and thermodynamic properties to enable thermodynamic modelling of multicomponent systems. The purchase of a calorimeter for the measurement of various thermodynamic properties and the development of the Smith thermal analysis technique for the determination of phase boundaries are recommended.

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by Dr C Lea, Head, Centre for Materials Measurement and Technology.

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Types of data required

An important application of thermodynamic data is for calculation of thermochemical equilibrium. A typical problem would be to calculate the nature and individual compositions of the phases present at equilibrium for a given overall composition and fixed temperature and pressure. Many variations are possible: for example it is possible to determine ;

- the temperature that will be reached when a combination of substances is reacted,
- the initial composition to ensure the presence of a given amount of a phase of arbitrary or defined composition,
- the partial pressure of gases needed to achieve a given product,
- the emf of cells.

The particular power of thermodynamic modelling derives from the fact that it is not necessary to have studied systems of more than 3 or 4 components in order to calculate the behaviour of higher order systems that are very common in commercial alloys and the norm in both primary and secondary pyrometallurgy.

The fundamental thermodynamic property that determines the phase equilibrium at constant pressure is the Gibbs energy, G . This is not an absolute quantity but requires a reference state such as that adopted within SGTE [91Din], the data for the pure chemical elements in their stable phases at 298.15 K. The Gibbs energy for a phase contains 6 main contributions.

- H The 'standard' enthalpy of formation of each pure component at 298.15 K and 1 atm pressure,
- S The 'standard' entropy of each pure component at 298.15 K and 1 atm pressure,

- C_p The heat capacity as a function of temperature of each pure component,
- G^P Terms that express the pressure dependence of the Gibbs energy,
- G^M Terms that express the change of Gibbs energy in a magnetic field,
- G^{ex} Terms that express the variation of the Gibbs energy with composition and temperature in non-ideal solutions, as for example in a single phase alloy. Terms involving 2 or 3 components are usual.

In the above 'pure components' may be compounds.

Just as it is possible to calculate phase equilibria using the thermodynamic functions, the reverse is also possible but with limitations.

- The observations must be sufficient to be able to refer the data back to common reference states, usually the elements in their standard states.
- The observations must be made over a sufficient range of temperature and composition so that all the terms above can be deconvoluted.

Unless these criteria are met it will not be possible to use the resultant thermodynamic data to model the behaviour of systems at temperatures, pressures and compositions different from those that have been measured. For example, phase equilibria measurements in Al containing systems determined for concentrations up to 10 %Al for application in calculations on steels would be of little use as a basis for calculations on aluminium alloys.

For generality it is much better to include, as part of an overall critical assessment of a system, measurements of the thermodynamic properties made independently, i.e. enthalpy, heat capacity and heats of mixing. These data provide an anchor for data derived solely from measurements of phase equilibria.

This said it must be remembered that data are needed for substances and conditions that are experimentally inaccessible. For example, in order to calculate the solution of chromium in austenitic steels it is necessary to include terms for the enthalpy and entropy and heat capacity of pure fcc chromium that cannot be

measured because fcc chromium is unstable. Such data may be derived by estimating the data from several starting points, including the effect of temperature and pressure on phase boundaries for a range of related systems. The more soundly based the data are for these related systems the more accurate will be the extrapolated data. Theoretical calculations, as they become more accurate, are also making increasing contributions to uncertain data.

In recent years there has been a tendency for fewer measurements to be made of the fundamental thermochemical data needed for thermodynamic modelling. Measurements of these data are now required in order to underpin predictive modelling of metallurgical processes. Also, because of the lack of measurements, the development of measurement methods has been neglected, so there are opportunities to exploit the general advances made in instrumentation and control systems in recent years.

The following types of data are needed.

- Enthalpies of reaction
- Enthalpies of mixing
- Heat capacity data for solids and liquids
- Measurements of phase boundaries
- Volumes as a function of pressure and temperature.

Table 1 summarises the main methods that could be used and their advantages and disadvantages.

Table 1 - Summary of experimental methods

Method	Property determined	Remarks
Calorimetry		
Drop calorimeter	Enthalpy increments, heat capacity	Direct but slow and complex
Solution calorimeter	Enthalpies of reaction and solution	Direct and indirect methods. In the indirect method substances before and after reaction are dissolved in a suitable solvent and the enthalpy difference determined.
Adiabatic calorimeters	Heat capacity, enthalpies of reaction and solution	Good accuracy but slow.
Differential scanning calorimetry	Heat capacity, transition enthalpies	Rapid but relatively low accuracy. Neighbouring transitions not well resolved.
Combustion bomb calorimetry	Enthalpies of formation for compounds	Primary method. A suitable combustion agent is needed.
Aqueous solution calorimetry	Enthalpies of solution and hydration	Limited new opportunities.
Calvet calorimeter	Heat capacities, enthalpies of reaction and solution	Many variants. High accuracy. Commercially available.
Smith thermal analysis	Phase boundaries, heat capacities, enthalpies of reaction	Phase transition temperatures well established. Neighbouring transitions very well resolved. Enthalpy data not of highest accuracy.
Equilibrium methods		
Vapour pressure	Gibbs energies of vaporisation	Vapour pressure may be measured manometrically or by mass loss and torsion. Species not determined. Measurement of vapour pressure of reactive gases difficult.
Effusion studies	Gibbs energies of vaporisation	Vapour species not determined (see above), requires calibration
Effusion with mass spectrometer	Gibbs energies of vaporisation	Equipment expensive and requiring extensive calibration
Isopiestic studies	Gibbs energies of solution	Specialised applications but accurate
Partial pressure measurements	Gibbs energies of solution or decomposition	Species need to be identified. Reactive gases difficult to handle. Compositions can be determined by "titrating" the gas.
Equilibration with flowing gas mixtures	Gibbs energies of solution and decomposition	Can mimic commercially important process. Species need to be identified. Reactive gases difficult to handle.

Reaction and transportation	Gibbs Energies of reaction and solution.	Indirect method in closed vessel with temperature profile. Mimics CVD. Data may be difficult to deconvolute.
Quenching studies	Compositions of phases in equilibrium. Gibbs energies of compounds and solution phases	The product must cool with minimal compositional changes. The composition of the phases must be determined or inferred. Chemical analyses can be undertaken by wet chemical analysis, x-ray fluorescence or in an electron microscope. Very suitable for silicate slags.
High pressure studies of phase equilibria	Gibbs energies as a function of pressure. Transition and reaction data.	Provides data for geology and HIP processing and extends data for phases that are unstable at ordinary pressures.
EMF studies	Gibbs energy differences	Very wide range of applicability but electrolytes must be carefully matched to the problem. The reversible reaction at each electrode must be established. Therefore most suitable for measurements in a single materials area.
Physical measurements		
Compressibility	Compression energy	High temperature facilities uncommon.
Dilatometry	Volume expansion coefficient with temperature	Problems with reactive and volatile materials.
High temperature X-ray diffraction	Temperature coefficients of volume and linear, possibly anisotropic, expansion.	High temperature X-ray studies difficult, very difficult on reactive materials.

In all the methods listed in Table 1 problems are found with containing reactive materials, characterising the materials, calibrating the equipment, determining sources of error and providing routes that enable the thermodynamic data to be referred back to the elements at 298.15K. These problems tend to become more severe at higher temperatures.

Experimental Techniques for Determining Phase Boundaries

The methods that can be used vary widely. There are techniques which measure a certain property of a sample as its composition or temperature changes, and rely upon this property changing discontinuously as a new phase appears. These techniques include thermal analysis, mechanical testing, x-ray diffraction and electrical resistivity measurements. Other methods, such as electron micrography, measure the compositions of the phases in equilibrium.

Conventional thermal analysis techniques

There are a number of thermal analysis techniques that can be used, of which Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) have emerged as the most popular. In a conventional DTA experiment the temperature of the furnace is raised or lowered at a fixed rate and the difference in temperature between the sample and an inert standard reference material is measured. When a thermal event, which can be either exothermic or endothermic, occurs within the sample, a difference in temperature is developed between the sample and the reference. With these methods the energy input to the furnace does not respond to the events taking place in the sample. As the temperature of the furnace changes, the temperature of the sample will change at a rate governed by the temperature difference between the furnace and the sample, as long as the sample remains single phase. When the sample undergoes a phase change, the rate of change of temperature in the sample slows or stops. As the furnace temperature continues to change at the same rate the temperature difference between the sample and the furnace increases, and so the rate of heat input into or removed from the sample increases. This causes the phase change to be accelerated which means that the sharpness of the effect is lost and so phase boundaries that are thermally close cannot be resolved. If the phase change is an invariant reaction then the situation can be made worse, as the rate of heat input into the sample increases with time. This problem can also cause very weak effects not to appear.

Other problems can occur within alloys that are susceptible to coring. Coring is the phenomenon when relatively large composition variations are generated within an alloy during solidification. Spurious thermal arrests can sometimes be indicated where no equilibrium phase boundary exists due to concentration variations within the specimen. This problem can be resolved by quenching the sample from a temperature above its liquidus when it is made, to produce a very fine grain size and so reduce coring. Possible thermal arrests are then analysed in a cyclic manner, by repeated thermal cycling through the temperature region of interest. If the effect is seen each time, the boundary is there, but if the signal gradually weakens and then disappears there is no boundary. This type of thermal cycling requires a furnace with a low thermal mass, and it is difficult to achieve using conventional DTA equipment.

DSC is a similar technique to DTA, but the measurement taken is the heat input required to keep the sample at the same temperature as a control sample. This technique has a great importance in the determination of heats of invariant reactions, which are very important values in the determination and the thermodynamic assessment of phase diagrams.

Smith Thermal Analysis (SMTA)

The problems associated with standard thermal analysis techniques, as outlined above, can be partly solved using a technique first proposed in 1940 [40Smi], now known as Smith Thermal Analysis (SMTA). The basic principle behind SMTA is to use the temperature of the specimen to control the temperature of the furnace. In practice the only control needed to achieve this is to maintain a fixed temperature difference between the sample and the furnace. This means that the rate of change of temperature of the furnace is not fixed, as in conventional methods of thermal analysis, but will change to match the rate of change of temperature of the sample.

Consider n moles of a specimen with cross section area A , contained in a furnace which has a thermocouple next to its windings a horizontal distance s from another thermocouple in the specimen. Assuming that heat transfer occurs mainly by conduction the amount of heat supplied to the sample, Q , in time δt is given by equation 1.

$$Q = k \cdot A \cdot \left[\frac{(T_{\text{specimen}} - T_{\text{furnace}})}{s} \right] \cdot \delta t \quad (1)$$

where T_{specimen} and T_{furnace} are the temperatures of the specimen and furnace respectively, and k is a constant dependent on the thermal conductivity of the furnace and specimen tube materials.

If the specimen has a molar heat capacity of C_p , the amount of heat supplied to it to produce a temperature change of δT is given by equation 2.

$$Q = n \cdot C_p \cdot \delta T \quad (2)$$

Equating the above two expressions for Q gives equation 3

$$\frac{\delta T}{\delta t} = \left[k \cdot A \cdot \frac{(T_{\text{specimen}} - T_{\text{furnace}})}{n \cdot s} \right] \cdot \frac{1}{C_p} \quad (3)$$

This equation mathematically describes the Smith Thermal Analysis technique. As stated previously the temperature difference between the sample and the furnace ($T_{\text{specimen}} - T_{\text{furnace}}$) is set for the duration of an individual experiment and for a particular specimen k , A , n and s will be constant, and so the term in square brackets is a constant for a given analysis. Therefore the only variable is the heat capacity of the material under test, C_P . If the temperature of the sample is measured over time the rate of change of temperature with time of the sample ($\delta T/\delta t$) can be determined easily.

For a single phase material, C_P is generally not strongly temperature dependent over a fairly small range of temperature so $\delta T/\delta t$ will be roughly constant. For two phase regions (in binary and ternary systems) and two or three phase regions (in ternary systems) the effective heat capacity of the sample will change as the fractions of the phases present in the sample change. The effective heat capacity of the sample will be a weighted average of the heat capacities of the phases in the sample plus an extra heat effect derived from the enthalpy of transformation of one phase to another.

When a phase boundary is crossed either a new phase will start to form or a phase that was decreasing in amount will disappear. This will cause $\delta T/\delta t$ to start to change at a different rate. This can be seen on a plot of $\delta T/\delta t$ versus time, so the temperature at which the change occurred, and hence the temperature of the phase boundary, can be found. When a phase boundary is crossed into a region with more phases, the new phase will not normally start to precipitate immediately as a temperature difference is required to generate a driving force for nucleation. When the precipitation does start there will be a sudden heat effect which will cause a peak in the $\delta T/\delta t$ curve. The formation of a peak when a phase boundary is being crossed into a region containing a greater number of phases, means that these boundaries are easiest to detect. Therefore liquidus and secondary phase separation temperatures are best detected on cooling and solidus temperatures are best detected on heating.

When an invariant reaction is encountered, all the heat put into or removed from the sample is the enthalpy of the invariant reaction with no changes in temperature of the sample. Consequently the effective C_p of the sample increases to infinity and, according to equation 3, $\delta T/\delta t$ drops to zero. However, as a fixed temperature difference is maintained between the sample and the furnace, the rate of change of temperature of the furnace will also drop to zero. This means that the invariant reaction is allowed to go to completion before the furnace temperature starts to change again, and then $\delta T/\delta t$ will change from zero to a new value depending on the heat capacities of the phases now present in the sample and any enthalpy of transformation between those phases. The conditions in the sample are therefore maintained much closer to equilibrium than in a conventional thermal analysis experiment where the furnace temperature would continue to change regardless of the temperature of the sample.

Since invariant reactions are allowed to go to completion the start temperatures of slower invariant reactions, phase boundaries and weak thermal arrests are not masked and so their temperatures can be determined accurately. Also invariant reactions that are very close in temperature can be resolved, as the first reaction is allowed to finish before the temperature of the furnace starts to change again. In a study of the Ag-Cd-In system the temperatures of two invariant reactions (a eutectic and a eutectoid) were resolved even though they are only 1.8 °C apart [92Hor/Hay].

It can clearly be seen that a very important aspect of this technique is the necessity for the furnace to respond very quickly, to match the changes in the temperature of the sample. Therefore the furnace needs to have a low thermal mass and the sample used is larger (1.5 - 2 g) than in conventional thermal analysis.

The low thermal mass furnace also allows thermal cycling over fairly small temperature ranges (20 - 30 °C), in order to repeat the same thermal arrest a number of times to confirm it. This enables the elimination of spurious thermal effects caused, for example, by coring, as effects like this will get smaller and then disappear when

repeated a number of times.

Recommendations for experimental capability

The basic requirement is to be able to model phase equilibria in multicomponent systems. Fundamental to this is the need to determine experimentally the phase equilibria of the subsystems. With this information it is possible to model these phase equilibria for the range of compositions and temperatures over which they exist in the sub-systems studied. However to use the data from the low order systems to model phase equilibria in the multicomponent systems, without experimental data in those systems, the most important additional need is for enthalpy and heat capacity data in the low order systems. These data can be determined by calorimetry. With these additional data the standard entropy and entropy of mixing can be determined.

Therefore the basic experimental requirements are :

- equipment for measurement of phase equilibria and characterisation of the substances involved.
- versatile calorimetric equipment.

Of the calorimetric methods described above, a variant of the Calvet calorimeter is probably the best choice because of its sensitivity. This type of calorimeter is available commercially and with appropriate modifications would be suitable for the measurement of various thermodynamic properties of interest. Instruments are available for measurements from room temperature up to about 1500 °C.

For the determination of phase equilibria the Smith thermal analysis technique is recommended to enable the accurate determination of phase boundaries, especially liquidus temperatures. This technique has been used with success at The Materials Science Centre of The University of Manchester / UMIST [92Hor/Hay, 94Hay/Cha1, 94Hay/Cha2], in particular with systems that have proved difficult to study with other thermal analysis techniques. The system is not available commercially so would need to be built in-house. The system in use at UMIST has not been developed to its full potential and would benefit considerably from modernisation of the control

and data logging systems.

The Smith technique could also be extended to measure heat capacities and enthalpies of invariant reactions to complement the calorimeter. Although the SMTA technique was not used in this way at UMIST, it was proposed as the principle use of the method in the original paper [40Smi].

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