

REPORT

UK requirements for thermodynamic data for high temperature processing of metallic materials

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UK REQUIREMENTS FOR THERMODYNAMIC DATA FOR HIGH TEMPERATURE PROCESSING OF METALLIC MATERIALS

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ABSTRACT

A survey of current and future use of thermodynamic data for modelling high temperature processing of metallic materials is presented. Thermodynamic and phase diagram data have been published in a variety of forms; raw experimental data, compiled, critically assessed, computer compilations of these and computer databases linked directly to sophisticated software for the calculation of phase equilibria. These sources of information are listed in this report and some indication given as to the quality of the information stored.

The report also explains the background to the calculation of phase equilibria and the benefits that can be obtained from use of such techniques.

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Approved on behalf of the Managing Director, NPL, by Dr C Lea
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UK REQUIREMENTS FOR THERMODYNAMIC DATA FOR HIGH TEMPERATURE PROCESSING OF METALLIC MATERIALS

1 Introduction

The aim of this document is to provide a survey of the current use in the UK of thermodynamic data used in the modelling of high temperature processing of metallic materials and to identify future requirements both in terms of the data and in terms of the software required for their application. The document also explains much of the background to the calculation of phase equilibria from thermodynamic data and the benefits that can be achieved by thermodynamic modelling of phase equilibria as well as the type and scale of the effort required to achieve those benefits. The detail of the thermodynamic methods is not covered.

A number of key papers are also listed which show how thermodynamics have been applied successfully to a number of problems associated with processing.

2 Background and principles

Thermodynamic data provide information both about the amount of heat associated with a given chemical reaction eg during melting of an alloy or conversely during casting, and the nature of the most stable or equilibrium phase assemblage. The data are fundamental properties that relate to all aspects of processing. The principles relating thermodynamic data and phase equilibria are so well established that it is tempting to believe that the whole subject area is well understood and that there are no major outstanding data requirements. There are, however, significant gaps in reliable thermodynamic data for certain classes of material. A belief that no major data requirements remain has led to far less attention being paid to the subject during undergraduate courses in recent years and a significant loss in experimental capability within the UK in the field of high temperature chemical thermodynamics. The other point that is worth making here is that raw experimental data themselves are of limited value. More important for industry is access to critically assessed values where all the experimental data for a particular substance or system have been analysed as a set to provide a self consistent description of the whole system. Such a description allows extrapolation and interpolation to allow prediction of properties even in regions where they are not covered experimentally. The process of extrapolation both as functions of temperature and composition is vital to the rapidly growing techniques for the calculation and application of phase equilibria. This requires good validated models which will depend intimately on the nature of the interactions at the atomic level.

3 Needs for thermodynamic data within the UK

Surveys were taken of known and potential users of thermodynamic data in the UK to ascertain their needs. A large variety of materials types were highlighted with specific needs ranging from comprehensive multicomponent databases to data for one or two key systems for use in conjunction with other extant data.

Comprehensive databases are required for:

- aluminium alloys (solidification modelling and recycling)
- nickel based superalloys (aerospace alloys)
- steel systems (modelling inclusion formation and recycling)
- copper alloys (recycling)
- molten salt systems (high temperature discharge lamps, coal combustion)
- amalgams and low melting alloys (solders, fluorescent lamps)
- slags and ceramics (pyrometallurgical extraction, refractories, glasses)
- TiAl based intermetallics (aerospace)
- magnesium alloys (aerospace)
- complex organic and organometallic species (recycling, waste incineration and disposal)
- aqueous solutions (corrosion, metal extraction and leaching)
- polymer solutions (textiles)

4 Calculation of phase equilibria

The phase equilibria (ie the phases that will form and their composition) in a chemical system can be calculated from a knowledge of the overall composition and thermodynamic data for the various constituents of the phases that might potentially form. For example in the system involving iron, copper and sulphur in contact with water at a known temperature it is possible to calculate the nature and composition of the solid phases, the composition, pH and Eh of the aqueous solution and the overall and molecular composition of the gas phase. The description of the solids would include the amounts of metal, oxide, hydroxide and sulphide phases present and the extent of solid solution in those phases.

The data are based on thermodynamic models, ie they comprise the coefficients of mathematical equations that allow the Gibbs energy of the constituents of the phases to be expressed as a function of temperature, pressure and composition. As a result of effort in many centres particularly over the last 25 years, these models have been thoroughly tested and found to be reliable to the extent that they can be used for extrapolation into multicomponent systems and beyond the limits of experimental data. The stored data are generated mainly by critical assessment of experimental data for subsystems: in this case H_2-O_2 , $Cu-H_2O$, $Cu-Fe$, $Cu-Fe-O$, $Cu-Fe-S$ etc.

For any new problem some of the critically assessed data will probably exist, in the above example most obviously those for H_2-O_2 and Cu-Fe. In some cases relevant experimental data may exist while the assessments may not have been undertaken. However, it often happens that experimental data for some key sub-systems are missing, in which case adequate assessments can sometimes be made using comparisons with chemically related systems or by theoretical methods. In most cases it is difficult to generate new experimental data on a time scale appropriate to the solution of industrial problems. Any experimental data for a higher order system such as Cu-Fe-O-S-H would normally be used only to validate the results of calculations.

It should be stressed that the original experimental data can seldom be used directly in the prediction of equilibria even of simple systems and still less so for calculations of higher order systems. In any case experimental data are always to some degree in error and sometimes grossly so. The materials may have been impure, equilibrium not fully established, interactions with containers ignored, phases present incorrectly identified, and temperatures and pressures incorrect. Errors are revealed when some data are shown to be inconsistent with others that have been critically assessed on the basis of a well established model. Without the thermodynamic models it is impossible to determine the degree of inconsistency in sparse data. With the models the value of the data are greatly enhanced.

Critically assessed data may also be in error for reasons other than the lack of or errors in the experimental data, which nevertheless are the most common cause of poor assessments. Problems will certainly occur if the model is inadequate, for example if data for a real solution is represented by an ideal model, internal magnetic interactions and pressure are ignored, solution on multiple sublattices is treated over-simplistically or the assessed data are used outside the range (T, P, x) of validity intended by the original assessor. Lack of care in the assessment, confusion of reference states, ignorance of experimental data or overlooking the existence of a compound phase also cause problems. The discipline of writing up assessments helps to avoid such errors as discussed further below.

5 Benefits and Problems - Examples of thermodynamic applications

The major benefits of the thermodynamic approach for industry and the environment arise because both industry and nature tend to be chemically complex. The exploration of a process such as copper extraction from scrap by smelting is likely to involve as many as ten significant components. It is simply impossible to study the system experimentally so as to cover all combinations of variables of temperature, fuel-air ratio and the compositions of the slag and scrap, whereas calculations of the effect of varying the conditions can be made relatively easily and, if necessary, within an urgent time frame.

Benefits of this kind have been realised by industrial users of MTDATA and NPL-based consultancy services in many aspects of technology in many industrial, environmental and defence sectors, including the following.

- Alloy development: superalloys, steels, casting alloys for nuclear fuel, codeposited magnesium alloys, aluminium alloys.
- Corrosion: hot corrosion of superalloys and steels, carbon deposition, aqueous corrosion particularly in energy conversion plant.
- Extraction and refining: particularly iron, zinc, aluminium, copper and platinum group metals.
- Polymers: analysis of processes in polymer "alloys".
- Lamp chemistry: quartz-halogen and discharge lamps.
- CVD: semiconductor development.
- Catalysis: improvements for vehicle exhausts.
- Waste: evaluation of treatment of toxic aqueous and solid waste.
- Atmospheric pollution: prediction of release of sulphur, fluorine, organochlorine, PAHs and other toxic organics
- Glass making: interactions of glass with tin and of gases with refractories, environmental control.
- Nuclear safety: analysis of the probable outcome in event of core melt-down.
- Refractories: compatibility of liquid metals and slag with refractories.
- Process modelling: Because the driving force for structural and chemical change is thermodynamic it is possible to apply the thermodynamic methods to process modelling and hence to process optimisation. To date the main applications of this type have been in metallurgical transformations, for example in welding, and lamp design.

The widest benefits are realised when data for the same and other combinations of the system are used to analyse a diversity of problems. For example, essentially the same data are required to analyse problems of hot corrosion of steel as are needed for the extraction and refinement of iron. Thus a project directed at recycling of steel will have benefits far beyond this application. Similarly data needed for the inclusion of small proportions of nickel in aluminium alloys are equally applicable to calculations on the effect of including aluminium in nickel alloys. These examples show that when data are derived for any particular customer, no restriction should be placed on their use for other customers. The details of the customer's problem can be confidential but normally the use of the data need not be closely restricted, except, for example, in the infield of the customer's application. When customers request that the data should be confidential it is necessary to point out that it would be quite impossible to solve their problem if previous customers had been restrictive.

Currently the main obstacle to the much greater use of thermodynamic methods is the lack of sufficiently comprehensive data. The difficulty is that in some cases the cost of undertaking the work necessary to generate thermodynamic data that cover all the important sub-systems, relevant to an individual, process may exceed the benefit that would be gained by undertaking calculations using these data. More often, however, either all the necessary data are present or relatively few are missing and these can be provided at a fraction of the cost of the benefits.

6 Organisation and methodology - Sources of data

6.1 Problems about compatibility

For reliable and effective use, the data for any particular set of calculations must be assessed using consistent models and reference states. Otherwise the data for the individual subsystems will be inconsistent with each other and calculations using the combined data will give wrong results. Furthermore, because the demands of industry are so varied and may require data for an unplanned combination of elements, it is very desirable that all data should be interconsistent.

There are two distinct problems which arise with respect to reference states. Firstly, different tabulations of data may use different reference states as a basis for their data eg The JANAF Thermochemical Tables (85cha/dav) provide data for the Gibbs energy of formation while the Barin and Knacke tables (73bar/kna) provide data for the Gibbs energy relative to the pure elements at 298.15 K. Mixing data from these two different sources will, unless corrected, give results which are in error. Secondly, data for solution phases (eg alloys and slags) are based ultimately on data for the pure components in the particular phase. The difference in Gibbs energy between two phases for a particular element (sometimes called lattice stability) is a fundamental set of standard reference data upon which a critical assessment of data or a thermodynamic database is built. Datasets which use different data for these pure components cannot in general be mixed. For alloy systems this has been resolved to a large degree through an initiative taken by SGTE (Scientific Group Thermodata Europe) whereby data for the various crystalline and liquid phases of the most important elements were critically assessed and published (91din). These are now established as the standard world-wide, to the great benefit of all, and most particularly to NPL, other SGTE members and licensees of databases, since their use adds to the volume of compatible assessed data for binary and higher order systems.

Models also need to be defined in such a way that compatibility is promoted. There has been good progress on models and solution data for alloy systems. Standards are less well established for other solution phases, especially for systems in which the interactions between components within a phase are

strong and where charged species are involved. Of particular current interest are liquid oxides for which four different models are being used by NPL, KTH Stockholm, IRSID Metz and Ecole Polytechnique Montreal. Another difficult area is that of concentrated aqueous solutions for which the models may need to cover many types of solute and extend to high temperatures and pressures as well as cases in which water is a minor component. From one perspective the multiplicity of models is unfortunate because the systems are difficult to model and the effort is multiplied. On the other hand it is desirable on balance for competing models to be developed so that the most useful can be established by peer evaluation and their effectiveness when applied to practical problems. Organisations such as CALPHAD (96din, 97din) serve to encourage discussion on the applicability of models for various types of phases. More recently workshops have been held specifically to obtain broad consensus on models and data suitable for use over the next 20 years (95sun/ald, 97sun/sei). Such ventures need to be encouraged.

6.2 International Collaboration

Ideally the effort needed to generate the large base of data required to tackle unanticipated problems should be undertaken in the context of international co-operation. In practice there is no possibility of the common funding that would encourage the adoption of common standards and the contribution of CODATA (89cox/wag, 89gar/par), though useful, is minor. Nevertheless, it is normal practice for research on models to be freely published. On the other hand data using those models are often published only selectively or in full after a significant time has elapsed, either because they were developed for a particular application or because of their value as part of a commercial database.

The cost per beneficiary can be reduced when projects are jointly funded like that on pyrometallurgical extraction (95atd/gis) organised by MIRO (RC81). Various types of consortia such as SGTE have arisen to enable a limited co-operation to be established within a framework of rules. COST507 (light alloys) is an example of a European project in which each country bears its own costs but all share in the benefits. The disadvantage of such groups is that the participants may be inhibited from enjoying the benefits of co-operation with or working for third parties. The international organisation CALPHAD, which runs a journal and whose participants have no formal agreement with each other but can get together at the annual meeting, has been very successful in advancing the methodology, raising standards through peer pressure and stimulating the flow of published data without these disadvantages. The Journal of Phase Equilibria also plays a valuable role in publishing compilations and assessments with a standard format. APDIC (88cha), (the Alloy Phase Diagram International Commission) is helping to co-ordinate effort on alloy systems world-wide. In the UK awareness and some degree of coordination is fostered by the Materials Chemistry Committee of the Institute of Materials.

6.3 The availability of experimental data

The period 1950 to 1970 was one where experimental methods were able to produce good quality results and much useful work was published. Unfortunately, since then there have been relatively few experimental studies on basic systems for two reasons:

- Experimental thermodynamic and phase equilibrium studies became less fashionable, especially as techniques for microstructural and kinetic studies blossomed. The provision of data was seen to be unoriginal and incompatible with study for a PhD.
- The trend was established to target research funds to applied ends and it became difficult to justify the funding of experimental thermodynamics because even a man year would seldom produce results that had any early impact.

The result has been that, even though many experimental data have been published but not yet critically assessed, there are now gaps in published experimental work relevant to important applications. Moreover, there has been a very great decline in the number of experimental facilities and the maintenance of those that are left so that when the need arises for experimental data to fill a gap no suitable equipment and associated expertise can be found.

6.4 Sources of thermodynamic and phase diagram data

Compilations of thermodynamic and phase diagram data are essential. In this section the various types of sources of data are identified and some indication is given of their relative strengths and weaknesses.

Ultimately nearly all data that are used originate from a journal or a report that is, in principle, publicly available. A literature search could be carried using the standard abstract services for relevant documents. This task has been made easier by use of publications such as those by Wisniak (81wis), Cheynet (89che) and Prince (78pri, 81pri) and equivalent computer based products (97ans) which provide a list of references for the thermodynamic and phase diagram information for a particular system but with no attempt to analyse or report the information given. The series of volumes "Phase Diagrams for Ceramists" (64lev/rob) provides further information concerning phase diagrams for oxide, sulphide and salt systems. Generally this information is abstracted from published papers and not critically assessed through comparison with other information on the same system. For alloy systems this service is also provided by the Ageev series (59age) also occasionally known as the "Red Book". They nevertheless provide a vital source of information.

The next most important source of data is the standard critically assessed publications. These include the JANAF (85cha/dav), Barin and Knacke (73bar/kna, 77bar/kna), NBS Tables of Chemical Thermodynamic Properties (65wag, 82wag/eva) series, Medved'ev (65med/ber), IVTAN (78gur/vei, 79gur/vei, 81gur/vei, 82gur/vei, 90gur/vey, 94gur/vey), Landolt and Börnstein, Kubaschewski et al (93kub/alc), Barin (89bar) and Knacke tables (91kna/kub) for thermodynamic properties. Separate data sources are available for nuclear materials (90cor/kon, 92gre/fug) and sulphides (74mil).

Thermochemical data for organic substances are rarely found in the major compilations discussed above. If any data are included there is usually an arbitrary cut off at say C_2 (65wag, 82wag/eva) with data for compounds containing more than 2 carbon atoms simply ignored. The NPL implementation of the SGTE Substance Database (see below) is actually distributed with data for C_4 and larger organic substances in a separate database (SGORG). In the main database there is no systematic coverage of low molecular weight organic compounds and the SGORG supplement essentially covers only hydrocarbons. This appears typical of the organic coverage of many fundamentally inorganic data sources.

Organic data compilations covering both enthalpy of formation and entropy are rare, a notable example being that of Stull, Westrum and Sinke (69stu/wes) which includes enthalpy, entropy and heat capacity up to 1000K for gaseous species. Compilations including enthalpy of formation of condensed and gaseous materials have been produced by Cox and Pilcher (70cox/pil) and more recently by Pedley and co-workers (77ped/ryl, 86ped/nay). Pedley has further updated these earlier compilations including data for over 3000 substances and a comparison with his own scheme of enthalpy of formation estimates. These sources have focused on data from experiments although there is no guarantee that all substances of interest, of a particular type, have been included. Thus there is a major difference in relation to inorganic data sources where the degree of coverage of relevant substances is more nearly complete or omissions are easily identified.

The Thermodynamic Research Centre of Texas A&M University has a long history of compiling thermodynamic data (and other properties such as density, dynamic viscosity, surface tension and refractive index) for organic substances. Tables are available in printed and on-line computer format for approximately 7000 substances.

Various sources of critically assessed phase diagram information are available. These include:

For alloy systems:

- Hansen and Anderko and its supplements (58han/and, 65ell, 69shu)
- Massalski (90mas/sub)
- Kubaschewski (82kub)

- The ternary alloys series (88pet/eff)
- Raynor and Rivlin (88ray/riv)
- Raghavan et al (87rag, 88rag1, 88rag2, 89rag)
- Chang et al for copper-metal (79cha/neu1) and copper-metal-sulphur (79cha/neu2) phase diagrams
- Compilations of ternary phase diagrams published by ASM (96vil/pri).
- PC based phase diagram compilations (TAPP, MSI, ASM)

For oxide systems:

- the Slag Atlas (95all/gay)

For binary halide systems:

- Posypaiko and Alekseeva (87pos/ale)

Certain compilations provide both thermodynamic and phase diagram information:

- Hultgren et al (73hul/des1, 73hul/des2) for a number of alloy systems.
- The series of monographs (87mur, 88nay/cla, 89smi, 91nas) published by ASM provide a review of the thermodynamic information for selected binary systems as well as phase diagram information.
- CALPHAD Journal and the Journal of Phase Equilibria also provide excellent reviews of data for various systems and often provide critically assessed data which can be used for the calculation of phase equilibria.
- IAEA monographs (66ran/liv, 68lav/ger, 72ger/lav, 73spe/gol, 75ran/gol, 76oet/ran, 76fug/oet, 78cor/oha, 80bre/lam, 81chi/akh) for nuclear related systems.

6.5 Computer databases

For the calculation of phase equilibria the sources identified above are rarely sufficient. While data for pure substances eg in the JANAF tables are provided in tabular form for discrete temperatures, for phase equilibrium calculations they are more generally required as expressions representing the variation of the thermodynamic properties with temperature. In a similar way the information for binary alloy systems is typically a relatively small number of coefficients representing the variation of thermodynamic properties of a particular phase as a function of composition and temperature. While many datasets have been published it is often a time consuming and frustrating task to validate these and combine them to permit calculations on a multicomponent system. This has led to the development of databases for specific types of materials which can be used with software such as MTDATA. Inconsistency between different reference states is one of the main limitations on the usability of published datasets.

The following table summarises the properties of many of the available computerised databases. A number of these databases have been surveyed in a recent NEA report (96nea).

Database Name	Origin	Size	Reference states	MTDATA	Quality
SGSUB	SGTE/NPL	4300 substances	✓	✓	✓
SGSOL	SGTE/NPL	230 systems	✓	✓	✓
UNARY	SGTE/NPL	76 elements	✓	✓	✓
COST	COST507	63 systems	✓	*	✓
MTOX	MIRO/NPL	15 components	✓	*	✓
MTAQ	MIRO/NPL	72 species, 109 interactions	✓	*	✓
SALTS	NPL	90 systems	✓	✓	✓
AQDATA	NPL	450 species	✓	✓	✓
HOTAQ	NPL	106 species	✓	✓	✓
NPLCORR	NPL	7 components	✓	✓	✓
IRSID	IRSID	7 components		✓	
KAUFMAN	Dr L Kaufman	14 components			
AL-DATA	ThermoTech	12 components	✓	✓	
NI-DATA	ThermoTech	13 components	✓	#	
FE-DATA	ThermoTech	15 components	✓	✓	
TI-DATA	ThermoTech	15 components	✓	✓	
FACT	Ecole Polytechnique	5000 substances and 80 systems			✓
MALT2	Japan Society of Calorimetry and Thermal Analysis	4931 substances			
HSC	Outokumpu	7600 substances			
TCRAS	IVTAN, Moscow	2300 substances			✓
NUCLMAT	AEAT	550 substances		✓	
NUCLOX	AEAT	13 component oxide		✓	
THERMOCOMP	Thermodata	4100 substances	✓		
THERMALLOY	Thermodata	470 systems	✓		
HATCHES	AEAT	772 substances, 1176 aqueous species		✓	

* available to members of the club project

available after permission from Rolls Royce

Information about the scope of each database is given here:

SGSUB (and SGORG) is a very general compilation of high quality data for over 4300 substances (version 6.0). Together, these data enable the Gibbs energy of the substance to be calculated as a function of temperature and hence for thermochemical software to perform equilibrium calculations and tabulations. The database contains data for pure substances and gases.

For each substance, the data consists of:

- the enthalpy of formation at 298.15 K relative to the pure elements;
- the standard entropy at 298.15 K; and
- the temperature dependence of the heat capacity from 298.15 K (all data at a pressure of 1 bar (NPL implementation at 101325Pa)).

SGSOL contains critically assessed data for over 230 binary and higher-order alloy systems modelled as non-ideal solution phases. Elements included in the current version (3.0) of the database are:

Ag, Al, Am, As, Au, B, Ba, Be, Bi, C, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, N, Na, Nb, Nd, Ni, Np, O, Os, P, Pa, Pb, Pd, Pr, Pt, Pu, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Yb, Zn, Zr.

The database comprises:

- data for the Gibbs energy (relative to the weighted sum of the enthalpies of the constituent elements) of the end-member species as a function of temperature; and
- data for the excess Gibbs energy for solution phases formed between the end-member species.

Specific subsets of the SGTE Solution Database for solders and low melting alloys, steels, precious metals, electronic materials etc are under development.

UNARY contains standard reference data for 76 key elements used as basis for the critical assessment of data for alloy systems. The UNARY database forms the foundation of SGSOL but the database is also used widely throughout the world. Since many of these assessments are published this provides an ever increasing quantity of consistent thermodynamic data.

The **COST** database arises from a joint European project COST507 aimed at providing a general thermodynamic database for light alloys. Round I of COST507 provided a database for 63 binary systems which, when used in combination, permit predictions of the properties of alloys based on Al, Mg and Ti. The database is consistent with the UNARY database. Round II of COST507, which is nearing completion, will result in an expanded database focusing on key multicomponent systems of industrial importance. The database resulting from Round I is available to users of MTDATA. At present the database from Round II is available to the project members only.

MTOX is the result of a project carried out at NPL since 1988 aimed at the development of a comprehensive database for multicomponent oxide systems of industrial importance. The project has attracted a large amount of industrial support coordinated through MIRO (Mineral Industry Research Organisation) and this is reflected in the scope of the database and the range of the systems covered. Initially the work was directed to deriving data for the key oxide system $\text{CaO-Fe-O-MgO-Al}_2\text{O}_3\text{-SiO}_2$. Later work has been concerned with the addition of data for ZnO , Cu-O , Mn-O , B_2O_3 , Na_2O , K_2O , ZrO_2 and sulphur. Data are available to members of the consortium although membership is not restricted.

MTAQ is the result of another project sponsored by industry through MIRO, this time concerned with the development of a database containing critically assessed data for industrial strength aqueous solutions over a relatively wide temperature range. The database is available to current and future sponsors of the project.

The **SALTS** database contains data for more than 90 binary systems formed primarily between alkali halides. The data includes representations of the Gibbs energies of the unary phases themselves as well as multicomponent solution phases. The binary systems included are taken from combinations of the following components:

LiF , LiCl , LiBr , LiI , NaF , NaCl , NaBr , NaI , KF , KCl , KBr , KI , RbF , RbCl , RbBr , RbI , CsF , CsCl , CsBr , CsI , CaCl_2 , MgCl_2 , ZnCl_2 , Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Na_2SO_4 , K_2SO_4 , Na_2CrO_4 , NaOH , InI , TlCl , TlI .

AQDATA contains data for over 450 aqueous species at 298.15 K, including ionic and neutral complexes of elements, oxides, hydroxides, halides, sulphates, sulphites, nitrates, nitrites, phosphates and many more. It can be used for calculations involving very dilute aqueous solutions.

The **HOTAQ** database contains many data for iron, chromium and nickel with carbon and sulphur in dilute aqueous solution from room temperature up to 573 K.

NPLCORR is a database for calculations involving metal oxygen systems. It includes a comprehensive dataset for the Cr-Fe-Ni-O system and other data for metal oxygen binary systems eg Al-O , Si-O , Y-O , Ca-O etc

IRSID is the original version of the IRSID slag database for the $\text{CaO-MgO-FeO-MnO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system as published by Gaye and Welfringer (84gay/wel) in their paper in the proceedings of the 2nd International Conference on Molten Slags and Fluxes in 1984. The reference state for the database is the pure oxides at the temperature of interest and is therefore not compatible with other databases. The database was developed for steelmaking slags and will give unreliable

results if used outside its intended composition range. The data were derived from an analysis of the thermodynamic properties of the slag phase - the properties of the crystalline phases may be inconsistent with data from other databases eg SGSUB.

KAUFMAN is a database compiled from the data published by Dr L Kaufman since 1970 for the system: Al-B-C-Co-Cr-Cu-Fe-Mn-Mo-Nb-Ni-Si-Ti-W. The reference state for the database is the pure elements at the particular temperature and is therefore incompatible with all the other databases used with MTDATA.

AL-DATA is a database for aluminium base alloys developed by ThermoTech Ltd. The elements considered are: Al-Cr-Cu-Fe-Mg-Mn-Ni-Si-Ti-V-Zn-Zr and the database covers 26 phases. It has been used with some success for modelling the solidification behaviour of a number of commercial alloys.

NI-DATA contains data for 15 phases in the Ni-Al-Co-Cr-Hf-Mo-Nb-Ta-Ti-W-Zr-B-C system developed by ThermoTech Ltd in conjunction with Rolls-Royce plc. It has been used with success for modelling equilibria such as γ/γ' , carbide formation and solidus/liquidus relations. Access to the database is restricted.

FE-DATA was also developed by ThermoTech Ltd in collaboration with the Royal Institute of Technology, Stockholm. The database was derived from data stored in the SGTE Solution Database for the system: Fe-C-Co-Cr-Cu-Mg-Mn-Mo-N-Nb-Ni-Si-Ti-V-W.

TI-DATA was developed by ThermoTech Ltd for calculation of phase equilibria in multicomponent conventional Ti-alloys. It covers the following elements: Ti-Al-Cr-Fe-Mo-Nb-Si-Sn-Ta-V-Zr-C-O-N-B and has been validated against information for commercial alloys.

FACT is a software/data product developed by Ecole Polytechnique, Montreal. It offers a substance database consisting of data for about 5000 substances and 80 binary and multicomponent systems. Of major interest is the database for the system: SiO_2 - Al_2O_3 -CaO-MgO-FeO-MnO- Na_2O - K_2O - TiO_2 - Ti_2O_3 - ZrO_2 which uses a modified quasichemical model for the liquid phase.

MALT2 is the product of the Japan Society of Calorimetry and Thermal Analysis and is a database for 4931 condensed and gaseous substances.

HSC is a software/data product created and marketed by Outokumpu Oy. It contains a database for over 7000 substances, crystalline, gaseous and aqueous although the quality of the database is thought to be relatively poor.

TCRAS is a computer database and associated calculation software for the PC (IVTANTHERMO-PC). It provides thermodynamic properties for about 2300 substances (containing 85 elements) over a wide range of temperature. This was developed at the Institute for High Temperatures in Moscow. The

content is based on the IVTAN tables (78gur/vey, 79gur/vey, 81gur/vey, 90gur/vey, 94gur/vey).

NUCLMAT is a nuclear materials database developed by AEA Technology and contains about 550 datasets for stoichiometric condensed substances and gaseous species.

NUCLOX is an oxide database containing data for some nuclear materials within the overall system: $\text{UO}_2\text{-ZrO}_2\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-BaO-La}_2\text{O}_3\text{-SrO-(Fe-O)-CeO}_2\text{-Ce}_2\text{O}_3$. Data for the $\text{CaO-MgO-Fe-O-Al}_2\text{O}_3\text{-SiO}_2$ system are not included directly. For general use the MTOX database must also be used in combination.

THERMOCOMP is a substance database supplied by Thermodata and contains data for approximately 4000 substances.

THERMOALLOY is a solution database marketed by Thermodata. The database contains data for approximately 470 binary systems.

HATCHES is a database developed by AEA Technology and Nirex containing data for aqueous and solid phase species involving the elements U, Th, Pu, Np, Am and Cm. The reference states used by HATCHES are different from those used in other commonly available databases and this database should therefore only be used in isolation.

CHEMVAL is the acronym for two EU funded projects (prime contractor W S Atkins Consultants Ltd.) that have resulted in a thermodynamic database (96fal/rea) applicable to radioactive waste disposal. The CHEMVAL2 project, which ended in December 1994, has produced a database covering 650 aqueous species and minerals. Although some specific ion-ion interactions have been considered in general the data are applicable only to dilute and low temperature aqueous systems.

NIST-JANAF Thermochemical tables is a computer database (computer readable file) providing coefficients (in Shomate and Cruise formats) that represent the tabulations in the 3rd edition of the JANAF Thermochemical Tables.

NIST Thermodynamics Database is a database (computer readable file) covering more than 15000 inorganic and organic compounds with up to 2 carbon atoms (dilution states of aqueous solutions counted) at 298.15K and 100kPa. Coverage of all thermodynamic functions (enthalpy of formation, entropy and heat capacity) is not complete. It appears that this database is a computer based version of the NBS Technical Notes (65wag, 82wag/eva).

NIST/DIPPR Properties of Aqueous Solutions Database is a database containing excess Gibbs energy data for single and mixed electrolytes from

25°C to 200°C and concentrations up to 12 molal. Approximately 350 single electrolytes and many of their mixtures are covered.

NIST Critically Selected Stability Constants of Metal Complexes is an aqueous database containing stability constants for the formation of metal and hydrogen ion complexes with over 5300 ligands. More limited data for the entropies of the association process are also available.

NIST Chemistry Web Book (www.nist.gov/chemistry) is a searchable database of over 4000 organic and a limited number of inorganic compounds. The enthalpy of formation is given for condensed and gaseous species. Extensive experimental bibliographic references are given to the original data sources. Although there is wide coverage of compounds with experimental data available not all thermodynamic functions (enthalpy of formation, entropy and heat capacity) are given.

NIST organic databases (Structures and Properties, THERM/EST, CHETAH) are databases combining experimental values of enthalpy of formation and entropy with Benson group estimation methods (70cox/pil). A large number of compounds are covered with the Structures and Properties database containing approximately 5000 compounds. Values of enthalpy and entropy of formation are stored, however it is likely that some of these are based on estimates. Many compounds are from NIST's Positive Ion Energetics Database.

TRCTHERMO is the on-line database of the Thermodynamic Research Centre of Texas A&M University. The database (available from a number of on-line sources such as the Chemical Property Data Network) contains thermodynamic and other data for approximately 7000 substances.

DETERM is a database provided on-line by Dechema e.V. (Information systems and Databases) for the thermodynamic properties of organic substances. This is very large database, focusing mainly on vapour-liquid-equilibrium and other phase and transport properties, however there are data for enthalpy of formation, combustion and entropy that allow chemical equilibria to be calculated. Data for about 20000 substances are stored compiled from experimental sources, although not all substances have the required enthalpy of formation and entropy data.

6.6 Ab initio calculations

To some extent it is now possible to calculate the thermodynamic properties of pure compounds and mixtures ab initio. The method is particularly relevant to the provision of data for substances that cannot be made experimentally. Traditionally data for an unstable phase, bcc copper for example, have been estimated from data for binary systems in which the component dissolves in the phase in question. Ab initio methods are steadily

improving in accuracy at decreasing cost but cannot, at least as yet, remove the need for experiment. Moreover, there is no prospect whatsoever of ab initio calculations on complete systems of several components and phases of the kind that would be important industrially. As discussed below, calculations of the kind made by MTDATA on such systems are far more efficient than either ab initio calculations or experiment.

7 The effort required

The effort that needs to be put into any particular system depends not only on its intrinsic complexity but also on the amount and quality of data in the literature and the accuracy required. If the data are to be used as part of a growing database, it is very desirable that they be assessed as rigorously as possible but, if the requirement is for the solution of an individual problem, a lower level of rigour may be warranted. If effort is put into the assessment of a new system, it is very desirable that the work be thoroughly documented and preferably published. Otherwise, when the data are used in the future there will be no basis to establish their quality, partly because they would not have been subject to peer review. Documentation adds significantly to the effort but the long term benefits make this worthwhile.

The effort required to assess a binary system might be as little as one day, or if the experimental data have been compiled even less, but more usually between 1 man-week and 2 man-months. However, some difficult systems such as Ti-O, in which there are many complex solution phases, might require longer still. An estimate of the effort necessary for any particular set of objectives therefore requires consideration of the intrinsic difficulty of the systems involved and the availability and quality of experimental data in the literature. The elapsed time necessary to accumulate information from the literature also needs to be considered.

8 Calculation methods

The focus of this discussion has been on the data but the successful use of the thermodynamic approach also depends on the existence and widespread use of the calculation methods. These must be capable of handling high order multicomponent systems and phases represented by a variety of models that reflect their chemical complexity. MTDATA provides such a facility. It is used by a large number of organisations world-wide many of them in the UK and is the most reliable system available. Moreover, it is developing in response to users needs both by providing versions suited to current operating systems and computer platforms and by expanding applications to non-equilibrium processes.

Significant added value is given to the results of calculations when these are presented in terms of immediate relevance to the user. This is best achieved if the calculations are made by the chemists, metallurgists or engineers concerned with the ultimate problem or by others interacting closely with

them. For this purpose the software needs to be easy to use. Moreover the data need to be very reliable as unspecialised users will be less likely to spot problems with the data. Because processes are very variable even from plant to plant in the same industry, it is desirable that the software includes modular kinetic tools that can be used by those with specific needs or that it can be linked with commercial process models. In at least one case MTDATA is used in real time to control an industrial process.

9 Strategy

The recommended strategy for consideration of individual problems is as follows:

Identify the application areas where problems amenable to thermodynamic analysis exist and review the following factors:

- The potential value of the benefits from thermodynamic analysis
- The appropriateness of existing thermodynamic models
- The availability of critically assessed data at present
- The potential for obtaining data by co-operative effort intra- and internationally
- Possibilities for estimation or ab initio calculations of data for which no experimental data exist
- The effort required to make the assessments
- The need for experimental studies to provide data for chemical equilibrium and the kinetic data needed to underpin process modelling
- The need to validate new data and methods
- The scope for publication of results to enhance the value derived from co-operation
- The potential additional value of the assessed data for future use (studies on americium would score low relative to aluminium for example)
- The need for any developments in software, for example to incorporate an additional model or to exploit the results for process control

Following considerations under these headings it is necessary to review with the customer the potential benefits in relation to the cost and to schedule the effort to achieve optimum benefits.

For an appreciation of the longer term needs and opportunities for thermodynamic modelling it is desirable to consider further points in addition to those identified above.

- The need to identify broad areas where gaps exist in the critically assessed database, taking note of areas of technology that presently cannot be tackled through lack of data.

- Evidence for lack of experimental data
- The value of maintaining experimental capability to enable rapid response to particular needs
- The future potential of ab initio calculations of fundamental data
- The need for new thermodynamic models
- The need for generic kinetic calculation modules and associated data
- The need for improved linking with process modelling and plant design packages
- Opportunities for national, European and international co-operation
- Scope for additional markets.

For these more general purposes close interaction between industry, environmental bodies and complementary organisations and data providers is essential.

10 Conclusions and recommendations

- The use of thermodynamic data in the modelling of high temperature processes is already widespread and is likely to increase.
- Experimental data are required in order to fill gaps in information available in the literature
- There has been a marked rundown in the capability within the UK to undertake experimental thermodynamic studies. NPL should develop some capability in this area to cover future needs.
- Industry require access to critically assessed data for use with software such as MTDATA. Databases should be developed for use on behalf of UK industry. International collaboration eg through SGTE is vital in order to develop these databases over a reasonable timescale.
- Software, such as MTDATA, needs to be developed to match the changing needs of UK industry.

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