



MTDATA - Thermodynamic and Phase Equilibrium Software from the National Physical Laboratory

R H Davies*, A T Dinsdale, J A Gisby,
J A J Robinson and S M Martin
NPL Materials Centre, National Physical Laboratory,
Teddington, Middlesex TW11 0LW, UK
*: Corresponding author's email: hugh.davies@npl.co.uk

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Abstract. In the past, the complexity of the chemical and phase equilibria established during many industrial processes has prevented the kind of in-depth understanding of their thermodynamics necessary for successful and efficient process control. Predictive thermochemistry, as embodied within MTDATA, makes such an understanding possible.

MTDATA allows equilibria to be calculated for multicomponent systems of practical interest, containing many different types of phase, from critically assessed data for their component binary and ternary subsystems. Very complicated calculations can be undertaken with as many as thirty different components and 500 phases being considered simultaneously. A number of modules are incorporated for critically assessing, manipulating and retrieving the data, making various types of calculation and plotting binary, ternary, multicomponent, and predominance area diagrams. Facilities are also available for users to link the complexities of phase equilibrium calculations within MTDATA to their own software or to third party commercial software packages enabling users to simulate unit operations within an industrial plant or to integrate kinetic effects. Special derivatives of MTDATA are also now being developed to provide the sophisticated capabilities within MTDATA to non-expert users for special applications using carefully designed graphical user interfaces, which are both easy to use, and which provide output specifically designed for the particular industrial need. © 2002 Published by Elsevier Science Ltd.

MTDATA has been developed over many years by the National Physical Laboratory, the UK's National Standards Laboratory, to the highest standards of Quality Assurance for which NPL has been accredited with ISO 9001 registration. MTDATA incorporates numerical analysis routines developed in-house to provide more reliable equilibrium calculations. A wide range of databases is available for use with MTDATA developed either in-house, through collaboration within international consortia or by other organisations but sublicensed for use with MTDATA. The code is available for licensing to industry, universities or other research bodies for a wide range of computer platforms.

In this paper the principles and operation of MTDATA are illustrated by reference to systems of practical importance involving oxides, alloys, molten salts and aqueous solutions.

1 INTRODUCTION TO PHASE EQUILIBRIUM CALCULATIONS

MTDATA is used as a tool in the analysis of diverse problems in chemistry, metallurgy and material science. Examples of areas of application include: extraction, refining, and recycling of metals, alloy development, process metallurgy, ceramics, refractories, cements and glasses, energy conversion, joining materials, corrosion and deposition, lamp chemistry, electronic and magnetic materials, pollution control, molten salt chemistry, hot and aqueous corrosion, coating, etching and crystal growth.

Practical problems in these areas generally involve many components, deliberate or accidental, as well as the product phases: gaseous, liquid and crystalline. The principle behind the operation of MTDATA is that mathematical models incorporated in the software enable equilibria in multicomponent systems to be calculated on the basis of critically assessed data for the thermodynamic properties of simpler systems. Thus, using the facilities within MTDATA [89Bar, 89Din, 90Dav, 91Dav, 90Tay, 91Tay, 92Bal, 93Bar, 93Gis, 94Bar, 94Dav, 95Din, 95Que, 97Din, 2002Gis], industries are able to explore compositions and conditions of temperature and pressure for which no direct experimental data exist and thereby gain much greater control over the factors that influence process operation. Thermodynamic modelling of materials and processes therefore provides a rapid and cost effective means of directing and reducing the complexity of experimental investigations leading to more efficient use of resources, cost savings and improved yield. Because MTDATA allows the user to monitor the results of equilibrium calculations in great detail and the effect of the thermodynamic data on these results, it is also a very useful educational tool and is already being used as such in a number of universities.

The principles of the calculation of chemical and phase equilibria are well established as described in the review of Bale and Eriksson [90Bal]. A large number of computer programs implementing these principles have been reported over the years. Many such programs were produced for handling specific problems with specific types of materials, some contained hard coded thermodynamic data. Most of the early programs were unable to calculate equilibria involving phases of variable composition (solution phases). Even though modern equilibrium programs can frequently handle solution phases, the nature of the equilibrium algorithms often place a heavy requirement on the provision of initial estimates of the equilibrium state; poor estimates result in non-convergence. Similar poor performance can also be found when calculating in systems that contain phases of the same basic structure but which may give rise to two or more variants with differing composition (a miscibility gap).

The aim of this paper is to provide a description of MTDATA, its various modules and the types of calculations it can undertake. A wide range of models are available within MTDATA to represent the thermodynamic properties of phases as a function of temperature, pressure and composition although they are not described here. MTDATA can be supplied with a variety of databases that use these thermodynamic models and permit calculations on real materials used in industry.

2 MTDATA

MTDATA is a single computer program comprising more than 150000 lines of Fortran 77 source code. About 1000 lines of code are specific to the computer/operating system hosting the program.

With the aim of developing a reliable tool for calculating phase and chemical equilibria for a wide range of systems and phase types with maximum ease and reliability NPL started development in the early 1980s on a completely new "equilibrium engine" for MTDATA. MTDATA had existed for a decade previously as a widely available service on various mainframe computers but which provided only limited capabilities for the calculation of chemical equilibrium. This new equilibrium algorithm (Multiphase) rapidly became the underlying engine for MTDATA's phase diagram and other application modules. As described later this algorithm is unique and does not work like other comparable programs in that it provides true Gibbs energy minimisation through solution of a non-linear optimisation problem with linear constraints. It uses the NPL Numerical Optimisation Software Library (NOSL) which guarantees mathematically that the Gibbs energy reduces each time it is evaluated and the result can be proven to be a solution to the posed problem. Another important feature of the algorithm is that no initial guess is required. The algorithm is tested aggressively and regularly for reliability against a range of datasets covering a variety of thermodynamic models with a success rate for pseudo random calculations of > 99.99% offering nearly 100% likelihood of convergence providing users with a high level of confidence.

Great efforts have been taken to cope with miscibility gaps or phases which have multiple minima in the Gibbs energy arising from internal degrees of freedom where the Gibbs energy is not an explicit function of system composition e.g. chemical ordering models.

The main function of MTDATA is the calculation of phase and chemical equilibria in multicomponent systems. For this purpose, it includes a flexible and powerful database management and software modules for manipulation of the data, the critical assessment of data, evaluation of thermodynamic functions, equilibrium calculation, and the plotting of results, as well as some utilities. Many of the modules feature a graphical "click and go" interface to calculations for ease of labelling. This can be used to initiate the calculation of a phase diagram although such diagrams can also be started automatically. It is normally used interactively via its Windows interface, but can also be driven in batch mode and in addition, macros can be used to customize the program or replace commonly entered sequences of commands. Users of MTDATA potentially have access to a wide range of critically assessed thermodynamic data.

MTDATA also contains facilities for linking process models to the equilibrium calculations through a self-documenting programming interface. A process model could be used to add and remove gas, slag, metal and heat as required or to determine the redistribution of components and heat by diffusion and convection, iteratively passing requests to MTDATA to calculate global or local equilibrium and heat generation. A typical use would be the determination of concentration profiles ahead of a crystallising melt. Non-equilibrium calculations can be undertaken by omitting phases or placing restrictions on the distribution of components (para equilibrium). Examples are the removal of sulphur as sulphur dioxide in the blowing of mattes, and counter current processes involving metal, slag and/or matte streams.

MTDATA is available for a range of machines and operating systems. The most recent implementation, MTDATA for Windows, combines the power and reliability of MTDATA with the ease of use and versatility of Windows 9x, ME and NT. This allows the user to benefit from the

opportunities for improved process control and understanding that MTDATA offers without devoting time to learning how to use the software. With just a few simple clicks of the mouse a phase diagram can be calculated, a series of complex equilibria computed, or the thermochemical properties of multicomponent industrial alloys examined.

MTDATA for Windows takes full advantage of the Windows interface, using a fully 32-bit optimising compiler for speed and reliability. The benefits that Windows bestows, such as drag-and-drop, context-sensitive help, multi-tasking and print formatting are automatically available. Windows standards of consistency and compatibility means that MTDATA for Windows is as intuitive and accessible for occasional as it is for regular users. The same program also has the capability for traditional interactive use via a powerful command language which allows the use of prompting, menus and access to the on-line help system at all times. Keywords are used for entering options in full or as unambiguous abbreviations. All user input is buffered so that more than one command sequence may be entered on a line of input. Those less familiar with MTDATA can enter the same set of commands on separate lines with prompting, menus and help being provided for each item as required. Groups of commands may be combined and stored in a file for subsequent execution as an MTDATA macro. Macros allow considerable customisation of the user interface with the options of inserting user input break points, extra prompting and explanatory text.

A record of the interaction between the user and MTDATA is logged automatically to an MTDATA log file which takes the form of an MTDATA macro. These log files can be used easily to repeat any calculations easily, to report any difficulties in the use of MTDATA to NPL and as a record of the calculations undertaken. All graphical output from MTDATA will contain a record of the name of the log file created in addition to the names of datafiles used or generated during the calculations.

MTDATA can calculate and display unary, binary and ternary phase diagrams, isopleths, isothermal sections through high order systems, liquidus projections, phase fractions diagrams and predominance area diagrams.

All versions of MTDATA can provide graphical output in Postscript, encapsulated Postscript, HPGL and Tektronix 4010 and, in MTDATA for Windows, any supported printer.

3 THEORY

MTDATA calculates equilibria using an extremely robust true Gibbs energy minimisation procedure developed by Hodson which requires no initial estimate of the equilibrium state [89Din]. In this way MTDATA differs from many of the other chemical and phase equilibrium programs available.

The equilibrium state of a metallurgical or chemical system may be determined by solving, for a given temperature and pressure, the following problem:

$$\underset{n}{\text{Minimise}} \quad G = \sum_{j=1}^N n_j \mu_j$$

such that
$$\sum_{j=1}^N a_{ij} * n_j = r_i \quad i=1,2,\dots,M \leq N$$

and
$$n_j \geq 0$$

 where

- G is the Gibbs energy which is to be minimised by varying the values of the $n_j, j = 1, 2, \dots, N$
- n_j is the amount in moles of species j present in the system; each chemical substance with a different phase designation being considered as a distinct chemical species,
- N is the number of species in the system,
- μ_j is the chemical potential of species j , which may be a function of some or all of the species amounts in the same phase; it also depends on temperature and pressure, (the form of μ_j depends on the model of the phase under consideration and is constructed such that $dG_j/dn_j = \mu_j$),
- a_{ij} is the number of units of component i per species j ,
- M is the number of components in the system,
- r_i is the number of moles of component i in the system.

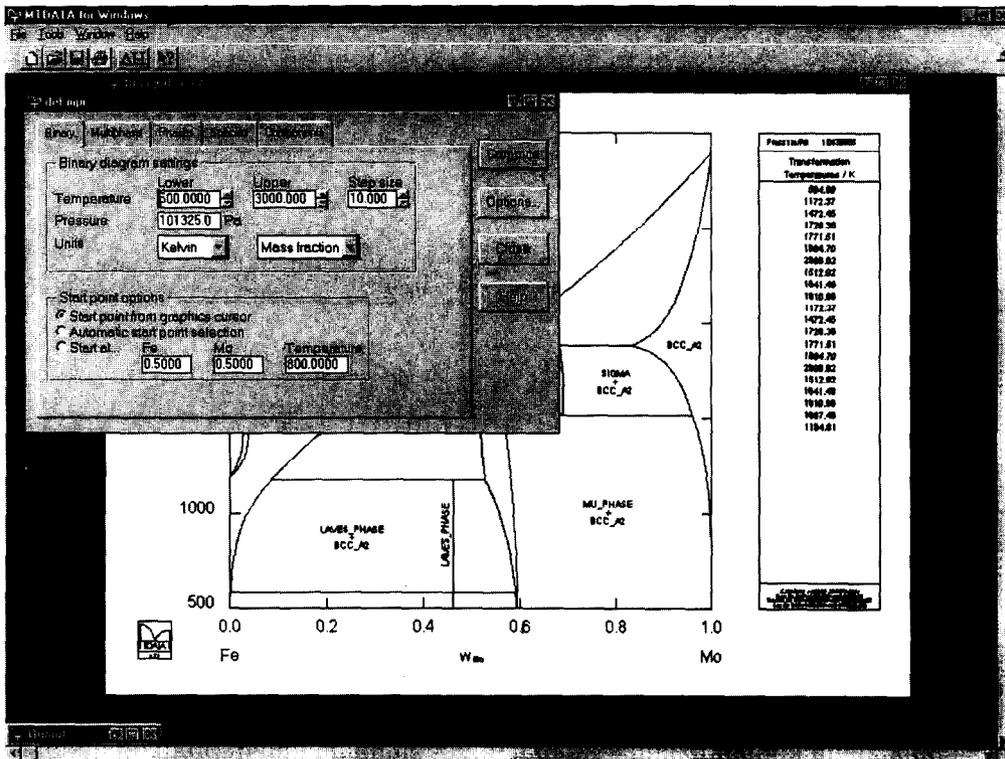


Figure 4.1 Screenshot of MTDATA for Windows with calculated binary phase diagram. The expression G is a non-linear function of the species amounts and is dependent on temperature, composition and pressure.

This optimisation problem is solved using methods based on aspects of NPL's NOSL (Numerical Optimisation Software Library) library. It is a feature of this method that a lower value of the objective function (Gibbs energy) is found at the end of each iteration while maintaining feasibility with respect to the constraints - one reason that the method is so reliable. More details of the method may be found in Gill, Murray and Wright [81Gil].

The methods described allow the calculation of phase and chemical equilibria in multiphase, multicomponent systems containing mixtures of gases, aqueous solutions, stoichiometric and solution phases (eg alloys, molten salts, oxides, polymers). It forms the basis of the calculation modules in MTDATA except Unary, Thermotab and Coplot.

4 USER ASPECTS AND AVAILABILITY

Most of the modules of MTDATA are fully documented and equipped with context sensitive help. The user guide incorporates information on the data structures, the thermodynamic models and the principles of operation of the modules, particularly MULTIPHASE. The cooperation of users in the improvement and development of MTDATA is encouraged through the thriving MTDATA Users Group.

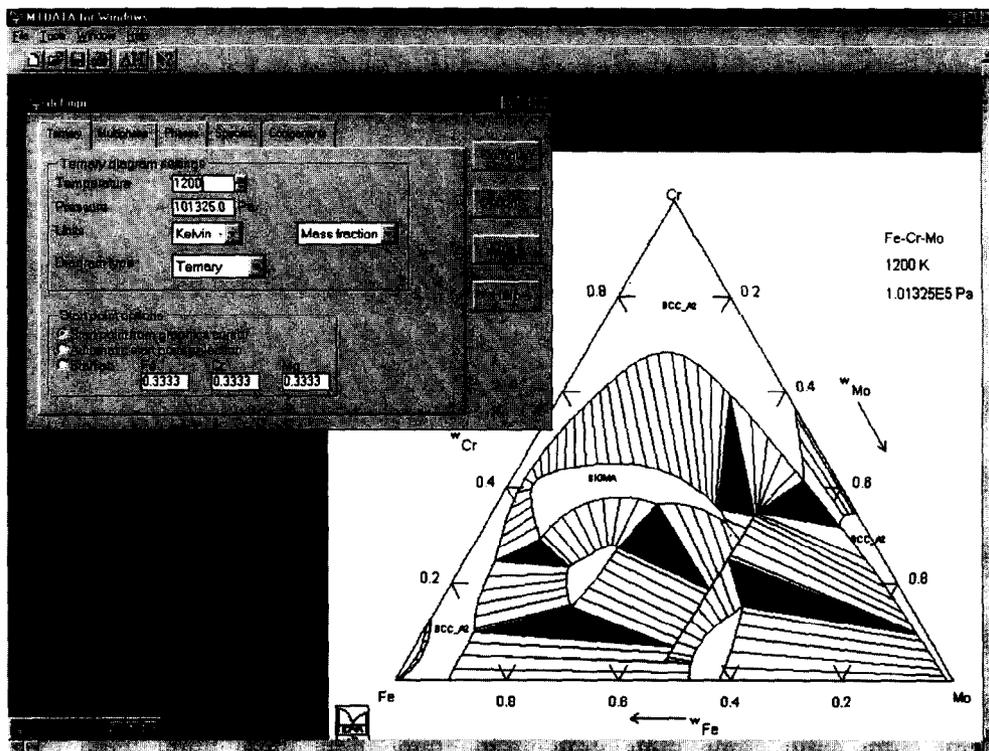


Figure 4.2 Screenshot of MTDATA for Windows with calculated ternary phase diagram. MTDATA is highly portable and is currently available for licensing for use on a range of computer platforms and operating systems including PCs running under Windows 9x, ME and NT and most popular Unix workstations and servers.

The screen shots (Figures 4.1, 4.2 and 4.3) give examples of the use of MTDATA for the calculation of binary and ternary phase diagrams and also complex gas phase speciation.

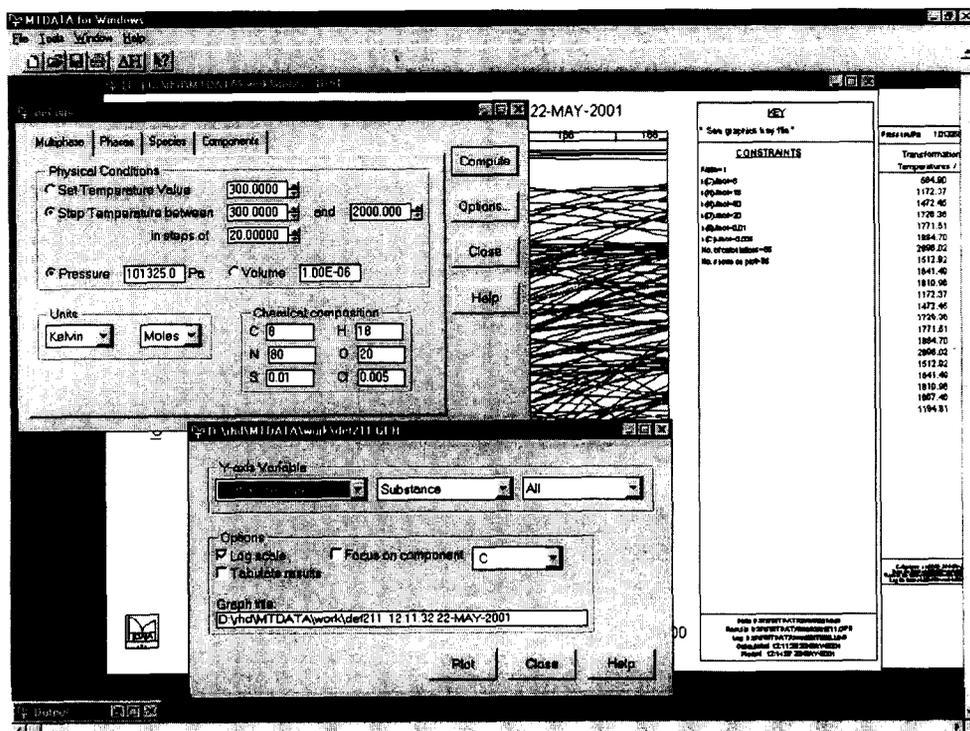


Figure 4.3 Screenshot of MTDATA for Windows with calculated MULTIPHASE speciation diagram

5 MTDATA DERIVATIVES

NPL has produced a number of MTDATA derivatives for the PC/Windows platform. These make use the core MTDATA thermodynamic model, Gibbs energy minimisation routines and database routines via a dynamic link library (DLL). The following sub-sections describe some of the applications.

5.1 NPL Virtual Measurement Systems

It is difficult and time consuming to measure all the thermophysical properties required for the modelling of solidification processes. Frequently the engineer, who may not be a specialist in thermodynamics, needs to obtain realistic estimates of these properties because he has no measured data.

The Virtual Measurement System designed by NPL predicts the enthalpy, heat capacity, fraction solid, density, thermal conductivity and freezing range. Solidification can be modelled either assuming equilibrium is maintained, with a Scheil model or with a fixed cooling rate.

The program has a clean, simple interface (see Figure 5.1.1) directed to the specific problem that is required to be solved. Reliability is provided by the MTDATA routines in the accompanying DLL. Output is produced in the required units and format including integration with MS Excel.

It is planned to produce systems for Al, Fe, Ni-base alloys and slags. An important part of this work is the validation of the estimated data with selected experimental measurements. The work is funded by the UK Department of Trade and Industry with substantial input from industry via an Industrial Advisory Group.

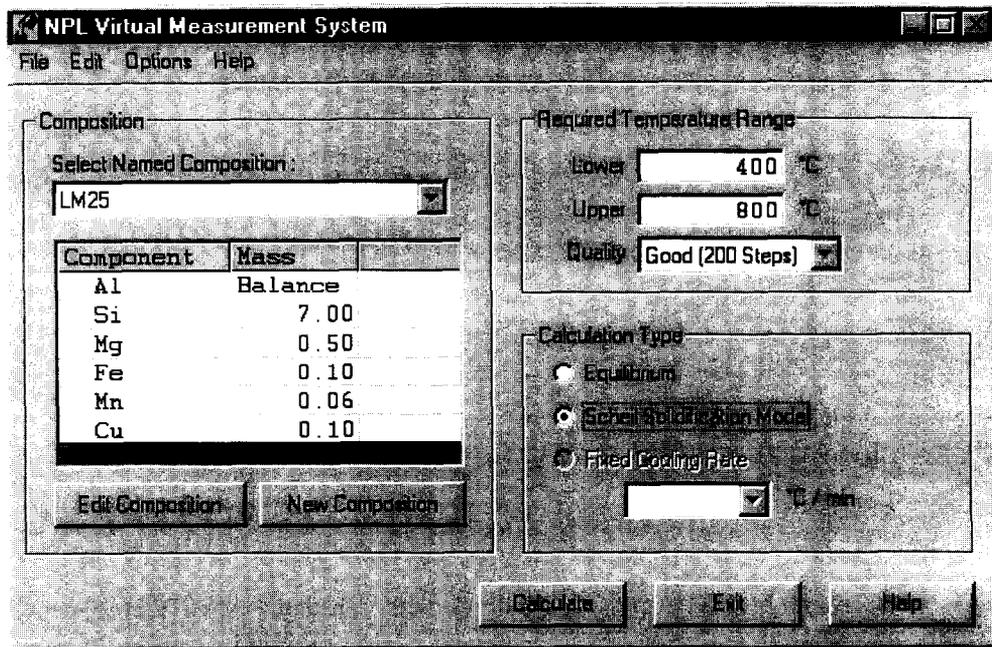


Figure 5.1.1 Screenshot of the Virtual Measurement System for Aluminium Alloys with LM25 alloy and Scheil solidification model selected

5.2 NPL Engineer's Tool Kits

For specific industries it is possible to produce highly customised MTDATA derivatives. One example of this is a software "toolkit" produced to aid lighting engineers in the development of fluorescent lamps (Figure 5.2.1). This application is interesting as it not only allows the engineer to calculate reliably the effect of amalgam composition on Hg vapour pressure, hence light output, but the toolkit also determines the best amalgam to use under the conditions selected.

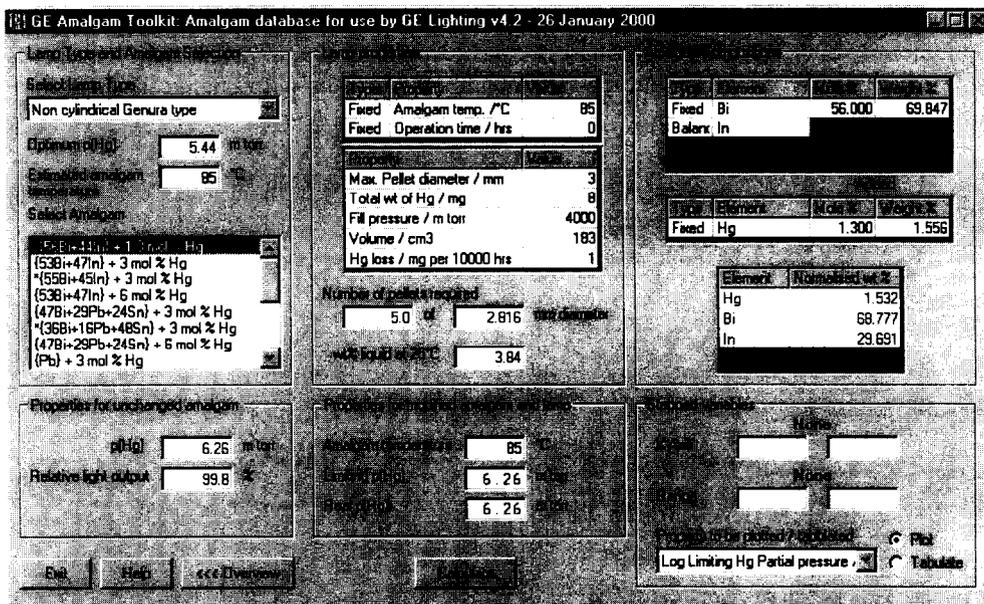


Figure 5.2.1 Screenshot of lighting systems design toolkit showing results of automatic materials selection of Bi-In-Hg amalgam

6 CHARACTER INTERFACE

The following shows how MTDATA can be used via the traditional character interface. Many of these interactions can be performed in a much simpler way using the graphical user interface in MTDATA for Windows but the text below will help to describe many of the facilities and concepts used by MTDATA. More complete descriptions can be found in set of the MTDATA handbooks.

Data are retrieved from one or more databases by means of the Access module. The system is chosen by a definition of its components, which may be elements or compounds. A typical command allowing data to be recovered for the CaO-FeO-Al₂O₃-SiO₂ system from the oxide database might be

```
define system = "CaO,FeO,Al2O3,SiO2" source = oxide out = "CFAS" !
```

Here, the command "define" is used to name the system, the source database, and the datafile that will be generated when the command "save" is issued. Any unique abbreviation of the keywords will suffice and four levels of user experience are catered for. The normal command sequence has the following syntax

```
command {parameter = value} !
```

The types of substance and phase/model for which data can be stored and retrieved include stoichiometric compounds, gases, aqueous species, other associates, non-ideal solutions, and phases with solution on fixed or variable sublattices.

The datafiles generated by the command "save" have a standard format and provide the input data used by Gplot, Binary, Ternary, Multiphase, Coplot, Application and Assessment - in fact, all the calculation modules in MTDATA except Thermotab, which deals with chemical equations rather than systems.

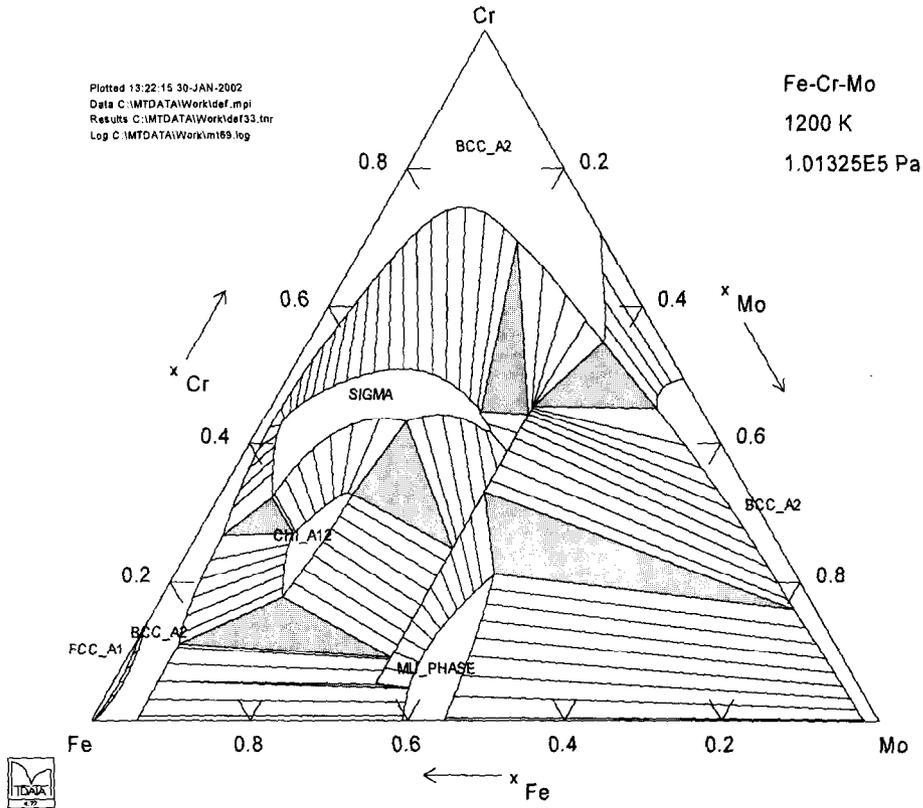


Figure 6.1 Calculated ternary phase diagram for the Fe-Cr-Mo system at 1200 K

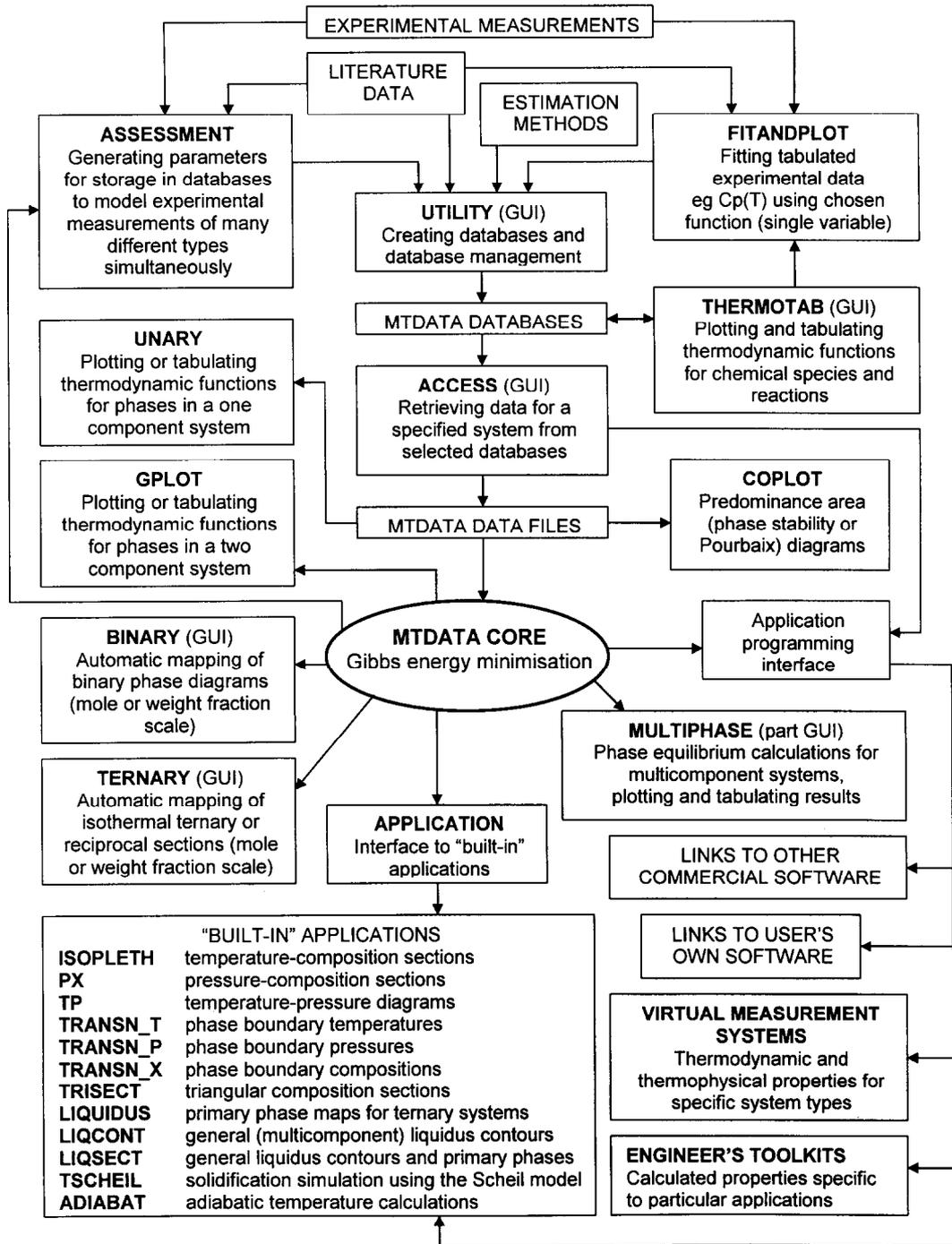
The following example of user input is all that is required to compute and plot a ternary diagram for the Fe-Cr-Mo system at 1200 K.

```
define system = "Fe,Cr,Mo" source = mtsol ! set temperature = 1200 ! compute !
```

In the sequence above, there are three commands, define, set and compute, each of which is terminated by an exclamation mark. If the default database is mtsol, the NPL Alloy database, the use of unambiguous abbreviations reduces the above to:

```
d sy "Fe,Cr,Mo" ! se t 1200 ! co !
```

Figure 7.0 MTDATA structure overview



After giving the compute command the screen changes to a graphical interface with the cursor controlled by a mouse or other pointing device. The single letter command S produces the diagram shown in Figure 6.1. Note that even non-contiguous phase fields are calculated.

Alternatively the whole diagram can be calculated automatically by entering:

```
d sy "Fe,Cr,Mo" ! se t 1200 ! co diag auto_ter !
```

7 MODULES

MTDATA comprises a number of modules (see fig 7.0 for an overview) for data retrieval, assessment and calculation, the TERNARY module being used in the above example. Each module will now be described and examples of use given. These examples have been selected to illustrate the way in which MTDATA works and are not necessarily taken from any specific practical application.

7.1 UTILITY

Data, in the form of assessed parameters for various models that describe the thermodynamic properties of phases, are stored in databases created and maintained by means of MTDATA's integral data management system. This allows large collections of data to be made readily available to the calculation modules of the databank. The UTILITY module is used for creating, loading and listing databases, which may include a user's own database or major data compilations such as those supplied by NPL. The listing of the contents of a user's own database is achieved as follows.

```
list database = my_data format = name !
```

Only the names of the datasets would be listed such as Fe<LIQUID>, C,Fe<LIQUID> and Fe:C<CEMENTITE:3:1>. Complete data from non-proprietary databases could be listed simply by using the keyword data in the place of name. Any data listed by the UTILITY module can also be loaded back into a database. These facilities in conjunction with macros allow a data manipulation environment to be built suitable for amending a single number in a dataset or managing large solution databases.

UTILITY also contains a facility for plotting graphics files that have been created by other modules and customised by the user to meet any requirement for publication, simplification or the highlighting of particular features.

MTDATA also incorporates utilities for manipulation, conversion and import of databases in other formats eg ThermoCalc tdb format.

7.2 ACCESS

The ACCESS module is used to retrieve thermodynamic data for systems of components from MTDATA databases. Some modules have direct database interfaces and can recover data

directly; however, it is often more appropriate to use the ACCESS module, especially when a system is being searched for across more than one database. The variety of databases available with MTDATA is discussed in a later section.

Specifically the ACCESS module allows the user to define a system and a list of databases from which to retrieve data. For example:

```
define system "Ca,K,Zn,Cl" source my_data sgte_sub !
```

Here a search for data would be carried out in the private database MY_DATA and also in the SGTE Substance Database. As the system definition is in terms of elements as components all species containing these elements would be recovered. Systems can also be defined in terms of non-elemental components such as "KCl,CaCl₂,ZnCl₂". Calculations for this system would be confined to the plane determined by the three components, whereas the definition in terms of elements would allow the proportion of chlorine to vary independently of the other components. Similar considerations apply when the model for a phase includes charged species. A facility is included that allows the user to determine whether charge is formally a component or present in species but constrained to zero in phases.

The ACCESS module allows items of data (for phases or their unary constituents) to be rejected outright or substituted, under user control, by data from a database lower on the search list. Data may then be saved into a text file for use by other modules.

7.3 THERMOTAB

This module is used for tabulating and plotting thermodynamic functions for individual substances or a chemical equation. The user enters chemical equations such as:

```
define equation "CO2<g> = CO<g> + 1/2 O2<g>" !
```

Equations are automatically balanced, if required, so the above equation could have been entered as "CO₂<g> + CO<g> + O₂<g> =" with THERMOTAB being left to insert the correct species multipliers. Data are automatically recovered from the chosen database and may be displayed in terms of the actual data stored in the database or tabulated and plotted to show the variation of the thermodynamic properties with temperature for chemical equations or individual substances. Users are at liberty to select from one of a set of standard table formats or, as illustrated in Table 7.3.1, to choose their own format. This feature enables easy comparison with established compilations which use a variety of tabulated thermodynamic functions. Plotting is equally flexible.

It is possible to select data from more than one database for different species in a THERMOTAB equation. This facility makes THERMOTAB very useful for the comparison of data from different sources as indicated by the following example, in which the data for substances 1 and 2 in the equation are derived from adata and bdata respectively.

```
define equation "H2S<g> = H2S<g>" ! use adata 1 bdata 2 !
```

Although THERMOTAB was originally designed to use data for pure condensed substances, ideal gaseous or aqueous species, the module's direct database interface allows all database data to be displayed. For example:

define equation "Fe,Ni:C<CEMENTITE:3:1"> ! list data 1 !

The equation keyword is used here to identify an interaction parameter for cementite, which is modelled in terms of two sublattices with site ratios of 3:1.

Table 7.3.1 Illustration of a user controlled format generated by THERMOTAB showing various thermodynamic properties as a function of temperature.

H2S<g> = H2S<g>

T K	Delta Cp J/K mol	Delta H J/mol	Delta S J/K mol	Delta G J/mol	Beta -G/RTln10
298.15	-6.75830E-02	98.400	-4.60052E-02	112.12	-1.96419E-02
300.00	-6.70942E-02	98.276	-4.64218E-02	112.20	-1.95357E-02
400.00	-6.80973E-02	91.870	-6.48386E-02	117.81	-1.53835E-02
500.00	-9.33523E-02	83.891	-8.25377E-02	125.16	-1.30751E-02
600.00	-0.12429	73.021	-0.10227	134.38	-1.16988E-02
700.00	-0.15456	59.059	-0.12373	145.67	-1.08699E-02
800.00	-0.18149	42.222	-0.14618	159.16	-1.03920E-02
900.00	-0.20443	22.915	-0.16889	174.92	-1.01516E-02
1000.0	-0.19159	1.1188	-0.19188	192.99	-1.00807E-02

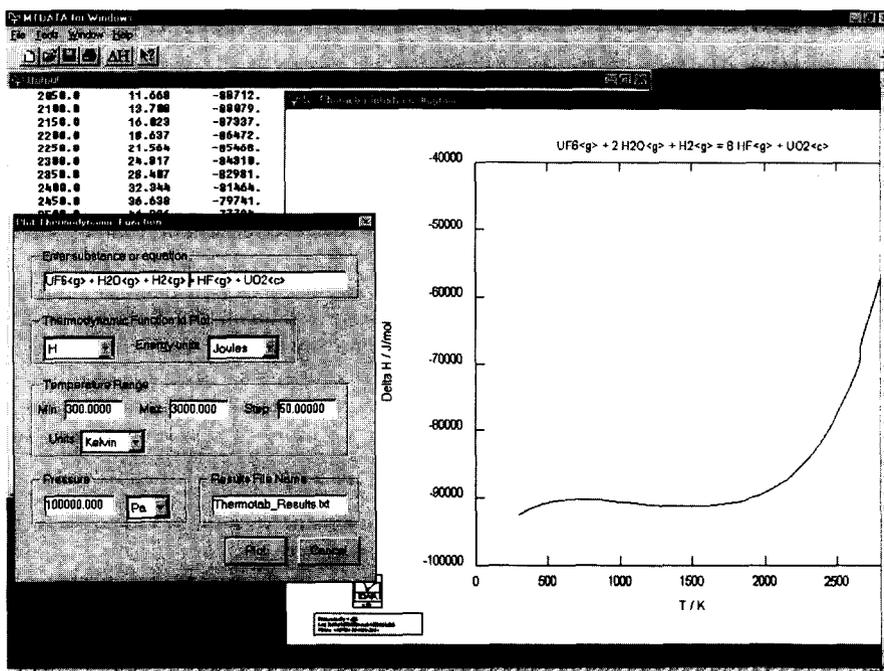


Figure 7.3.1 Screenshot showing calculation of thermodynamic functions for a chemical reaction using MTDATA for Windows

There is convenient, simple to use graphical user interface to these calculations from MTDATA for Windows and shown in Figure 7.3.1.

7.4 UNARY

The UNARY module is used for the calculation of thermodynamic properties for individual phases in a one component system.

The development of a thermodynamic database that can be used in the calculation of equilibria in multicomponent systems requires that all the data are consistent. This is achieved by building the data from a foundation, preferably those agreed internationally, for pure components and their binary combinations. The components include the elements [91Din] and important compounds such as salts and oxides.

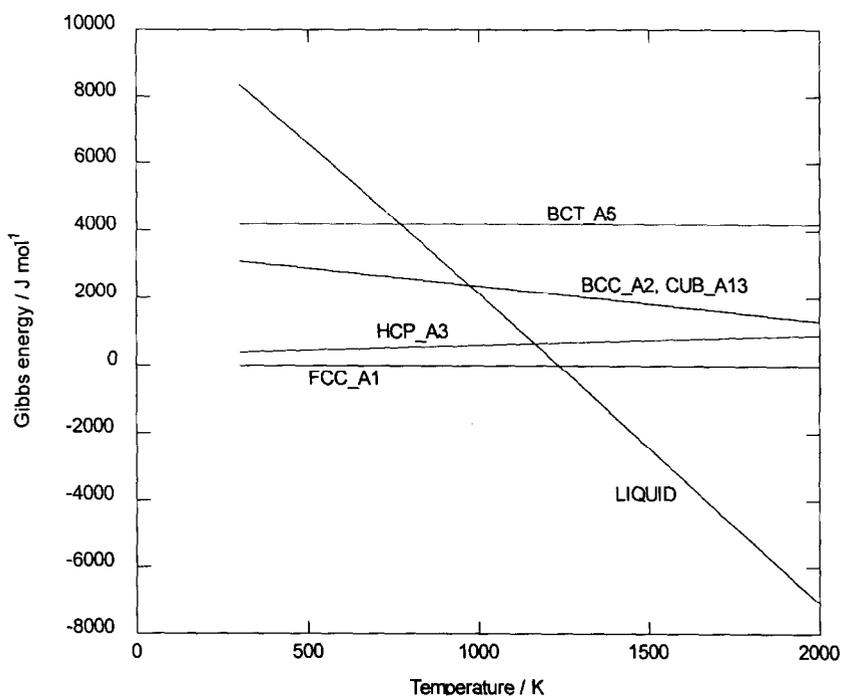


Figure 7.4.1 Gibbs energy of various phases of Ag relative to fcc_a1 as a function of temperature.

Figure 7.4.1 shows the Gibbs energy calculated by UNARY as a function of temperature for the stable phases of silver, liquid, and fcc, as well as the unstable phases, hcp, bcc, bct_a5 and cub_a13. The Gibbs energy curves are plotted relative to the fcc phase and cross at temperatures corresponding to the transition temperatures.

UNARY can also be used to examine other properties. Figure 7.4.2 shows the variation of the molar volume of the various phases of uranium as a function of temperature.

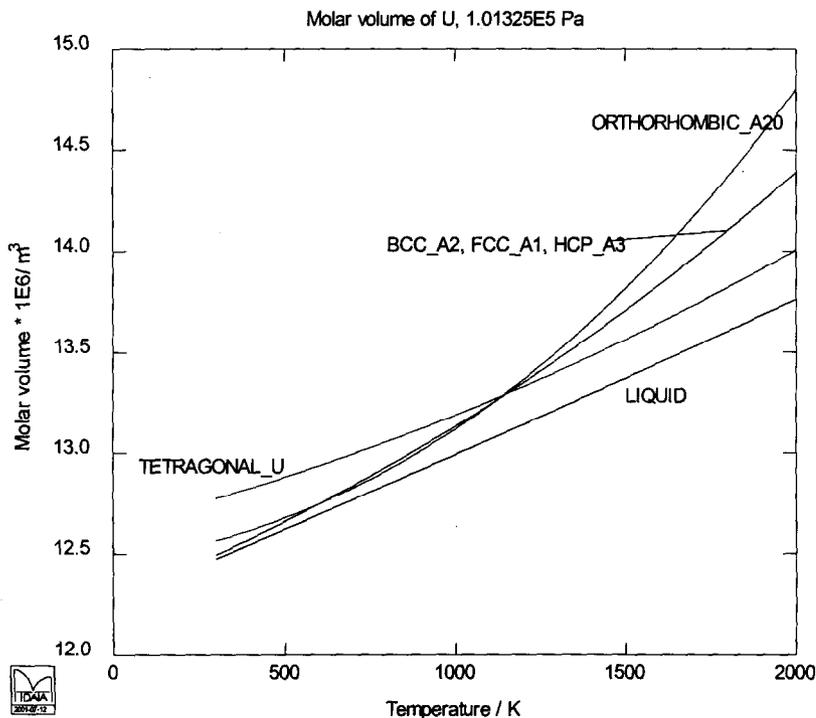


Figure 7.4.2 Calculated variation of the molar volume of the various phases of uranium as a function of temperature

7.5 BINARY

The fcc or γ -phase of pure iron is stable over the temperature range 1184.8 K to 1667.5 K. Titanium dissolves in the fcc phase but only to a limited extent. Figure 7.5.1 shows the use of BINARY to provide a very simple mechanism to calculate the binary phase diagram. Regions of the diagram can be expanded to display the shape of the γ -loop and to compare the result with experimental data. Once the user has retrieved the data, calculations can be initiated automatically by moving the cursor to a suspected two-phase field and pressing a defined key. The data used in the calculation of Figure 7.5.1 have been used in the prediction of phase equilibria in multi-component steels [89Bar, 89How].

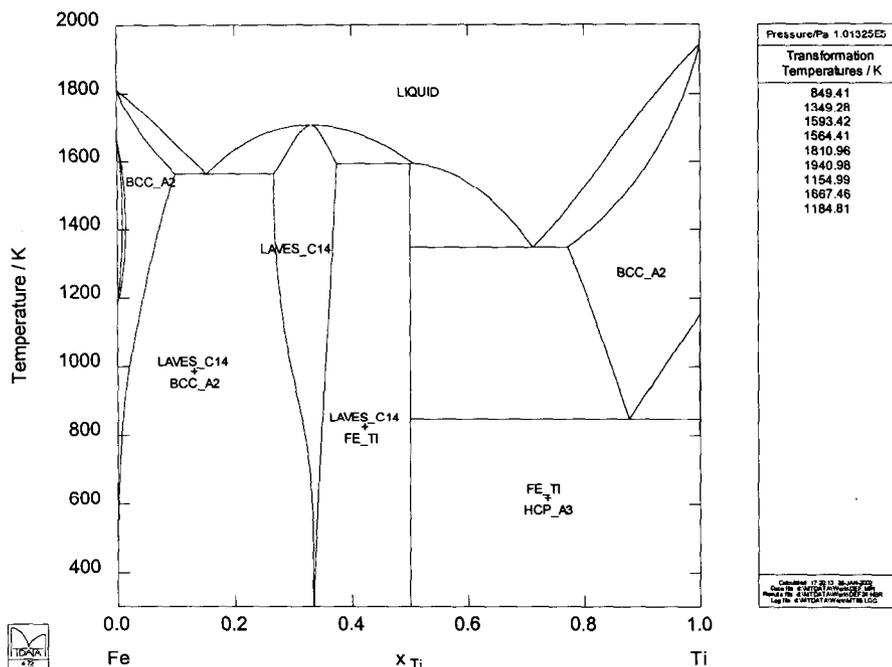


Figure 7.5.1 Calculated phase diagram for the Fe-Ti system

7.6 GPLOT

GPLOT is used for tabulating and plotting thermodynamic properties for purposes of data assessment, mainly, but not exclusively, for binary systems. The assessments are based on all the available thermodynamic and phase equilibria data and, where these are insufficient or of doubtful validity, on well-established methods of estimation. In the Fe-Mo system the sigma phase and a number of other phases are stable over a limited range of temperature and composition. Figure 7.6.1 shows that, in the middle of the composition range, the Gibbs energy of the sigma phase is lowest, whereas, on either side, a two-phase combination of the sigma and bcc, and sigma with other phases are stable. GPLOT may be used together with UNARY, BINARY, MULTIPHASE and ASSESSMENT modules in the computer-aided assessment of data.

7.7 MULTIPHASE

The principal calculation module of MTDATA is MULTIPHASE. As the name suggests, this can solve equilibrium problems involving many phases and components. Given the composition, temperature and pressure (or volume) of the system, MULTIPHASE will calculate the equilibrium state in terms of the distribution of components and species between the stable phases. The volume or pressure will also be determined. Output may be tabular or graphical, the latter allowing a large number of plots to be drawn for the same set of equilibrium calculations.

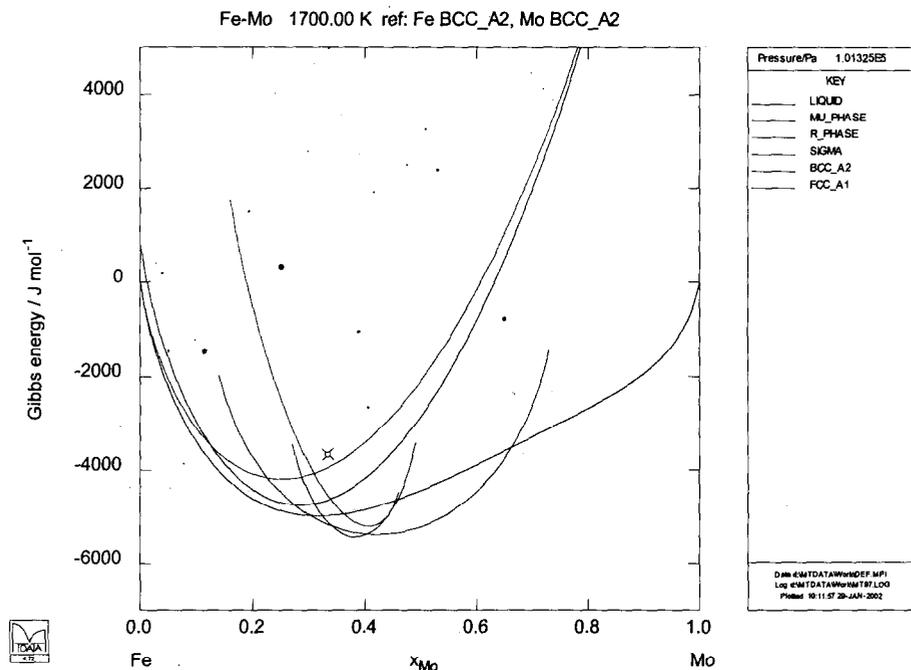


Figure 7.6.1 Plot of Gibbs energies of various phases in the Fe-Mo system at 1700 K

MULTIPHASE allows composition, temperature, pressure or volume, partial pressures, and activities to be set and one independent variable stepped. Amounts can be specified in terms of mass or moles and can be stepped in multidimensional component space. Depending on the nature of the problem, either or both of two calculation stages can be used. The first employs a particularly reliable method of determining equilibrium when all component and phase amounts are greater than 10^{-6} mol. The second stage, similar to other established chemical equilibrium programs [90Bal], may be invoked to give extra accuracy in small species amounts when each thermodynamic component has a well-established and independent activity in the system. Instead of the results being available to a constant tolerance in species amount, Stage-2 determines the speciation to a tolerance on a logarithmic scale. No start points are required to initiate the calculations. However means are provided to make the calculations more efficient by using results or the program variables from previous calculations as a starting point for the next calculation.

The calculation of equilibria in a system of many components generates an enormous quantity of information that can rarely be displayed on a single graph and would be difficult to assimilate in tabular form. For this reason MULTIPHASE incorporates flexible procedures to control what is to be plotted from the graph files calculated previously. Amounts of phases or substances (individually, in a phase, compounds of a particular component, or all), component distribution between phases or within a phase, component and compound activities, molalities, partial pressure, Gibbs energy and other thermodynamic quantities can all be plotted. The axis

scales can be varied and made logarithmic, and amounts can be expressed in moles or mass terms irrespective of the way the problem was formulated. Moreover, the abscissa of the graph can be changed from the originally stepped variable to one of the calculated variables.

A typical use of MULTIPHASE is to define the system composition and calculate the chemical and phase equilibria over a range of temperatures. Figure 7.7.1 shows the results from a calculation of the combustion of a dirty fuel in air between 300 and 2000 K. As a large number of species (165) and phases (24) were considered during the calculation figure 7.7.1 has been plotted to show the partial pressures of only species containing sulphur. The labelling of curves is automatic and the full traceability information is shown to the right of the graph.

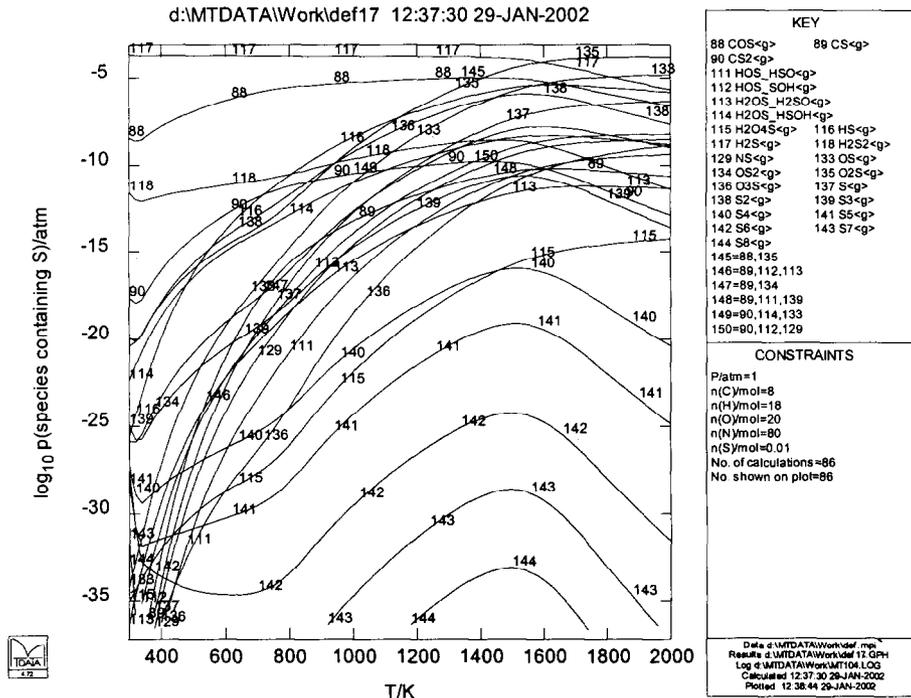


Figure 7.7.1 Calculated partial pressures of sulphur containing species on combustion of a dirty fuel

In the example illustrated in Figures 7.7.2-7.7.4 equilibria have been calculated across the ternary system CaO-FeO-Fe₂O₃-Al₂O₃-SiO₂ between a start and final composition. In order to display the often very extensive results of such calculations MULTIPHASE offers many plotting options. The example illustrates just three of these.

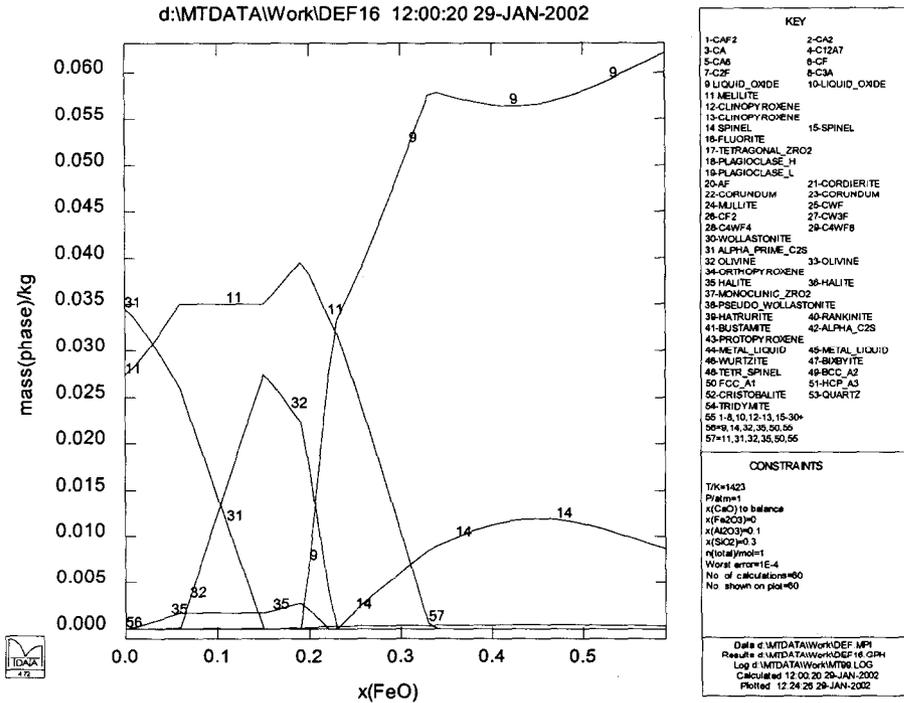


Figure 7.7.2 Calculated masses of the phases in the CaO-FeO-Fe₂O₃-Al₂O₃-SiO₂ system as a function of composition.

Figure 7.7.2 shows the masses of the phases present and Figure 7.7.3 the distribution of SiO₂ between the phases. The composition of the liquid phase in terms of the components (the user has elected to confine the plot to the range over which the liquid is stable) is plotted in Figure 7.7.4. This final diagram of the set shows the species present in the liquid, some of which, for example Ca₂SiO₄ are associates. This type of diagram can be used in data assessment since it enables the user to monitor which constituents of the solution and therefore which interactions are making a significant contribution to the Gibbs energy.

MULTIPHASE can also be used to calculate various properties associated with solidification of commercial alloys. In the example illustrated in Figure 7.7.5 equilibria in a 9 component commercial Aluminium alloy have been calculated as a function of temperature. The results showed display the heat capacity of the equilibrium alloy. Simulations of Cp for various alloys are currently being compared, at NPL, with precise measurements of Cp as part of a UK Government funded programme on the measurement of data for process simulation.

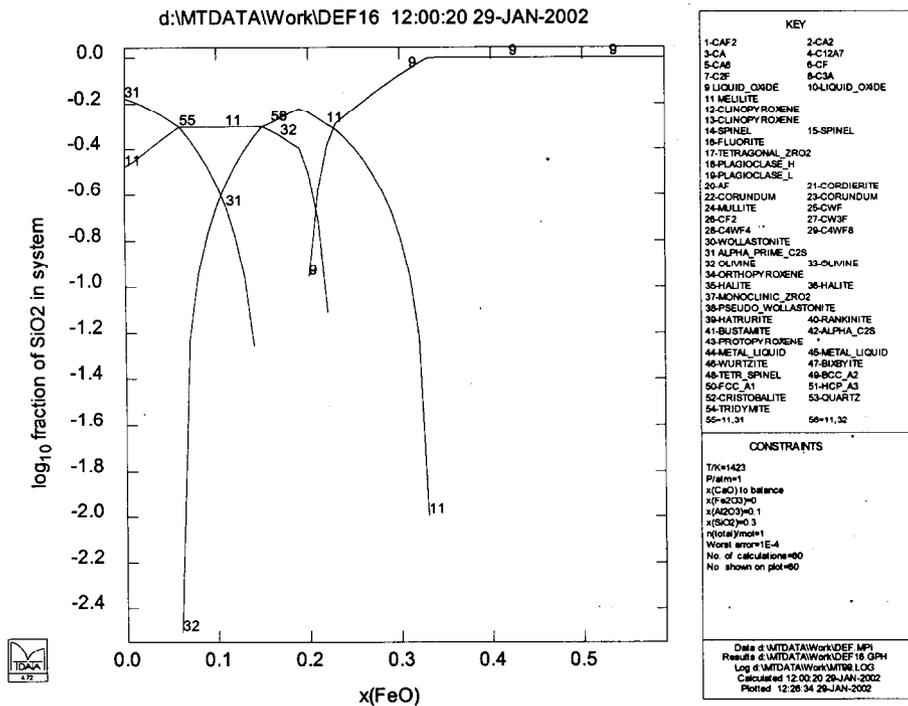


Figure 7.7.3 Calculated distribution of SiO₂ between phases in the CaO-FeO-Fe₂O₃-Al₂O₃-SiO₂ system as a function of composition.

For purposes of data assessment and exploration of metastable phenomena it is possible to suppress individual substances or phases from the calculation. Hayes et al [90Hay] have used this facility to model metastable phenomena in steels.

If some information about the equilibrium state is available it may be useful to evaluate equilibria applying this information as a constraint. For example the oxygen partial pressure, the pH or the mole fraction of iron in the liquid phase may have been measured. It is almost always best to express the problems posed to MULTIPHASE in terms that match as closely as possible the experimental or actual conditions. This ensures that the problem has a solution and that the results are pertinent to the real situation.

In addition to constraints on composition or activity the problem may be posed with a constraint on the enthalpy. This allows the simulation of an adiabatic process where the system maintains a constant enthalpy and as a result a rise or fall in temperature occurs. Examples of these types of process would include combustion for the former and evaporation for the latter. Figure 7.7.6 shows the calculation of the adiabatic temperature resulting from the combustion of carbon in oxygen.

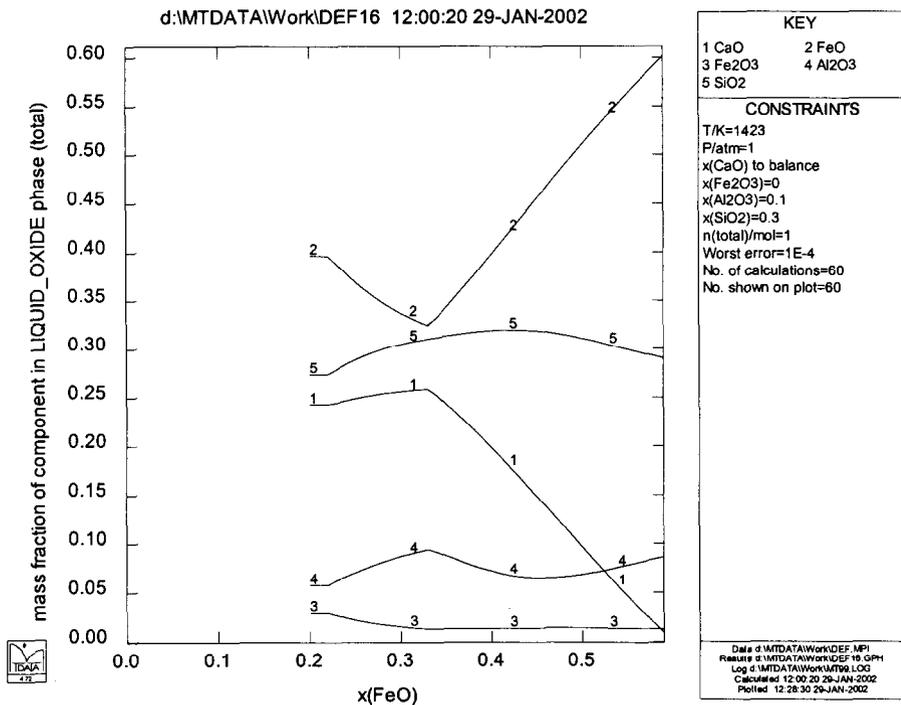


Figure 7.7.4 Calculated composition the liquid phase in the CaO-FeO-Fe₂O₃-Al₂O₃-SiO₂ system as a function of composition.

7.8 TERNARY

The TERNARY module calculates and plots isothermal ternary phase diagrams via a simple graphical interface. The diagram and the process of calculating interlinked two and three phase regions is automatic. Facilities are provided, by the graphical interface, for labelling phase fields semi-automatically. Diagrams may be replotted with magnification, component rotation and experimental data overlaid. Examples of the output have already been given in figures 4.2 and 6.1. Figure 7.8.1 shows a calculated phase diagram for the K₂O-Al₂O₃-SiO₂ system at 1273 K, which is based on assessments for the three binary subsystems and some experimental studies of the ternary system.

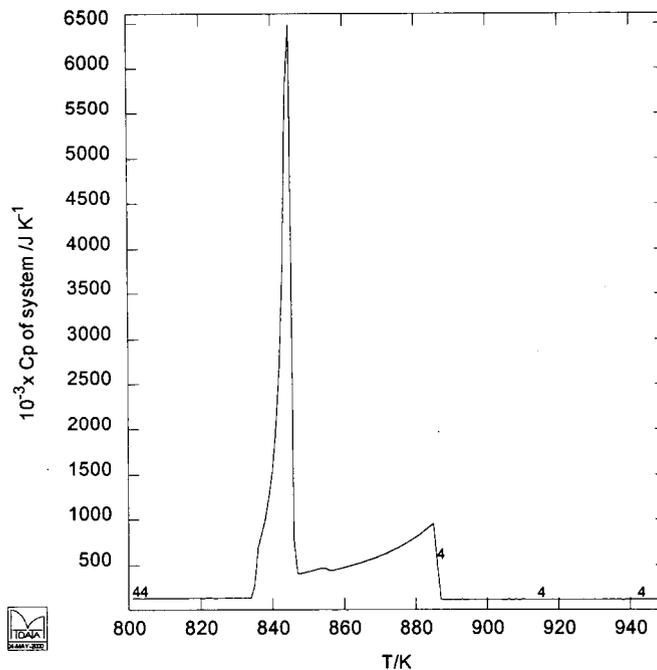


Figure 7.7.5 Calculated heat capacity of a 9 component aluminium alloy assuming the alloy remains in thermodynamic equilibrium

TERNARY also allows diagrams for reciprocal systems to be calculated and plotted. Figure 7.8.2 illustrates this for the NaCl-KCl-NaBr-KBr system. In systems of this type there are only three independent components but symmetry demands that the diagram should be plotted on a square rather than a triangle. The model for the solid solutions allows independent mixing on two sublattices. In this particular case, because all the ions are univalent, the same simple model can also be used for the liquid phase. The parameters were assessed or validated from published information. At lower temperatures the calculated diagram shows the existence of miscibility gaps emanating from the NaCl-NaBr and KCl-KBr systems. The predictions for the reciprocal system bear all the features indicated by experimental studies [35Rad]. If polyvalent ions were involved the variable site two-sublattice and other models could be used, thereby making it easy to compare the ability of the various models to represent the overall phase equilibria.

Figure 7.8.3 shows a diagram calculated by TERNARY for the FeO-Fe₂O₃-SiO₂ system. In this system iron is present in two valence states and the equilibria are not confined within the system FeO-Fe₂O₃-SiO₂ because iron and oxygen are implied by making the amounts respectively of Fe₂O₃ or FeO negative. The diagram shows that at compositions along the boundaries of the region corresponding to the liquid phase, the slag is in equilibrium with variously bcc iron, cristobalite and wüstite and spinel (magnetite) solid solutions. The compositions of the coexisting phases correspond with the positions of the ends of the tie-lines.

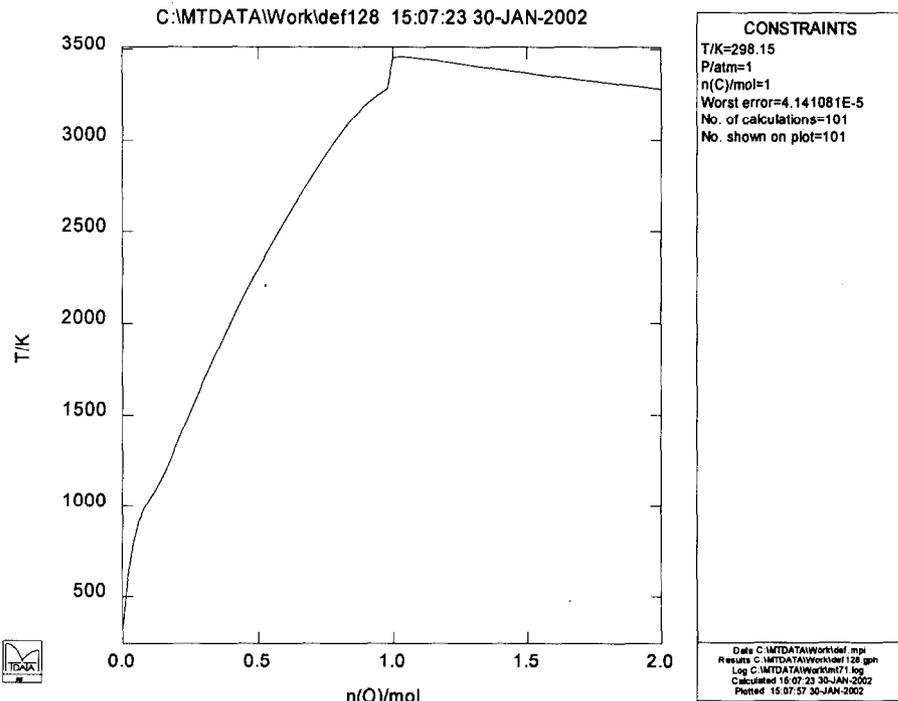


Figure 7.7.6 Calculated adiabatic temperature resulting from the combustion of carbon in oxygen

7.9 APPLICATION

The APPLICATION module has two purposes. Firstly it provides access to a number of standard "built-in" applications distributed with MTDATA but which have not yet been built into the general MTDATA framework. It also provides access to an interface that allows user supplied Fortran 77 code to be linked with MTDATA. A set of "tools" (the Application Interface, see section 8) is provided to facilitate the writing of user applications. The applications may involve extensive computation, effectively using MTDATA as a set of subroutines to solve equilibrium or non-equilibrium problems.

A simple example of a standard application is the calculation of the temperature for which a defined proportion of a given phase is calculated to be in equilibrium. This has been used to calculate a composition surface for a range of slags. Another example is a facility for calculating the phases present as a function of temperature across a multicomponent system (isopleth). Figure 7.9.1 shows an example for the join between two compositions in the Fe-Al-O system. The diagram gives a general impression of the phase equilibria but not of the proportions or compositions of the coexisting phases. MULTIPHASE should be used for detailed calculations. Other standard applications include Scheil solidification modelling, adiabatic calculations with multiple feeds that can themselves be equilibrated and phase diagram calculation for high order

systems (T-P, T-x, P-x, x-x), with interactive graphical interfaces similar to Binary and Ternary. An example of a calculated T-P phase diagram is shown in figure 7.9.2 for Fe.

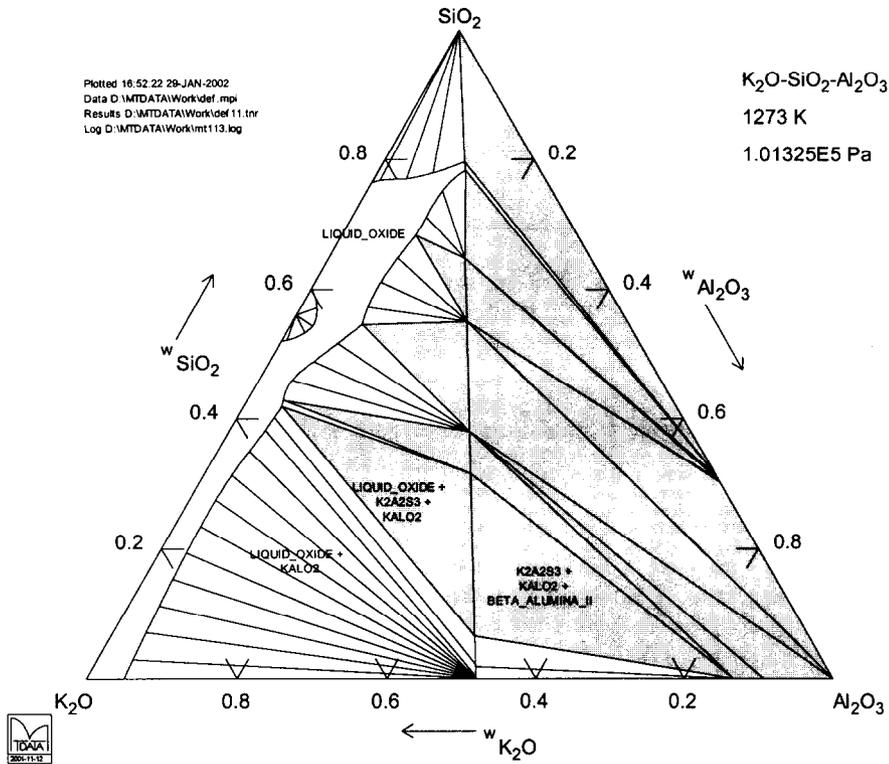


Figure 7.8.1 Calculated phase diagram for the K₂O-Al₂O₃-SiO₂ system as 1273 K

In addition to sections through phase diagrams the APPLICATION module also contains facilities for the calculation of projections of liquidus surfaces. A simple example is given in Figure 7.9.3, for a 3-component system. MTDATA can also perform similar projections in higher order systems which may include temperature contouring.

Pressure composition sections through 3-component or higher order systems may also be calculated. An example showing the oxidation phase behaviour of an Fe-Cr alloy is shown in figure 7.9.4.

The full list of built-in applications is given below.

Simple one dimension applications

- TRANSN_X - phase boundary compositions - fixed T and P
- TRANSN_T - phase boundary temperatures (eg liquidus and solidus temperatures) fixed P and x

- TRANSN_P - phase boundary temperatures - fixed T and x
- Projections**
- LIQUIDUS - Primary phase fields for a ternary system at a fixed pressure
 - LIQSECT - Liquidus contours and primary phase fields for a triangular cut in composition through a multicomponent system
 - LIQCONT - Liquidus temperature contours for a triangular cut in composition through a multicomponent system
- Sections**
- ISOPLETH - Temperature - composition diagrams at fixed P
 - TRISECT- Pseudo ternary sections at a fixed T and P
 - PX - Pressure - composition diagrams at a fixed T
 - TP - Temperature - Pressure phase diagrams for a fixed composition
- Solidification simulation**
- TSCHAIL - Recommended Scheil simulation with constant temperature steps
 - SCHEIL - Scheil model with constant proportion of liquid solidifying
 - CPSCHAIL - SCHEIL but also calculates the enthalpy and heat capacity associated with the solidification
- Miscellaneous**
- ADIABAT - Adiabatic temperature calculations for the mixing of different reaction streams

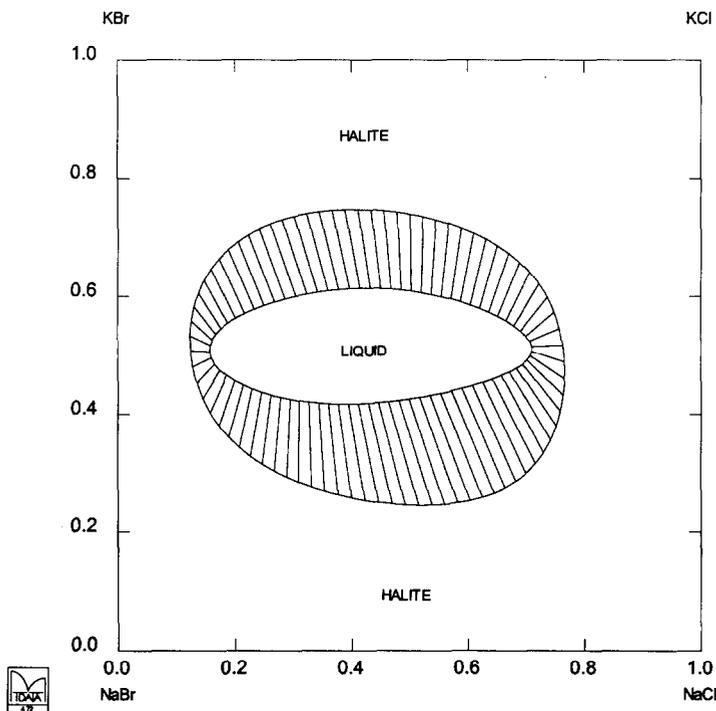


Figure 7.8.2 Calculated phase diagram for the NaCl-KCl-NaBr-KBr system at 900 K

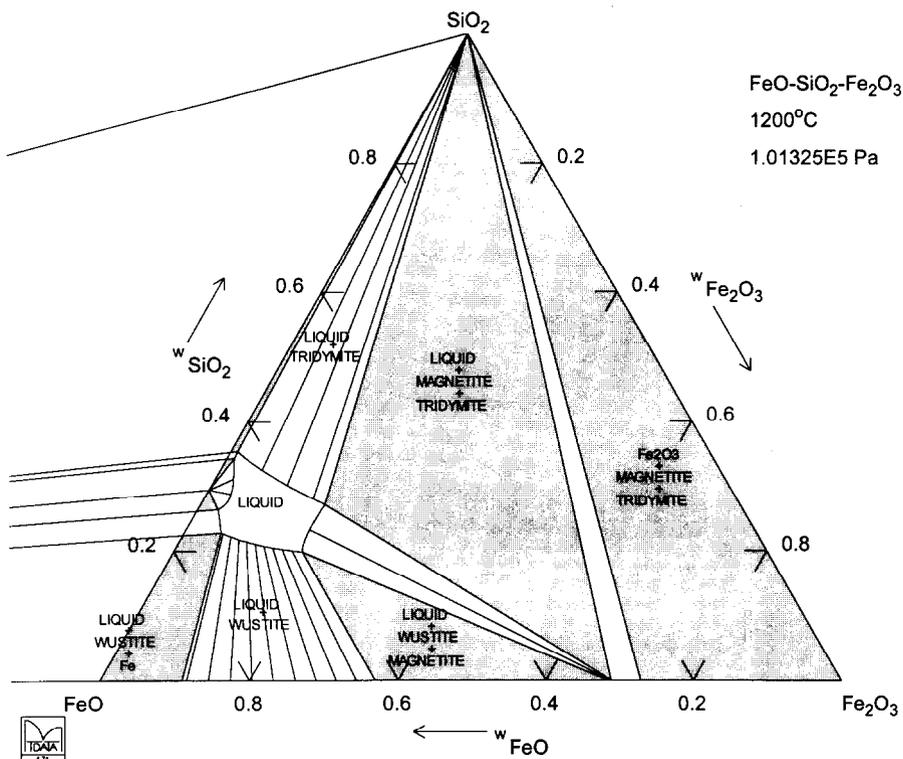


Figure 7.8.3 Calculated phase diagram for the FeO-Fe₂O₃-SiO₂ system at 1200°C

7.10 COPLOTT

COPLLOT calculates and plots predominance area or Pourbaix diagrams for systems involving stoichiometric substances, gases, and ideal aqueous solutions. These types diagrams are much used by those concerned with hot and aqueous corrosion [87Bar] and with hydrometallurgy. The chemistries of more than one element can be explored at the same time. The application of MTDATA to the redox chemistry of H₂S in contact with water is described by Kelsall and Thompson [93Kel]. An example of a Pourbaix diagram is given in Figure 7.10.1. Two components, iron and sulphur, are present in an aqueous environment. The diagram shows the dominant phases, containing respectively iron and sulphur, found within the range of applied pH and E_h. COPLLOT has been written so as to allow the components whose behaviour is being investigated to be set by amount relative to 1kg of water and a gas phase of variable volume. This enables the module to be used to explore very rapidly a wide range of conditions, for example where sulphur and/or iron is present in solution at very low concentrations, as is important for corrosion avoidance. COPLLOT displays only the solid phases or "predominant" aqueous or gaseous species, thus, once the most important variables have been established, MULTIPHASE should normally be used to obtain more detailed information. Although the

example shown here is for an aqueous system COPLLOT may also be used for calculation of predominance area diagrams in systems containing ideal gaseous species and stoichiometric solids. In this case axis variables such as $\log_{10}P$ for O_2 and SO_2 could be used.

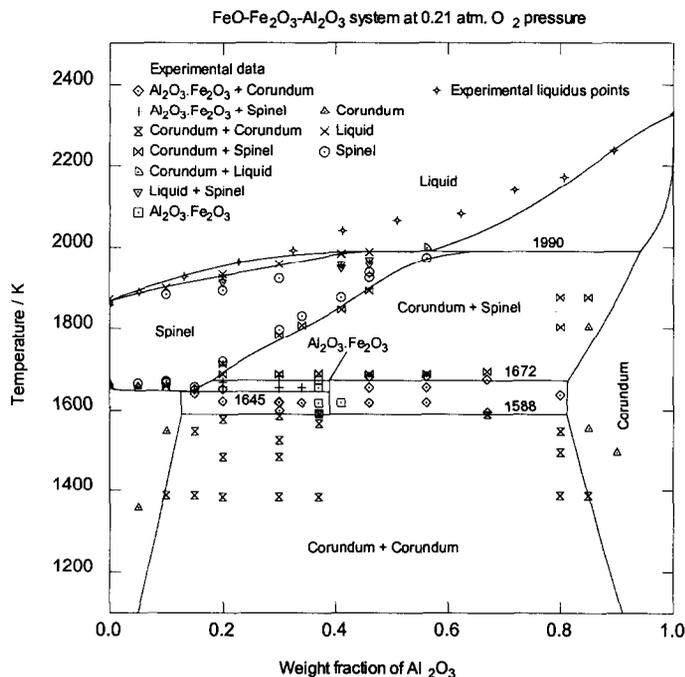


Figure 7.9.1 Calculated isopleth between Fe₂O₃ and Al₂O₃ in air

7.11 FITANDPLOT

FITANDPLOT provides a generalised multi-range data fitting capability for heat capacity, enthalpy and Gibbs energy data for substances tabulated as a function of temperature. It integrates with other MTDATA modules. The user determines the function and manipulates the closeness of the fit either by selecting the functional form, setting a tolerance or fixing the splitting points between ranges. Errors in the input data can be exposed by means of a difference method and, if desired, semi-automatically corrected. As the name suggests the module provides an immediate graphical view of the results showing data points, fitted curve, user inputted splitting points and automatically determined splitting points.

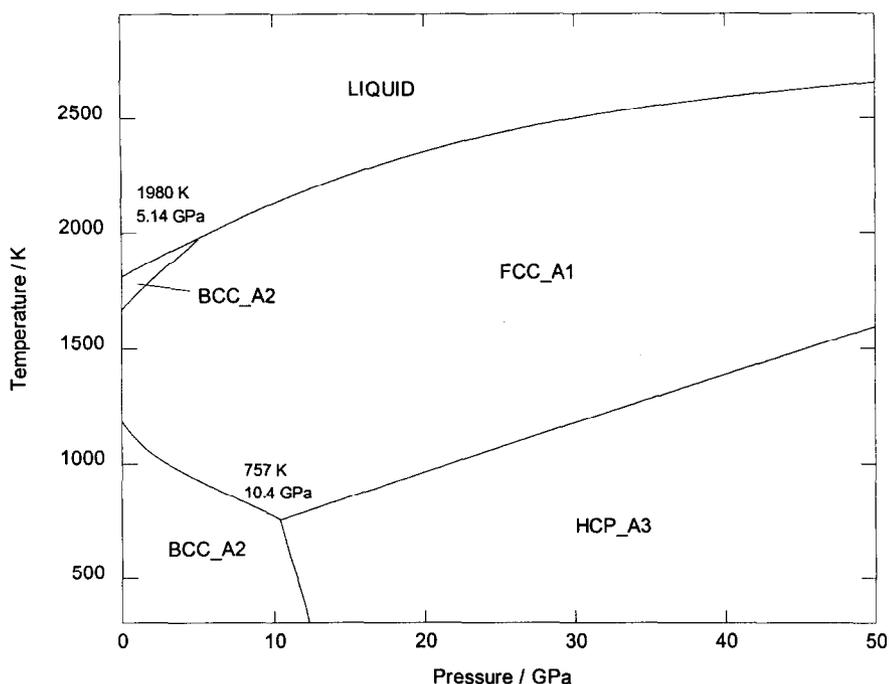


Figure 7.9.2 Calculated temperature - pressure phase diagram for Fe

7.12 ASSESSMENT

The ASSESSMENT module provides tools to help in the task of deriving values for thermodynamic model parameters, which, when used as a basis for phase equilibrium calculations, give the best possible representation of a collection of experimental measurements obtained for a particular chemical system. This overall task of gathering data and generating values for parameters is referred to as data assessment or sometimes critical assessment since it involves comparing data of many different types, from many different sources, obtained using many different experimental techniques. The specific task of generating model parameters appropriate to a set of experimental data is called optimisation.

Experimental data for a particular system are supplied to the ASSESSMENT module via an experimental data file. Any property or combination of properties that can be calculated using MTDATA can feature in this file, which takes the form of a macro giving instructions for the calculation of each property and associating each calculation with an experimental value and uncertainty (using the LIST command). Properties typically considered in experimental files include activities, heats of mixing, equilibrium phase compositions and phase boundary temperatures and compositions. Best results are obtained where a good mix of thermodynamic measurements and phase equilibrium data are available.

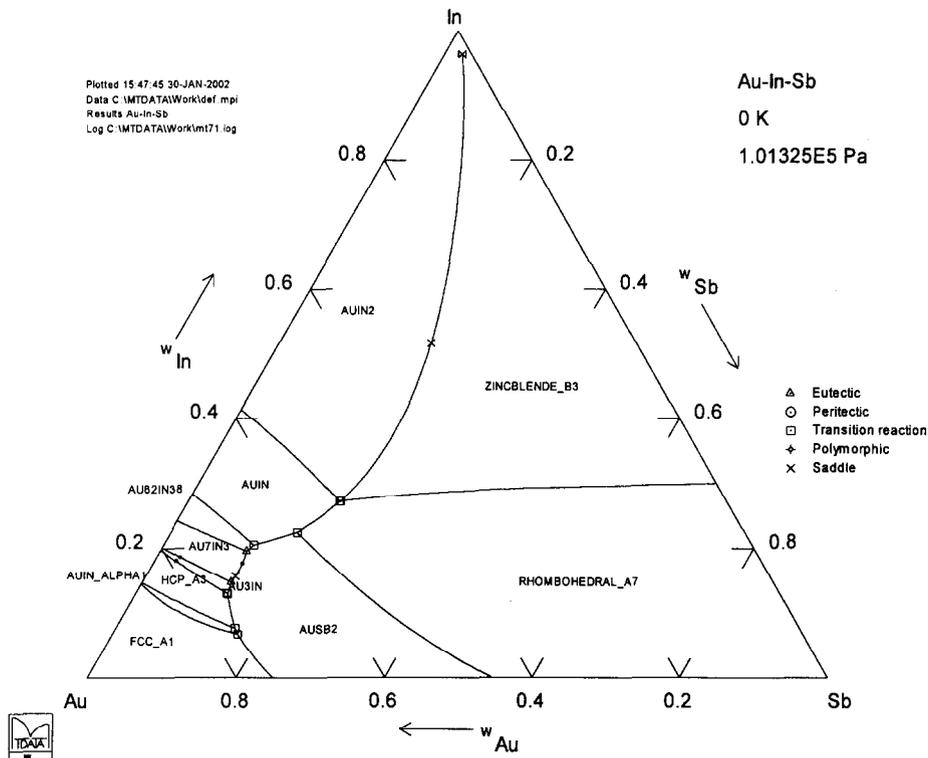


Figure 7.9.3 Liquidus projection for Au-In-Sb showing primary phase fields

Individual thermodynamic parameters from the data input (.mpi) file are referred to by number (or index) during the process of setting up an optimisation run. The SHOW command is used to reveal the index appropriate to each parameter. Once a parameter's index is known the parameter can be flagged for possible change during an optimisation run using the MODIFY command. Sets of parameters, which span temperature ranges, will be linked together such that any change made to one will be mirrored in its partner(s).

Three algorithms are available for the optimisation. An optimisation run is initiated using the OPTIMISE command. During such a run the values of parameters flagged for optimisation are changed automatically to minimise differences between calculated properties defined in the experimental data file and their experimental values. The actual function minimised is the weighted sum of squared errors where an error is defined as the difference between calculated and experimental values of a property divided by the stated experimental uncertainty. The is given by:

$$\text{Weighted sum of squares of errors} = \sum_{i=1}^N W_i \left(\frac{C_i - E_i}{U_i} \right)^2$$

where n is the number of properties considered in the optimisation run, C_i is the calculated value of property i , E_i is the experimental value of property i , U_i is the uncertainty associated with E_i and W_i is the weight assigned to property i .

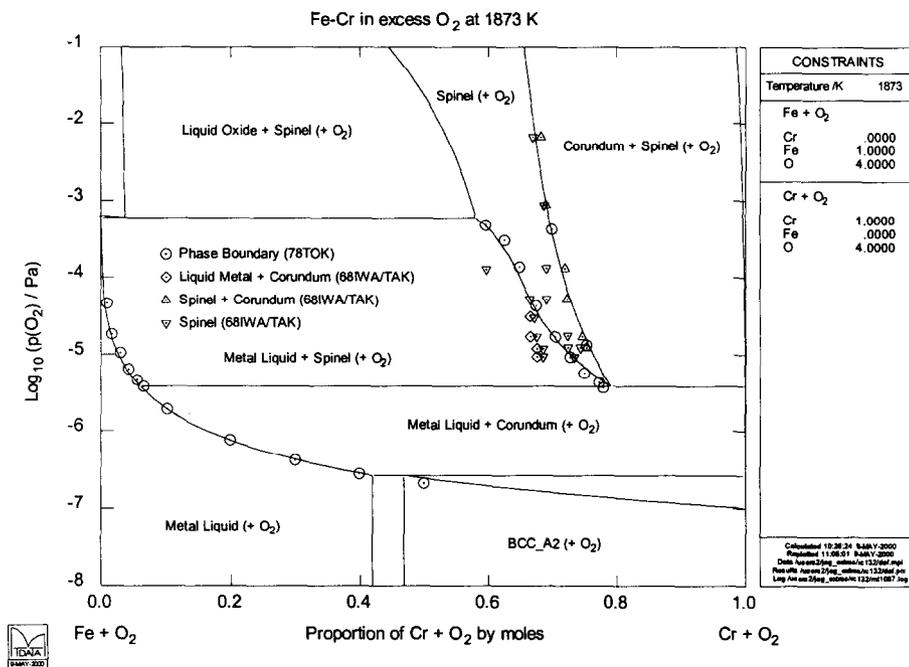


Figure 7.9.4 Pressure composition diagram at 1873K in the Fe-Cr-O system

Optimisation runs can be monitored graphically or by means of text output. In the former case plots illustrate changes in the optimised parameters and corresponding changes in the weighted sum of squared errors as they happen (see Figure 7.12.1). Typically an assessment will involve many optimisation runs with different numbers of parameters being changed and more experimental data being added at each stage.

As a prelude to an optimisation run it is often useful to obtain a crude impression of the effects of varying individual thermodynamic parameters. This helps in selecting suitable parameters for change. To facilitate this, one or two parameters can be flagged for stepping using the MODIFY command. On issue of the STEP_PARAMETER command the values of these parameters are varied automatically based upon a specified SCALE (magnitude of changes) and number of steps, a comparison between calculated properties and experimental data being made at each stage.

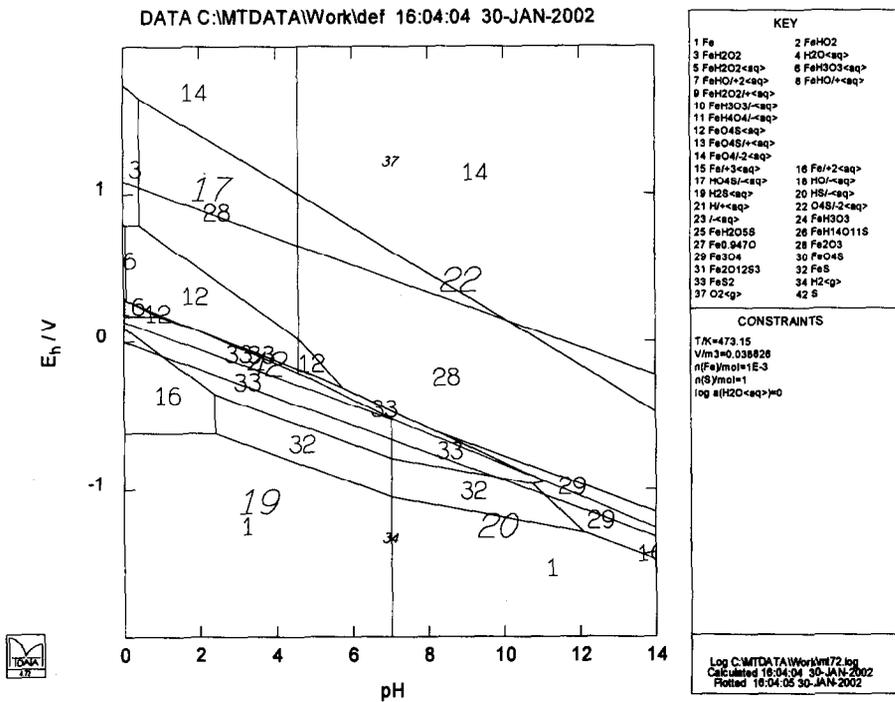


Figure 7.10.1 Pourbaix diagram for the Fe-S-H₂O system at 200°C

Properties calculated using parameter values resulting from an optimisation run can be compared with experimental data graphically using the PLOT command (see Figures 7.12.2, 7.12.3 and 7.12.4) or in the form of a results table using the LIST command. In order to make more complex calculations using the new parameters it is possible to SWAP to other MTDATA modules while still retaining the optimised data in memory. If the new parameters are found to be unsatisfactory, perhaps due to a lack of experimental data to constrain their values, it is possible to UNDO the effects of an optimisation run and recover the parameter values appropriate at its start.

Optimised values of parameters can be saved in an in-memory store or saved in a data loading file for the purposes of updating an MTDATA database. Alternatively a set up file (MTDATA macro) can be written, allowing the exact state of the existing optimisation to be recreated at a later date.

```

; Water activity data at 298.15 K
;
; Macro      T/K  molality act(H2O)  uncert  reference
``actH2O.mac`` 298.15  0.1  0.998004  0.0001  ``actH2O-298:74PIT/MAY``
``actH2O.mac`` 298.15  0.2  0.99639  0.0001  ``actH2O-298:74PIT/MAY``
``actH2O.mac`` 298.15  0.3  0.994889  0.0001  ``actH2O-298:74PIT/MAY``
``actH2O.mac`` 298.15  0.4  0.993443  0.0001  ``actH2O-298:74PIT/MAY``
``actH2O.mac`` 298.15  0.5  0.99202  0.0001  ``actH2O-298:74PIT/MAY``

; NiSO4 enthalpy of formation at various concentrations [82WAG]
;
; Macro      n(H2O)  DfHsol  uncert  reference
``DfHdil.mac`` 200.0  -958505  500  ``DfH-298:82WAG``
``DfHdil.mac`` 300.0  -958672  500  ``DfH-298:82WAG``
``DfHdil.mac`` 400.0  -958797  500  ``DfH-298:82WAG``
``DfHdil.mac`` 500.0  -958906  200  ``DfH-298:82WAG``
``DfHdil.mac`` 800.0  -959169  200  ``DfH-298:82WAG``

; NiSO4 solubility [65LIN, Vol II, p1219] for equilibrium aq + NiSO4(H2O)7<c>
;
; Macro      T/K      wt fraction  uncert  reference
``T-W1.mac`` 273.15  0.216  0.005  ``Solub-NH5:65LIN``
``T-W1.mac`` 278.15  0.231  0.005  ``Solub-NH5:65LIN``
``T-W1.mac`` 283.15  0.246  0.005  ``Solub-NH7:65LIN``
``T-W1.mac`` 288.15  0.261  0.005  ``Solub-NH7:65LIN``

```

The example above shows at typical layout of an MTDATA Assessment module experimental file. Note macros (eg "actH2O.mac") are used to calculate properties for comparison with experiment.

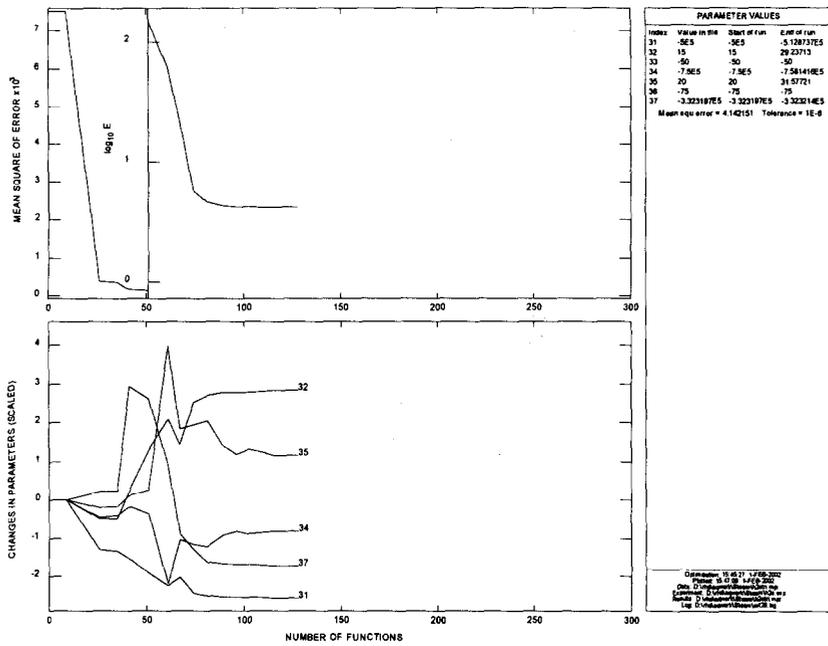


Figure 7.12.1 Real time display of objective function (top) and scaled parameters values
 Assessment Module: Correlation Plot

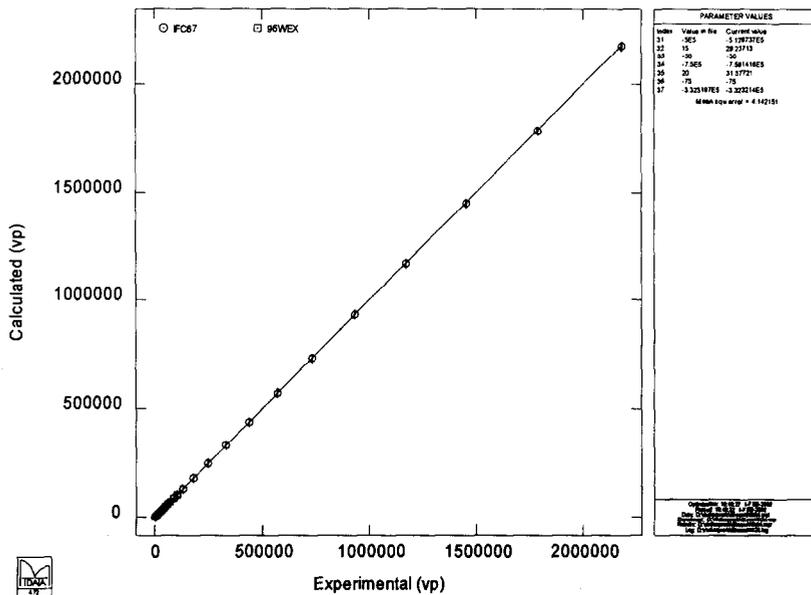


Figure 7.12.2 Correlation plot showing calculated versus experimental values of property

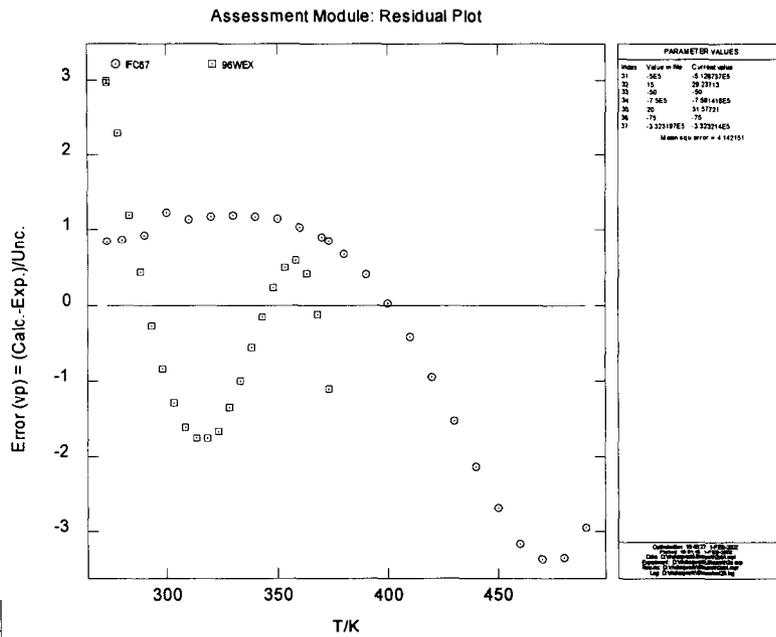


Figure 7.12.3 Residual plot showing differences between each calculated and experimental values of property "vp" (water vapour pressure)

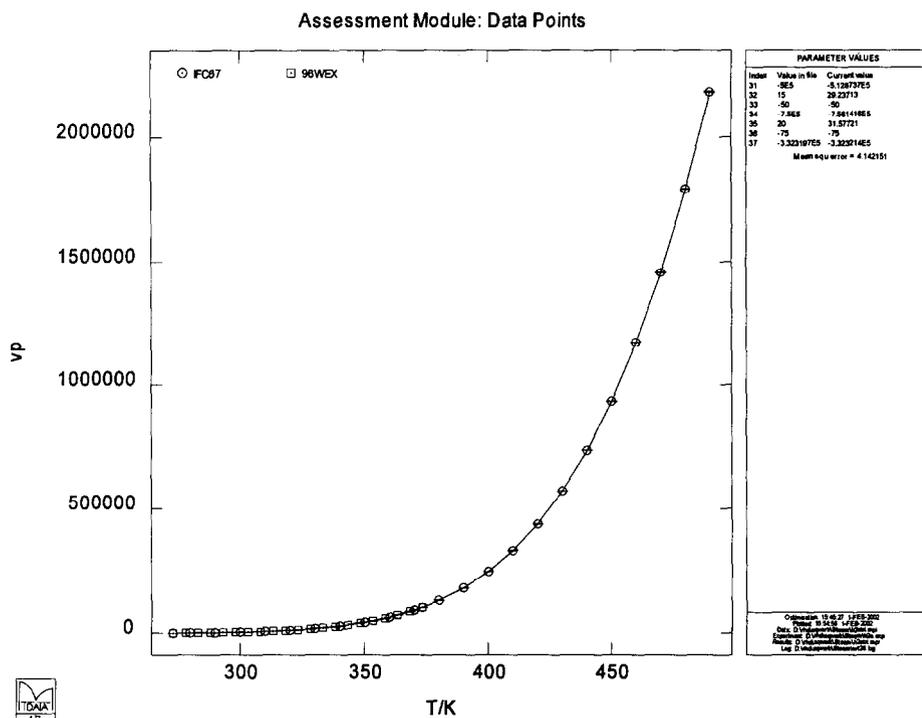


Figure 7.12.4 Plot of calculated property values showing experimental data as symbols

8 APPLICATION PROGRAMMING

The aim of the MTDATA Application Interface is to allow users to write software of their own, specific to particular applications, which makes use of the existing functionality of MTDATA. It also allows users to link MTDATA with third party software, such as kinetics, fluid flow or plant simulation and management packages. The Application Interface takes the form of a series of functions and subroutines which are documented in a programming guide.

Two different styles of application are available. The simplest is where the user builds some of their own code into MTDATA's Application Module (MTDATA as MASTER). The user applications then appear very similar to the NPL written ones described in Section 7.9 above. In this style of application the user only needs to concentrate on numerical problems as MTDATA provides a command line interpreter to handle database searching, phase classifications, setting up initial conditions and plotting of results.

The second style of MTDATA application is where the user is responsible for writing a new Main program (MTDATA as SLAVE). The diagrams below illustrate both of these styles of application with some examples of typical subroutine calls.

Built-in MTDATA applications such as the Scheil solidification simulation are written using the structure show in Figure 8.1 (see also section 7.9) and stand alone applications, such as the NPL Virtual Measurement Systems, use the structure shown in Figure 8.2 (see also section 5)

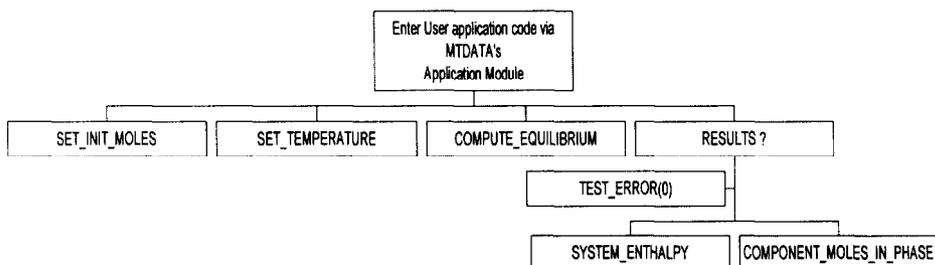


Figure 8.1 Layout of MTDATA-MASTER Application

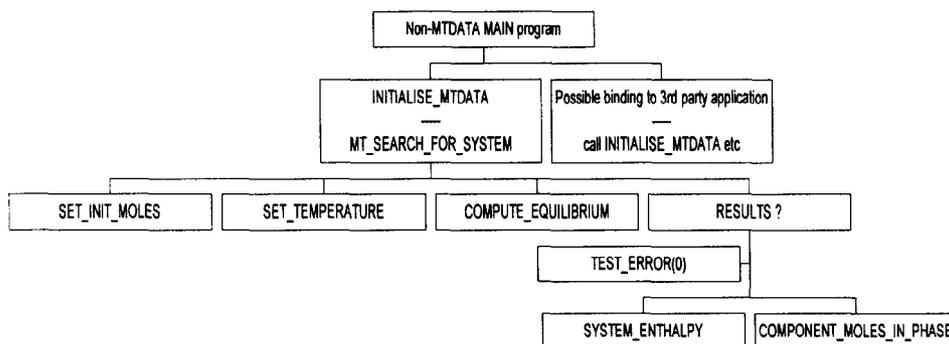


Figure 8.2 Layout of MTDATA-SLAVE Application

9 DATABASES

9.1 UNARY

The SGTE unary database contains data for around 78 elements in a form appropriate for phase diagram modelling. SGTE [87Ans] is an international consortium of leading organisations involved in the critical assessment of thermodynamic data and their use in the calculation of phase equilibria. Assessed data are provided for stable and metastable phases for each element from 298.15 K, or in some cases 200 K. In some cases, additional terms are included to describe the pressure or magnetic contributions to the Gibbs energy. The data have been published in a

paper by Dinsdale [91Din] but have been revised a number of times since then. The database is consistent with ITS90. The current version of the database is 4.4.

9.2 SGSOL

The SGTE solution database contains data for multicomponent, non-ideal solution phases. Elements included in the current version (3.01) 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, Y, Zr.

Between these elements, there are assessed data for over 230 binary and higher-order combinations. For example, taking aluminium alone, there are data for liquid, solid-solution and stoichiometric phases in the following systems:

Al-Ag, Al-As, Al-Bi, Al-Ca, Al-Cr, Al-Cu, Al-Fe, Al-Ga, Al-Ge, Al-Hg, Al-In, Al-Mg, Al-Mn, Al-Ni, Al-P, Al-Pb, Al-Sb, Al-Si, Al-Sn, Al-Ti, Al-V, Al-Zn, Al-Ca-Si, Al-Mg-Si, Al-Si-Zn.

The database comprises:

- expression 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.
- expressions for the excess Gibbs energy for any solution phases formed between the end-member species. These expressions are derived from various thermodynamic models.

There has been no update of SGSOL since version 3.0 was released in 1993.

9.3 MTSOL

The NPL Alloy Solution Database, MTSOL, is a general purpose database for use with MTDATA for the calculation of phase equilibria and thermodynamic properties for a wide range of alloy systems. The database is particularly strong for steels, aluminium alloys and 3-5 semiconductor systems and contains good coverage of binary data for low melting point systems, eg solders. MTSOL incorporates the latest SGTE Unary data (v4.4). MTSOL contains data for 423 binary and ternary systems assessed either at NPL, within SGTE or taken and validated from the published scientific literature. Version 1.2 of the database is being tested at the moment and release is expected in April 2002. MTSOL has been built upon SGSOL, the SGTE Solution Database, although all the datasets have been validated recently at NPL and corrected where appropriate.

9.4 MTSOLDERS

The database is designed for use in the calculation of phase equilibria involving solders and other low melting alloy systems. Alloys containing the following elements may be considered:

Ag, Al, Au, Bi, Cu, Ge, In, Pb, Sb, Si, Sn, Zn

The database contains critically assessed thermodynamic data for the 12 elements, all except one (Au-Zn) of the 66 binary systems and five ternary systems (Ag-Cu-Pb, Al-Cu-Si, Al-Sn-Zn, Au-In-Pb and Bi-In-Pb). The database may be used to make predictions of liquidus temperatures and phase equilibria in systems containing these elements but the results are likely to most reliable close to the binary and ternary systems covered explicitly by the database. The database is valid for temperatures between 50°C and 1000°C.

9.5 MTAL

The MTAL database is designed to allow calculations of phase equilibria to be carried out in Al-base alloys. At present the released version of MTAL (version 5) allows calculations in the 7 component system:

Al-Fe-Mg-Mn-Si-Cu-Zn

The database is also being extended incrementally with the addition of Ti, Ni and Cr

The MTAL database comes in two forms - a full version which includes data for phases not likely to be seen in aluminium system, and a reduced, released version with these phases taken out. In practice the results from the use of these two databases for aluminium alloys should be identical. Both versions of the database include pressure dependence of the Gibbs energy which allows calculations of the density and the effect of pressure on the phase diagram.

9.6 TCFE

This database has been developed by Thermo-Calc Software AB in conjunction with the CAMPADA project at the Department of Materials Science and Engineering, KTH. It is based on the TC-FE92 database and includes new assessments carried out up to 1998 for systems relevant to steels. The following system is covered:

Al-B-C-Co-Cr-Cu-Fe-Mg-Mn-Mo-N-Nb-Ni-O-P-S-Si-Ti-V-W

Based on the complete set of critical assessments of binary and a large number of relevant ternary assessments with special emphasis on some higher order systems in the iron rich corner, the database is however eminently suitable for calculations in the iron rich corner with a Fe minimum of 50wt %. It has been translated and tested for use with MTDATA.

9.7 TCNI

This database for Ni-based superalloys has been developed by TCAB and Dupin [2001Dup]. The thermodynamics of the γ and γ' phases are modelled with a single Gibbs energy function taking into account the crystallographic relations between these two phases after Ansara et al. [97Ans]. Calculations using the current database for multicomponent systems have validated its ability to extrapolate over a wide range of composition of interest for Ni-based superalloys both for equilibria in the solid state as well as for modelling solidification behaviour (liquidus temperature and partition ratios). The database has been translated and tested for use with MTDATA. At present the database contains 7 elements: Al Co Cr Ni Ti W Re

9.8 FEDILSOL

This database contains data for the dilute solution of 26 elements in liquid iron modified according to the modified Wagner model. It can be used in conjunction with SGSUB or with NPLOX to calculate the solubility of trace elements in liquid iron in equilibrium with a gas phase or a slag.

9.9 MTSEMI

The database contains data for condensed phases and gaseous species for system:

Al-As-Ga-In-P-Sb

and will allow exploration of the condition appropriate for the formation of the zincblend phase by chemical vapour deposition processes.

The data have been gleaned from the literature. The data for the elements are from the SGTE Unary database [91Din] and data for binary condensed phases eg liquid, zincblend, fcc, rhombo_a7 [94Ans]. Data for the ternary systems are taken from a number of sources; Ga-In-Sb from Yang and Watson [94Yan], Ga-In-P, Al-As-Ga, Al-Ga-Sb, Al-In-Sb, As-Ga-Sb, As-In-Sb, As-Ga,P, Ga-P-Sb, As-In-P, In-P-Sb, Al-As-In, As-Ga-P, Ga,P-Sb, As-In-P, In-P-Sb, Al-Ga-P, Al-In-P, As-Ga-In, Al-As-P, Al-P-Sb, Al-As-Sb and As-P-Sb [98Zha] and Al-Ga-In [78Ans].

9.10 NPLOX

This database contains data for liquid oxides and crystalline phases within the Na₂O-CaO-Fe-O-MgO-Al₂O₃-SiO₂ system. It represents a subset of a database developed mainly at NPL under an industrially funded project coordinated by the Mineral Industry Research Organisation. This enlarged database also covers Li₂O, K₂O, Cu-O, PbO, Mn-O, Cr-O, NiO, B₂O₃ and ZrO₂, containing systems, the modelling of hydrated systems and mattes.

Combined with existing data for alloys and gases, the database has already been used successfully to solve problems associated with iron formation in zinc blast furnaces, to assist in the extraction of copper and precious metals, to provide information on liquidus temperatures and primary phases of relevance to glass making, to assess the consequences of a nuclear reactor core meltdown and to model the behaviour of fly ash in coal combustion.

9.11 SALTS

The salts database contains data for more than 140 binary systems and includes representations of the Gibbs energies of the unary phases themselves as well as data for 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, CaCl₂, MgCl₂, ZnCl₂, Li₂CO₃, Na₂CO₃, K₂CO₃, Na₂SO₄, K₂SO₄, Na₂CrO₄, NaOH, InI, TlCl, TlI. A limited number of metal-salt systems have also been included.

9.12 AQDATA

AQDATA contains data for over 450 aqueous species, including ionic and neutral complexes: elements, oxides, hydroxides, halides, sulphates, sulphites, nitrates, nitrites, phosphates and many more. The database contains data valid only at room temperature and for dilute solutions.

9.13 HOTAQ

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

9.14 MTSPCRT

The MTSPCRT database is the MTDATA implementation of the high temperature dilute aqueous solution database (Slop98) developed for use with the SuperCrit program. It has enthalpy, entropy and heat capacity data for 1335 aqueous species mixing ideally. The reference states have been made consistent with other MTDATA databases.

9.15 MTCHVAL

The MTCHVAL database is the MTDATA implementation of the ChemVal database which was developed during a European Union project. The database contains data valid only at room temperature and for dilute solutions of 1356 aqueous species for nuclear environmental modelling.

9.16 MTCORR

This database contains data for metal oxygen systems eg Cr-Fe-Ni-O, Si-O, Al-O, Mn-O useful for the modelling of high temperature corrosion processes.

9.17 SGSUB

The SGTE pure substance database contains data for pure substances and gases. For each substance, the data consist of:

- the enthalpy of formation at 298.15 K relative to the pure elements
- the standard entropy at 298.15 K and a pressure of 101325 Pa
- the temperature dependence of the heat capacity typically from 298.15 K
- temperatures and enthalpies of transition for non gaseous substances

These data allow the Gibbs energy of each substance to be calculated as a function of temperature and so enable MTDATA to perform phase equilibrium calculations and tabulations. The present version of the pure substance database (version 10.0) contains assessed thermochemical data for over 4200 substances.

9.18 SGORG

SGORG is an organic supplement to the SGSUB database containing organic species containing more than 3 carbon atoms.

10 CONCLUSIONS

MTDATA is a general tool for calculating phase, chemical equilibria and thermodynamic properties with very high reliability with no need for initial guesses of the system/phase composition. A wide range of models and databases allow application to a large number of different types of problem.

In addition to the flexibility of the interactive version of MTDATA complex user applications can also be built using calls to MTDATA routines via the Application Programming Interface. A number of applications, using MTDATA technology but with customised user interfaces, are currently under development at NPL.

MTDATA is produced by NPL the UK National Standards Laboratory with ISO 9001 registration.

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