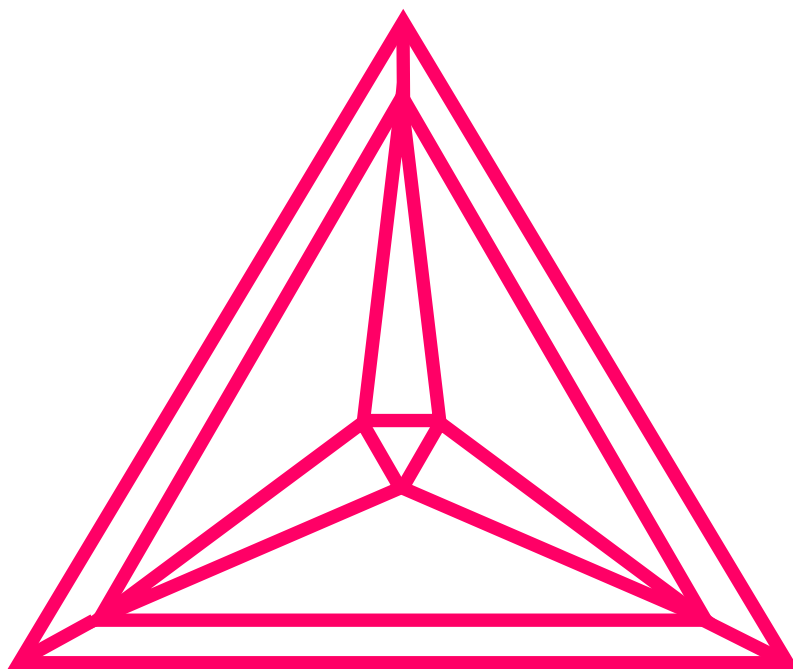# Thermo-Calc®™

Software System

(Thermodynamic Framework and Data)

Thermo-Calc Software AB
Norra Stationsgatan 93, 5 tr.
SE-113 64 Stockholm, Sweden

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There may be some minor differences in contents between this **Thermo-Calc Software System** and the actual appearance of the program as seen on the screen when running either **Thermo-Calc** or **DICTRA** software. This is because that some of the contents may need to be updated in the program's on-line help and in the future release of the program. Please visit the Thermo-Calc Software web site (www.thermocalc.com) for any patch (with modifications and/or improvements that have been incorporated into the program and its on-line help), or any amendment that have made to the content of the User's Guides and Examples Books, or to the FAQ lists and other technical information publications.

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Availability of This Document:

For the purpose of environment-friendlessness, this **Thermo-Calc Software System** and all other operational manuals (User's Guides and Examples Books), as well as Reference Lists and other technical documentations, for the TCS-provided software, databases and programming interfaces are provided along the delivered TCS Standard Products CDs and installed on each of designated installation, which can be reviewed and accessed easily and conveniently. If desired and preferred, a user can locally print such a manual BUT it is only for the purpose of the user's internal use. For a hard copy of such a manual physically printed and delivered by TCS, a certain fee shall be applied.

To make manual updating more prompt and efficient, the later manual revisions or additions will be made available on the Internet. Our users may therefore download such revised documents from our company's web site www.thermocalc.com.

Editors of This Document:

Dr. Pingfang Shi
Thermo-Calc Software AB (TCS)
Norra Stationsgatan 93, 5 tr.
SE-113 64 Stockholm, SWEDEN
   E-Mail: pingfang@thermocalc.se

Prof. Bo Sundman
Dept. of Materials Science & Engineering
Royal Institute of Technology (KTH)
SE-100 44 Stockholm, SWEDEN
   E-Mail: bosse@mse.kth.se

Contents

1   Introduction

1.1   Purposes of the Thermo-Calc Software System

The research and development linking materials science and engineering with computer calculations and simulations in the last decade have given birth to a revolutionary approach for quantitative conceptual design of various materials. A comprehensive combination of thermodynamic and kinetic models makes it possible to predict material compositions, structures and properties resulting from various materials processing.

The increased importance of mathematical modelling for product development and process control has proven the high need for thermodynamic calculations and kinetic simulations. Modern quantitative conceptual design of advanced materials has tremendously benefited from computational thermodynamics and kinetics.

The information about the equilibrium or partial-/local-equilibrium state of specific elements/species/phases in a heterogeneous interaction system and about kinetics of phase transformations (as well as chemical reactions, surface reactions, nucleation, particle growths/dissolutions, fluid flow, *etc.*) in a certain materials process, which can be provided by a software system, is essential for solving many real problems ranging from materials design and process development in chemical, metallurgical, automobile, aerospace and electronic industries, to resource exploitation, energy conversion and waste management in natural and environmental engineering. An important feature of a thermochemical/kinetic databank is that it also provides an easy way, compared to experimental work, to investigate how the equilibrium or partial-/local-equilibrium state and dynamic process can be affected by various external and internal factors. Moreover, a computerized thermochemical/kinetic databank has the great advantage, compared to handbooks, in providing the user with self-consistent, reliable and the most recent data.

A general thermochemical/kinetic databank must have high-quality and internally-consistent data for a number of fields that traditionally have been regarded as separate, *e.g.,* metallurgy, steels/alloys, ceramics, high temperature gas phase equilibria, aqueous chemistry, and geochemistry. In most applications, the number of components in a heterogeneous interaction system/process is so large that the equilibrium or partial-/local-equilibrium state and process kinetics can be efficiently and reliably calculated/simulated only by using computer software. The establishment of the Thermo-Calc$^{®™}$ and DICTRA$^{®™}$ databank systems is a successful attempt to provide such powerful and sophistic software systems, which are easy to learn and use for all kinds of thermochemical calculations and for some types of kinetic simulations.

Thermochemical calculations by Thermo-Calc, and kinetic simulations by DICTRA, can dramatically enhance your capacity in designing/developing new materials, selecting temperatures for heat treatments, optimising yields of manufacturing processes, supervising materials applications, protecting environments, *etc*. These comprehensive software/database/programming-interface packages have been proved worldwide to be the most powerful and flexible engineering tools that help eliminate expensive and time-consuming experiments, improve quality performance, and control environmental impacts.

One of the main purposes of the Thermo-Calc/DICTRA packages is in its use for planning and reducing the need for new costly experiments. By calculation it is possible to predict the results of an experiment and this can limit the number of experiments that eventually have to be made. It may even be found that the calculations alone give results that are reliable enough to be used directly.

1.1.1   Thermo-Calc Software

Thermo-Calc is a general and flexible software system (Sundman *et al.,* 1985; 1993; Jansson *et al.,* 1993; Sundman and Shi, 1997, Shi *et al.,* 2004), for all kinds of calculations of thermodynamic properties (as functions not only of temperature, pressure and composition, but also of magnetic contribution, chemical-/magnetic-ordering, crystallographic structures/defects, surface tension, amorphous glass-formation, mechanic-induced deformation, electro-static state, electronic potential, *etc.*), equilibrium and partial/local-equilibrium quantities, chemical driving forces (thermodynamic factors), and for various types of stable/meta-stable phase diagrams and property diagrams of multicomponent systems for many types of materials. It can efficiently handle a very complex multicomponent and heterogeneous interaction system defined with up to 40 elements, 1000 species and many different solution or stoichiometric phases. There are also powerful facilities to calculate many other types

of diagrams, such as CVD/PVD depositions, CVM calculations of ordering/disordering phenomena, Scheil-Gulliver solidification simulations (with or without back-diffusions of fast-diffusing components), liquidus surface, Pourbaix diagrams, Ellingham diagrams, partition coefficients, partial pressures in gases, and so forth. It is the only software that can calculate arbitrary phase diagram sections with up to five independent variables in a defined system (which, is very useful, for instance, in finding the lowest melting temperature in a multicomponent alloy that has up to five independently-varying compositions), as well as the only software that can calculate chemical driving forces (thermodynamic factors, *i.e.,* the second derivatives of Gibbs free energy with respect to compositions) which are important fundamental information for kinetic simulations (such as in diffusion-controlled phase transformation, nucleation, particle growths/dissolutions, and so on).

Linked with various databases and interfaces, it stands for the **Thermo-Calc Software/Database/Programming-Interface Package**, or the *Thermo-Calc Databank*. The most important aim of the Thermo-Calc package is to make efficient and quick thermodynamic calculations available for applications in science and industry. The Thermo-Calc software system is based upon a powerful Gibbs Energy Minimizer, which has been further enhanced by the so-called Global Minimization Technique (that has been implemented in the current version). The Thermo-Calc software is especially designed for complex heterogeneous interaction systems with strongly non-ideal phases (which are specifically handled by a very wide range of sophistic thermodynamic models), and can use many different thermodynamic databases, particularly those developed by the SGTE organization (*Scientific Group Thermodata Europe*, an international organization for collaborations on thermodynamic database developments) and CALPHAD community (*CALculations of PHase Diagrams*). Furthermore, there are several powerful application programming interfaces of the Thermo-Calc software engine, which can be utilized for user-written application programs or within third-party software packages for materials property calculations and materials process simulations.

There had been two different user-interface types of the Thermo-Calc software, namely ***TCC*** (Thermo-Calc Classic; also being referred as to the 1st generation of Thermo-Calc) and ***TCW*** (Thermo-Calc Windows; also being referred as to the 1st generation of Thermo-Calc). The first version of TCC was released in 1981. Since 1999, TCW (as the second generation of the renowned Thermo-Calc software), with a completely GUI-driven (Graphic User Interface), had been made available to our users. Any modern PC (MS-Windows 7/Vista/XP/2000/NT4, Linux) and UNIX workstation (SUN Sparc, Solaris, HP, IBM AIX, DEC Alpha OSF1, SGI) can be used for running the Thermo-Calc and DICTRA software/database/programming-interface packages. However, since TCCP (Thermo-Calc Classic version P) and DICTRA22 (DICTRA version 22), some UNIX platforms (SUN Sparc, HP, IBM AIX and DEC Alpha OSF1) are not supported any more. The classical version TCC (and DICTRA) has an interactive user interface, extensive documentation, and on-line help facilities. The general GUI-driven (Graphic User Interface) version TCW had been made available for MS-Windows environments.

Thermo-Calc 3 is the 3rd generation of the Thermo-Calc software, which merges the TCC and TCW versions altogether. The TCC becomes the Console Mode and the TCW becomes the Graphical Mode inside this united Thermo-Calc 3 version; moreover, the user-interfaces have dramatically changed and enhanced, as well as many other significant improvements inside the software have been implemented. From now on, all the further developments regarding new/improved/modified models, modules, features and so forth will be continuously put into this united version and its future versions. Thanks to the uses of many modern software-engineering tools and of JAVA language, the Thermo-Calc 3 and its future versions will be made available for a wide range of computer operation systems (such as MS-Windows, Linux/UNIX)for details please refer to the formal _Thermo-Calc Software Release Notes_.

Thermo-Calc has gained a worldwide reputation as the best software for calculations of multicomponent phase diagrams. There are more than 2000 installations all over the world today, including academic institutions (universities and governmental institutes) and non-academic organizations (industrial companies and research companies), and is a reference in technical literature. It is the only software that can calculate chemical driving forces (thermodynamic factors, *i.e.,* the second derivatives of Gibbs free energy with respect to compositions) and arbitrary phase diagram sections with up to five independent variables in a very complex multicomponent and heterogeneous system (up to 40 elements in the Thermo-Calc Console Mode and 20 elements in the Thermo-Calc Graphical Mode, and up to 1000 species). There are also facilities to calculate many other types of diagrams, such as CVD depositions, Scheil-Gulliver solidification simulations, Pourbaix diagrams, partial pressures in gases, *etc*. Many application examples are given inside the **_Thermo-Calc (Console Mode) Examples Book_** and **_Thermo-Calc (Graphical Mode) Examples Book_**, and can also be found at our web site (www.thermocalc.com).

1.1.2 Thermo-Calc Databases

A thermodynamic software package is useless if without accurate and validated databases. Thermo-Calc allows you to utilize many critically-assessed and high-quality databases from our R&D groups at TCS and KTH-MSE and from various other sources (such as SGTE, CAMPADA, CCT, CSU, USTB, ThermoTech, NPL, NIST, MIT, Theoretical Geochemistry Group, *etc.*). Such databases use different thermodynamic models for each phase in a certain heterogeneous interaction system. Currently-available Thermo-Calc databases cover a wide spectrum of materials, including steels, alloys, ceramics, melts, slag, slats, glasses, hard materials, semi-/super-conductors, solders, gas/fluids, aqueous solutions, organic substances, polymers, nuclear materials, earth materials, as well as geochemical and environmental systems, which can be applied to research and development in industrial engineering and natural systems: for instance, the SSUB/SSOL (general) databases for substances and alloy solutions in inorganic and metallurgic systems, TCFE for steels and Fe-alloys, TCNI/TTNI for Ni-based superalloys, TCAL/TTAL for Al-based alloys, TCMG/TTMG and Mg-based alloys, TTTI for Ti-based alloys, TTZR for Zr-based alloys, SLAG for slags, ION/TCOX for carbides/nitrides/oxides/silicates/sulfides (solids, liquids/slags, gases), TCFC for solid-oxide fuel cells, TCSC for superconductors, SMEC for semi-conductors, TCSLD/NSLD/USLD for lead-free solders, SNOB for noble metals, NUCLEA/MEPHISTA/NUMT/NUOX for nuclear substances, nuclear alloys and nuclear oxides, TCMP/TCES for materials processing and applications to environmental problems associated with metallurgical, chemical and waste-treatment processes (particularly in recycling, remelting, sintering, incineration and combustion), GCE for minerals, and TCAQ/AQS for aqueous solutions, *etc.* For more details on various available databases, please see the ***Thermo-Calc Database Description Forms***, which the users can always find the most-recently updated information (and more detailed descriptions for some databases) on our website www.thermocalc.com/Databases.htm or obtain related materials from our Local Sales Representatives (at www.thermocalc.com/LocalSalesRepresentative.htm).

The Thermo-Calc and DICTRA groups at KTH-MSE have initiated and participated in many national and international projects in order to create general and validated databases. TCS is now actively devoted to developments of more application-oriented databases of various industrial interests, through internal R&D projects or external collaborations. There are also many users in various academic societies and industrial companies all over the world who have established their own databases or datasets under the assistance of the Thermo-Calc and DICTRA packages.

Both the Thermo-Calc and DICTRA software also provide the users with a unique tool (the ***PARROT*** module) for critical assessment based upon varied experimental data such as PVT-EOS, thermochemical properties, phase equilibria, phase diagrams, diffusivity, and so on. By means of this module the user can efficiently expand some databases or reliably create various datasets or databases for some specific materials and applications. As a matter of fact, many of the existing databases and datasets for various materials are really the products of R&D activities using the PARROT module.

1.1.3 Thermo-Calc Programming Interfaces

Any software has its limitations; this also applies to the Thermo-Calc and DICTRA software (and their associated databases). Many types of thermodynamic calculations and kinetic simulations can be efficiently and reliably performed with these two software; however, some of our uses may wish to extend the Thermo-Calc and DICTRA capacities in order to additionally to handle some other properties/systems/processes or in a different way to treat some problems. Application programming interfaces of the Thermo-Calc and DICTRA software with other user-written programs or third-party software packages for materials property calculations, materials structure simulations and materials process controls, have been rapidly developed. There are now different ways of conducting such application-oriented programming.

Two flexible programming interfaces (*i.e., **TQ*** and ***TCAPI***) allow the users to write their own application programs. TQ is available for all modern computer platforms (programming in FORTRAN), and TCAPI is currently for Windows and Linux based systems (programming in C/C++, VC, VB, JAVA or any other modern language). Powered by the Thermo-Calc software engine (plus some DICTRA extensions), such programming interfaces provide various kinds of calculations both for thermodynamic quantities and for local-/partial-equilibria and driving forces, which are needed by other user-written programs or third-party software packages in complex property modelling and process simulations. These facilities will greatly help you to reliably predict material compositions, structures and properties, and to efficiently optimise material processing and performance. The most

successful examples are the comprehensive DICTRA$^{®™}$ package, *TC-PRISMA$^{™}$ and PrecipiCalc$^{™}$* (coupling via TCAPI) and *MISCRESS$^{™}$ software* (coupling via TQ).

Another powerful toolbox that is connected with specific third-party software (*i.e.,* **TC-MATLAB Toolbox** in the MATLAB$^{®™}$ software package) is also available. This unique toolbox has been developed, using the TCAPI programming interface. It allows an application (using this toolbox) to conduct all kinds of thermodynamic calculation precisely, which in return will enhance the performance of the MATLAB$^{®™}$ applications in materials property calculations, materials process simulations and materials production controls. Recently, there have also been many other developments on coupling the Thermo-Calc/DICTRA engines through such programming interface with third-party software packages such as Fluent$^{®™}$ and Phoenix$^{®™}$, as well as with FEM/PDE calculations and with Phase-Field simulations.

More sophisticated materials interface (using both Thermo-Calc and DICTRA as thermodynamic and kinetic engines) will be further developed.

1.1.4 Continuous Developments of the Thermo-Calc Package

Thermo-Calc and its sister software **DICTRA** (for Diffusion-Controlled phase TRansformation) have been developed originally at the *Department of Materials Science and Engineering of KTH (Royal Institute of Technology)*, Stockholm, Sweden, and since 1997 further by our company **Thermo-Calc Software (TCS)**. They are the results of more than 40 years and 300 man-years R&D and many national/international collaborations through various R&D projects.

The copyrights for the Thermo-Calc and DICTRA software and several related databases belong to a non-profit organization, *Foundation of Computational Thermodynamics* (STT), Stockholm. Since 1997, the further developments, marketing/sales, technical supports and all other activities concerning the Thermo-Calc and DICTRA packages are managed by our company TCS that is also owned by STT.

As mentioned above, there has been an update (normally as a major-version) almost every year. Such a great effort has efficiently been in place, not only for the Thermo-Calc and DICTRA software, but also for the application programming interfaces (TQ, TCAPI and TC-MATLAB Toolbox). Furthermore, some patches of various software and/or programming interfaces are released rather often, which our users can download from our web page (www.thermocalc.com/Patches.htm) to replace some executable files in their existing installations, and can use such patches, if there is a relevant license (for the corresponding major-version) that is granted to the user, plus if there is a valid Software/Interface Maintenance & Support Subscription. This is why we encourage our users (who have valid licenses for the most-recent major-versions) to keep their eyes open on our web site for possibly available patches. We keep in mind that newly-implemented and improved features/functionality, as well as necessary adjustments and corrections, made in an updated version (either a major-version or patch) of the Thermo-Calc/DICTRA software, should usually be synchronized and transplanted into the new version of the programming interfaces, too.

Some of the existing Thermo-Calc databases are also updated sometimes, but on a rather irregular basis due to the fact that a database update normally involves a tremendous amount of development work (assessments/evaluations and compilations) and validation tasks (testing, editing and applications), and often requires a long-enough period for many fruitful collaborations and discussions among our R&D partners and with some of our users. The major-version releases of such updated are promptly announced at our web page (www.thermocalc.com/Databases.htm) or in our company newsletters (which are also available at www.thermocalc.com/News.htm) when they become available to our users (in cases of a public database, the updated major-version is freely and automatically included in a release/installation of the relevant major-version of the Thermo-Calc/DICTRA software; whilst for a commercial database, a database version-upgrade can be applied to the existing users who have a valid license for an earlier version of a particular database). Sometimes, sub-versions of certain major-versions of particular databases may be made available: for instance, SLAG3.2 is the second sub-versions of the third major-versions of the SLAG database. Such a database sub-version may cover some necessary improvements, adjustments, corrections, and occasionally additions (of parameters/functions, species, phases or even elements). A commercial database is always sold and licensed (via a new database license or a database version-upgrade) as of a major-version (*e.g.,* SLAG3), while any database sub-version (*e.g.,* SLAG3.2) is automatically distributed/installed together within a newly-purchased license for a corresponding database major-version, and/or is often freely (if not automatically then a special request can be placed to TCS or its agents by the users who have the

corresponding database major-version) distributed/installed along with a renewed/enhanced license for a Thermo-Calc/DICTRA software package (through a valid Software Maintenance & Support Subscription, a Software License-Upgrade, or a Software Version-Upgrade). For all kinds of details on updated databases (as of either major-versions or sub-versions) and for the possibility of getting a database version-upgrade (from an older major-version to the recent major-version) or obtaining a database version-enhancement (from an older sub-version to the recent sub-version, while remaining as of the same database major-version), please contact us at TCS and/or its agents.

At present and in future, TCS, STT and KTH-MSE are highly devoted to the further development on the Thermo-Calc and DICTRA software, as well on various databases and interfaced programs for different materials and processes. The continuous and close cooperation with many international R&D partners and Thermo-Calc and DICTRA users all over the world are very important for ensuring such developments.

The mission of Thermo-Calc Software is *to be extensively utilized as a powerful research and development tool for scientists and engineers in their daily work in laboratories or factories, and in teaching and training activities to bring new insight into realistic problems by linking fundamental models and critically assessed thermodynamic and kinetic data.*

The ultimate purpose of Thermo-Calc Software is *to assist you, to the highest degree, to save time and money in materials design, engineering and applications.*

The development strategy of Thermo-Calc Software is *to provide multiple applicability and increased efficiency to the materials industrials and R&D community.*

1.2   About This Document

This ***Thermo-Calc Software System*** document is a supplementary part of the following manual sets:
- ***Thermo-Calc 3.0 Console Mode Manual Set (User's Guide)***;
- ***DICTRA26 Manual Set (<u>DICTRA26 User's Guide</u>*** and ***<u>DICTRA26 Examples Book</u>)***.

It gives the details of the entire Thermo-Calc software/database/programming-interface package and of various terms/concepts within the thermodynamic framework and data strategies applied within the Thermo-Calc software as well as within the DICTRA and TC-PRISMA software, and within the TC-PI Application Programming Interfaces (TQ, TCAPI and TC-MATLAB Toolbox).

Extensive descriptions and many application examples of the Thermo-Calc software/database/programming-interface package are given inside the ***Thermo-Calc (Console Mode) Manual Set*** and ***Thermo-Calc (Graphical Mode) Manual Set,*** which can be found within the Thermo-Calc 3.0 installation and also (for free reviewing/downloading) at our company's web page (<u>www.thermocalc.com/Library.htm</u>).

Editors of This Document:

Dr. Pingfang Shi   Prof. Bo Sundman
Thermo-Calc Software AB (TCS)   Dept. of Materials Science & Engineering
Norra Stationsgatan 93, 5 tr.   Royal Institute of Technology (KTH)
SE-113 64 Stockholm, SWEDEN   SE-100 44 Stockholm, SWEDEN
   E-Mail: <u>pingfang@thermocalc.se</u>   *E-Mail:* <u>bosse@mse.kth.se</u>

2 Some Thermodynamic Terms

This section gives a basic introduction and an overview of some thermodynamic terms used in the Thermo-Calc Software/Database/Programming-Interface Package. The following presents a starting point to understand how Thermo-Calc treats reality and thermodynamics.

2.1 Thermodynamics

Users of Thermo-Calc may have different backgrounds, and the word "*thermodynamics*" will probably not have the same meaning to all of the users. In order to understand some terms used in the Thermo-Calc package, these will be explained in the context of a general presentation of what could be called *classical thermodynamics*. How this description can be extended to situations outside the scope of classical thermodynamics will also be discussed.

It is worth remembering that thermodynamics is a phenomenological theory derived from two very simple observations: (1) heat and work are just two different forms of energy, and (2) heat flows from a hot body to a cold body. These observations are simplified versions of the first and second law of thermodynamics, but must, of course, be refined in order to be practically useful.

It is then necessary to introduce, in the following, some concepts of the ***physico-chemical properties*** of matter in order to make thermodynamics applicable in practice. In *Chapter 11 - Gibbs Energy System Module (GES)* and *Chapter 8 - Equilibrium Calculation Module (POLY)* of the *Thermo-Calc Console Mode User's Guide*, more details will be given on how the Thermo-Calc package employs such thermodynamic terms.

Some references of good textbooks on thermodynamics or physical chemistry or materials thermodynamics are recommended below:

Atkins, P.W. (1982) *Physical Chemistry (2nd Edition),* Oxford University Press.

Burshtein, A.I. (1995) *Introduction to Thermodynamics and Kinetic Theory of Matter*, New York, John Wiley & Sons.

Hillert, M. (1998) *Phase Equilibria, Phase Diagrams and Phase Transformations – Their Thermodynamic Basis.* Cambridge University Press.

Lukas, H., Fries S.G., and Sundman B (2007) *Computational Thermodynamics. The Calphad Method.* Cambridge University Press.

Klotz, I.M. and Rosenberg, R.M. (2000) *Chemical Thermodynamics: Basic Theory and Methods (6th Edition),* New York, John Wiley & Sons.

Kondepudi, D. and Prigogine, I. (1998) *Modern Thermodynamics – From Heat Engines to Dissipative Structures,* New York, John Wiley & Sons.

Prigogine, I. And Defay, R. (1958) *Chemical Thermodynamics,* London, Longmans.

2.2 System, Components, Phases, Constituents and Species

In thermodynamics, there is always a ***system***, which can be closed or open for exchange of matter, heat and work with its surroundings. A thermodynamic system is made up of components and phases, expressed as either homogeneous or heterogeneous states.

A ***component*** is a system wide entity; sometimes calling it a ***system component*** emphasizes this fact. A component has a unique name with some characteristic thermodynamic properties, such as amount, activity or chemical potential. At equilibrium, the activity and the chemical potential of the components are constants in the entire system.

In a system, the matter will always appear in one or more stable or meta-stable ***phase*** (a homogeneous part of the system). The same phase may often appear in many separate places in a volume, *e.g.,* dust particles in air. ***Homogeneous*** means that the system is uniform in composition, temperature and pressure, and has the same structure everywhere. By contrast, a ***heterogeneous*** system consists of at least two phases.

A phase is quantified by its composition in the amounts of components, enthalpy content, volume and other properties. The phase has ***constituents*** that may be different from its components. The constituents have a stoichiometry that can be expressed in terms of the components and possibly a charge. For instance, condensed phases may have an internal structure like sublattices or clusters (which may be modelled as constituents).

The constituents can either be the elements [*e.g.,* Fe, Si, C, O] or molecular-like aggregates that can be neutral [*e.g.,* Fe_3C, FeSi, $Fe_{0.87}O$, SiO_2, H_2O, CH_3COOH] or charged [*e.g.,* Fe^{+2}, Fe^{+3}, HO_2^{-1}, OH^{-1}, $Fe_2(OH)_2^{+4}$]. All such constituents are called ***species***. A species can be a constituent of one or several phases, and its presence in a phase can be real or fictive (postulated from a corresponding thermodynamic model for the phase).

In order to appropriately express the stoichiometry of a charged species in a phase and to describe the electro-state and electro-potential of a phase, a special species is used for the ***electron***, normally denoted as either `/-` or `ZE`, which is usually a part of phase constituents. The Thermo-Calc package denotes `/-` for charged constituents in gaseous, liquid or solid phases, and `ZE` in an aqueous solution phase. Corresponding to this special assignment, the stoichiometry of a negatively charged species can be expressed as *e.g.* `H1O2/-1` or `H1O2ZE-1`, and `CR1O4/-2` or `CR1O4ZE-2`, while the stoichiometry of a positively charged species as *e.g.* `FE1/+2` or `FE1ZE2`, and `FE2O2H2/+4` or `FE2H2O2ZE4`.

Another special species used for modelling is the ***vacancy***, always denoted as `VA`. The vacancy is used as a constituent of sublattices where there are sites that normally are empty or have defects. `VA` is by default defined as a system component, and its chemical potential is always set to zero.

Both vacancy (`VA`) and electron (`/-` in gaseous, liquid or solid phases or `ZE` in an aqueous solution phase) can be entered as "*special elements*" in definitions of some databases. Whenever `ZE` and `VA` (but not `/-`) are defined in a system, they are by default also regarded as ***special components*** in the defined system, while only `ZE` has a unique chemical potential and other thermodynamic properties, calculated by the GES module using an appropriate model associated with the aqueous solution phase and REF_ELECTRODE phase (*i.e.,* the hypothetical electrode); see *Section 8.11 – Aqueous Solution* of the *TCCS User's Guide.*

Therefore, a system component is normally an element in a defined system (especially for alloys), but it can also be an existing species in a defined system: *e.g.,* for an aqueous-free Cr-Fe-O-H system, the system components (in addition to the default defined `VA` for vacancy) can be defined as [`Fe, Cr, O and H`], or [`Fe, Cr, O2 and H`] or [`FeO, Cr2O3, O2 and H2`] or another set; for an aqueous-bearing Cr-Fe-O-H system, the system components (in addition to the default defined `VA` for vacancy) are normally defined as [`H2O, H+1, Cr, Fe and ZE`]. One can even define a system component as an appropriate combination of defined elements (*e.g.,* `CrC` and `FeC` in an Cr-Fe-C system) and have electron (`/-` or `ZE`) as a part of chemical formula for an element-combined component (*e.g.,* `H1O2/-1` and `FE1/+2` in a gaseous mixture phase, or `H1O2ZE+1` and `FE1ZE-2` in an aqueous solution phase), but the reference state of such a component must always be SER (Stable Element Reference).

Please not that for a heterogeneous interaction system without considering `ZE` as a special component, the number of components is equal to the number of elements in the system; while for an aqueous bearing heterogeneous interaction system, `ZE` is considered as an additional system component, and thus the number of components is equal to the number of elements in the system plus one.

2.3   Structure, Sublattices and Sites

It was mentioned above that a phase should have a structure. ***Structure*** is used in a broad sense and thus even the gas and liquid phases are considered to have structures. A structure can normally be described by one or several ***sublattices or sites***, which build up the phase in a certain manner. The importance of the structure of the phase is that it gives an idea of how to model the thermodynamic properties of the phase from its other physical properties.

To explain this, one may consider a phase where the thermodynamic properties do not simply depend on the amount of the components in the phase. In many cases there are internal degrees of freedom in the phase, *e.g.,* formation of molecules in a gas or ordering on sublattices in a solid. In such a case, it is simpler to model the composition dependence of the properties of the phase in terms of the constituents of the phase or of its sublattices instead of the components. The number of constituents of a phase can be larger or smaller than the actual number of components.

2.4   Composition, Constitution, Site Fractions, Mole Fractions and Concentration

The ***composition of a system*** is defined as the amount of each element/component in the whole system, and the ***constitution of a phase*** is defined as the amount of each constituent or species on a specific sublattice of the phase. Both the composition of a system and constitution of a phase can be described in many different ways. The choice of variables to present composition or constitution may differ from one type of phase or phase-assemblage to another. However, there are always common ways to express the system compositions or phase constitutions of different types by using conversion factors.

The most usual ways for describing the *composition of a system* are: the overall mole fraction (denoted as *X*) of the components, or overall mass fraction (denoted as *W*) of the components, which are defined by:

```
X(component) = N(component) / N
W(component) = B(component) / B
```

where `N` and `B` stand for the total mole number of components or total mass (in gram) the defined system, respectively; and `N(component)` and `B(component)` present the mole number or mass (in gram) of a specific component in the system.

The *constitution of a phase* is given by the ***fractions*** of the constituents in the phase or its sublattices if there are such. The Thermo-Calc package always expresses these parts in ***site fractions*** (denoted as *y*), to distinguish from ***mole fraction*** (denoted as *X*) of the components in the phase consisting of more than one sublattice, or from ***overall mole fraction*** (also denoted as *X*) of the components in the whole system. The site fraction is defined as the fraction of sites on a sublattice occupied by a certain constituent. If a phase has several sublattices, the constitution is given by the site fraction for each constituent on each sublattice. If a phase has no sublattices, the site fraction and the mole fraction are the same.

Such fraction quantities in a particular phase are usually expressed, using the mole numbers of the species on a specific sublattice, *i.e.,* `N(constituent#sublattice)`, in the defined phase:

```
y(phase,constituent#sublattice) = N(constituent#sublattice) / ν(sublattice)
```

or using the mole numbers or masses (in gram) of each of the elements/components, *i.e.,* `N(phase,component)` or `B(phase,component)`, in the defined phase:

```
X(phase,component) = N(phase,component) / NP(phase)
W(phase,component) = B(phase,component) / BP(phase)
```

where `ν(sublattice)` stands for the stoichiometric coefficient of specific sublattice site in the defined phase; and `NP(phase)` and `BP(phase)` present the mole number and mass (in gram) of the phase.

An aqueous solution system, however, needs extended terms for describing its composition or constitution, due to the traditional treatment methods, especially those used in aqueous chemistry. The concept of ***concentration*** has to be introduced in order to describe the extent of solving capacity of the solvent water, or dissolving behaviours of solute species in the water, under a certain temperature and pressure condition. The Thermo-Calc software applies the one-sublattice assumption to an aqueous solution phase; thus, the site fraction is identical to the mole fraction of the species in the aqueous phase. Moreover, the concentration of a species is also expressed as ***molality*** (m, the mole number of a solute species dissolved in 1 kg of solvent water), rather than ***molarity*** (M, the mole number of a solute species dissolved in 1 dm^3 of aqueous solution). For details on various aqueous solution quantities, please refer to *Section 2.6 - Derived Variables* (*Partial Derivatives*) in this document.

2.5   Equilibrium State and State Variables

The Thermo-Calc software uses *Classic Thermodynamics* that deals only with systems that are in equilibrium, *i.e.,* in a state stable against internal fluctuations in a number of variables, such as temperature and composition. These variables that have defined values or properties at the equilibrium state are called ***state variables***. Other examples of state variables are pressure (P), and chemical potential (μ). Thermodynamics provides a number of relations between these state variables that make it possible to calculate the value of any other variable at equilibrium.

A state variable can be of two types, extensive or intensive. The value of an ***extensive variable***, *e.g.,* volume, depends on the size of the system, whereas the value of an ***intensive variable***, *e.g.,* temperature, is independent of the size of the system. Each type of state variable has a complementary variable of the other type. The variable complementing the volume is pressure, while the variable complementing the composition of a component is its chemical potential.

It is worth mentioning here that the activity of a component can always be obtained from its chemical potential using a simple mathematical relationship. It is also possible to choose any convenient reference state for the activity or the chemical potential. One of the advantages with a thermodynamic databank on a computer is that, in most cases, such reference state changes can be handled internally without troubling the user.

If the work that can be exchanged with the surroundings is limited to pressure-volume work, the state of equilibrium of a system can be obtained by assigning values to exactly *N+2* state variables where *N* is the number of components of the system.

Note that the Thermo-Calc software distinguishes between *components* of a system and *constituent* (*i.e., species*) of a phase in the system. Many state variables require one or the other. By default, the elements are defined as the system components, but this definition can be changed with the POLY command `DEFINE_COMPONENT`; however, one cannot change the number of components when using this command. For instance:

➢ If the elements are Ca, Si and O, another set of components can be defined as `CaO`, `SiO2` and `O2`;
➢ In a pure water system, the components are normally defined as `H2O`, `H+` and `ZE` (the specially-assigned component for accounting the electro-static state in water); while a number of elements are added into the dissolving H_2O system, the component set should be `H2O`, `H+` and `ZE`, plus the relevant components for the additional elements.

A state variable is a defined thermodynamic quantity under a certain equilibrium state, either for the whole system, or for a component in the system, or a species in a specific substitutional phase, or a constituent (i.e., a species on a specific sublattice site) in a specific phase.

The basic intensive and extensive variables which are suitable in the Thermo-Calc package are listed and briefly described in *Table 1*, and are also be dealt with in some relevant chapters in the *Thermo-Calc Console Mode User's Guide*.

Please note that in order to have clearer physical meanings for various normalizations of system quantities and phase quantities, the following general rules have been enforced since:
➢ For system quantities, they should be normalized by the total system size (in terms of N, B or V), *as usual*;
➢ For phase quantities, they should be normalized by the phase amount [in terms of `NP(ph)`, `BP(ph)` or `VP(ph)`], except for the normalized `NPM(ph)`, `BPW(ph)` and `VPV(ph)` quantities [as well as for the normalized `DGM(ph)`, `DGW(ph)`, `DGV(ph)` and `DGF(ph)` properties] where the suffixes M, W, and V still mean the normalizations are performed with regard to the total system size (in terms of N, B and V, respectively).

Table 1.   **State Variables that can be used in the Thermo-Calc Package**

Name	*Mnemonic*	*Possible Units*	*Meaning*	*Comments*
Intensive variables				
T	`T`	K, °C, °F	Temperature	of the whole system
P	`P`	Pa, bar, psi	Pressure	of the whole system
μ	`MU(comp)`	J/mol, cal/mol	Chemical potential	of a component in the system
	`MU(sp,ph)`			of a species *relative to* a solution phase
a	`AC(comp)`	*dimensionless*	Activity	of a component in the system
	`AC(sp,ph)`			of a species *relative to* a solution phase
	`LNAC(comp)`		ln(Activity)	of a component in the system, in natural logarithm (`lnAC=MU/RT`)
	`LNAC(sp,ph)`			of a species *relative to* a solution phase, in natural logarithm (`lnAC=MU/RT`)
Extensive variables – Energetic (for the whole system or for a phase)				
V	`V`	m³, dm³, cm³	Volume	of the whole system
	`V(ph)` *or* `VP(ph)`			of a phase
G	`G`	J, cal	Gibbs energy	of the whole system
	`G(ph)`			of a phase
A	`A`	J, cal	Helmholtz energy	of the whole system
	`A(ph)`			of a phase
U	`U`	J, cal	Internal energy	of the whole system
	`U(ph)`			of a phase
H	`H`	J, cal	Enthalpy	of the whole system
	`H(ph)`			of a phase
S	`S`	J/K, cal/K	Entropy	of the whole system
	`S(ph)`			of a phase
C_p	`HM.T`	J/mol/K, cal/mol/K	Heat capacity at constant P	of the whole system
	`HM(ph).T`			of a phase
C_v	`HM.T`	J/mol/K, cal/mol/K	Heat capacity at constant V	of the whole system
	`HM(ph).T`			of a phase
D	`DG(ph)`	*dimensionless*	Driving force *(thermodynamic factor)*	of a phase *(already divided by RT)*. *Note this must be used together with a normalizing suffixes, M, W, V or F (see below).*
Extensive variables – Compositional (overall-components amount/size for the whole system, or amount of a component in the system or in a phase)				
n	`N`	mole	Moles	of all components in the system
	`N(comp)`			of a component in the system
	`N(ph,comp)`			of a component in a phase
	`NP(ph)`			of a phase
b	`B`	gram	Mass	of all components in the system
	`B(comp)`			of a component in the system
	`B(ph,comp)`			of a component in a phase
	`BP(ph)`			of a phase
x	`X(comp)`	*dimensionless*	Mole fraction	of a component in the system
	`X(ph,comp)`			of a component in a phase
w	`W(comp)`	*dimensionless*	Mass (weight) fraction	of a component in the system
	`W(ph,comp)`			of a component in a phase
$x\%$	`X%(comp)`	*dimensionless*	Mole percent	of a component in the system
$w\%$	`W%(comp)`	*dimensionless*	Mass (weight) percent	of a component in the system
u	`u-f(ph,comp)`	*dimensionless*	u-fraction	of a component in a *stable* phase
in	`IN(sp)`	mole	Input mole number	of a phase species into the system
im	`IM(sp)`	gram	Input mass unit	of a phase species into the system

Extensive variables – Constitutional Composition (amount of a constituent/species on a sublattice site in a phase)				
y	`Y(ph,cons#sub)`	*dimensionless*	Site fraction	of a constituent on a sublattice site (denoted by # and a digit) in a phase
Special quantities				
Q	`QF(ph)`	*dimensionless*	Phase stability function	of a phase *(being negative when the phase composition is inside a spinodal and positive everywhere else)*
T_c	`TC(ph)`	K	Curie temperature	of a phase
M_b	`BMAG(ph)`	*dimensionless*	Bohr magneton number	of a phase

Notes: Suffixes may be used to some intensive variables and all extensive variables, as described below.

1) <u>Normalizing suffixes **M**, **W**, and **V** for *energetic extensive variables* of **a system**</u>:

Normalizing suffixes like M (per mole), W (per mass in gram) or V (per volume in m³) *of the whole system (including all the components)* can be supplied on all following energetic extensive variables *for the system*:

```
Z = G, A, U, H, S, V                              → ZM, ZW, ZV
```

Such suffixed quantities are calculated via the first derivatives of the energetic extensive variable Z with regard to the total system size [in terms of N or B or V] in the whole system. For instance,

GM = $\partial G / \partial N$		Gibbs energy per mole of the system (J/mol)
GW = $\partial G / \partial B$		Gibbs energy per mass of the system (J/g)
GV = $\partial G / \partial V$		Gibbs energy per volume of the system (J/m³)

Note that VV is always as unit so it is unnecessary to evaluate such a quantity in the program.

2) <u>Normalizing suffixes **M**, **W**, **V** and **F** for *energetic extensive variables* of **a phase**</u>:

Normalizing suffixes like M (per mole), W (per mass in gram), V (per volume in m³) or F (per mole formula unit) *of a phase* can be supplied on all following energetic extensive variables *for the phase*:

```
Z = G(ph), A(ph), U(ph), H(ph), S(ph), V(ph)  → ZM, ZW, ZV, ZF
```

Such suffixed quantities are calculated via the first derivatives of the energetic extensive variable Z with regard to the phase amount [in terms of `NP(ph)` or `BP(ph)` or `VP(ph)`] for the phase. For instance,

GM(ph) = $\partial G(ph) / \partial NP(ph)$	Gibbs energy of the phase per mole of the phase (J/mol)
GW(ph) = $\partial G(ph) / \partial BP(ph)$	Gibbs energy of the phase per mass of the phase (J/mol)
GV(ph) = $\partial G(ph) / \partial VP(ph)$	Gibbs energy of the phase per volume of the phase (J/mol)
GF(ph) = $\partial G(ph) / \partial NP(ph)$ *NA	Gibbs energy of the phase per formula unit of the phase (J/mol) (where NA stands for total atomic number in the phase formula)

One shall note that: if a phase is unstable in the system, and thus its `NP(ph)`, `BP(ph)` and `VP(ph)` values equal to zero, `G(ph)`, `A(ph)`, `U(ph)`, `H(ph)`, `S(ph)` and `V(ph)` are all assigned with zero value. However, `GM(ph)`, `AM(ph)`, `UM(ph)`, `HM(ph)`, `SM(ph)` and `VM(ph)`, as well as all the W/V/F-suffixed quantities are precisely calculated and stored in the workspaces, according to the thermodynamic model used for the phase, using the first derivatives of the Gibbs energy expressed for the phase with respect to the current composition in the system.

Also note that `VV(ph)` is always as unity so it is unnecessary to evaluate such a quantity in the program.

3) <u>Normalizing suffixes **M**, **W**, **V** and **F** for the *energetic extensive variable* **DG** of **a phase**</u>:

Normalizing suffixes like M (per mole), W (per mass in gram), V (per volume in m³) or F (per mole formula unit) *of a phase* **must always** be supplied on the energetic extensive variable DG *for the phase*:

```
Z = DG(ph)                        → ZM, ZW, ZV, ZF      (Note this can not be used as condition)
```

Theoretically, such suffixed quantities can calculated via the first derivatives of the energetic extensive variable `DG(ph)` with regard to the total system size [in terms of N or B or V] in the whole system. For instance,

DGM(ph) = $\partial DG(ph) / \partial NP(ph)$	driving force for precipitation of the phase per mole of components
DGW(ph) = $\partial DG(ph) / \partial BP(ph)$	driving force for precipitation of the phase per mass of components
DGV(ph) = $\partial DG(ph) / \partial VP(ph)$	driving force for precipitation of the phase per volume of components
DGF(ph) = $\partial DG(ph) / \partial NP(ph)$ *NA	driving force for precipitation of the phase per formula unit of components

However, please note that the `DG(ph)` is never directly calculated in the program, and thus the above four quantities are not calculated followed these equations. Instead, these driving force quantities for a specific phase are calculated precisely using the second derivatives of the Gibbs energy expressed for the phase with respect to the current compositions in the equilibrium state of the system.

4) <u>Normalizing suffixes `M`, `W` and `V` for *compositional extensive variables* of **a system**</u>:

Normalizing suffixes like M (per mole), W (per mass in gram) or V (per volume in m³) *of the whole system (including all system components)* can be supplied on all following compositional extensive variables *for the system*:

> `Z = N, B`   → `ZM, ZW, ZV`

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable `Z` with regard to the total system size [in terms of `N` or `B` or `V`] in the whole system. For instance,

$NW = \partial N/\partial B$ Mole number of components per mass of the system (mol/g)

$NV = \partial N/\partial V$ Mole number of components per volume of the system (mol/m³)

$BM = \partial B/\partial N$ Mass (gram) of components per mole of the system (g/mol)

$BV = \partial B/\partial V$ Mass (gram) of components per volume of the system (g/m³)

Note that the followings:
  - `NM` and `BW` for overall amount (size) of the system are always as unity (so it is unnecessary to evaluate them);
  - `NW` and `BM` can not set as conditions;
  - `BV` is the density of the entire system

5) <u>Normalizing suffixes `M`, `W` and `V` for *compositional extensive variables* **a component in the system**</u>:

Normalizing suffixes like M (per mole), W (per mass in gram) or V (per volume in m³) *of the whole system (including all system components)* can be supplied on all following compositional extensive variables *for a component in the system*:

> `Z = N(comp), B(comp)`   → `ZM, ZW, ZV`

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable `Z` with regard to the total system size [in terms of `N` or `B` or `V`] in the whole system. For instance,

$NM(comp) = \partial N(comp)/\partial N$ Mole number of a component per mole of the system (*mole fraction*)

$NW(comp) = \partial N(comp)/\partial B$ Mole number of a component per mass of the system (mol/g)

$NV(comp) = \partial N(comp)/\partial V$ Mole number of a component per volume of the system (mol/m³)

$BM(comp) = \partial B(comp)/\partial N$ Mass (gram) of a component per mole of the system (g/mol)

$BW(comp) = \partial B(comp)/\partial B$ Mass (gram) of a component per mass of the system (*mass fraction*)

$BV(comp) = \partial B(comp)/\partial V$ Mass (gram) of a component per volume of the system (g/m³)

Note that some suffixed extensive variables stand for certain special quantities, as listed below:
  - `NM(comp) = X(comp)`   for mole fraction of a component in the system;
  - `BW(comp) = W(comp)`   for mass fraction of a component in the system.

6) <u>Normalizing suffixes `M`, `W` and `V` for *compositional extensive variables* of **a phase in the system**</u>:

Normalizing suffixes like M (per mole), W (per mass in gram) or V (per volume in m³) *of the whole system (including all system components)* can be supplied on compositional extensive variables `NP(ph)` and `BP(ph)` [as well as the `VP(ph)` quantity] *for a phase*:

> `Z = NP(ph), BP(ph), VP(ph)`   → `ZM, ZW, ZV`

Such suffixed quantities are calculated via the first derivatives of such extensive variable `Z` with regard to the phase amount [in terms of `NP(ph)`, `BP(ph)` or `VP(ph)`] of the phase, except for the normalized `NPM(ph)`, `BPW(ph)` and `VPV(ph)` quantities where the suffixes M, W, and V still mean the normalizations are performed with regard to the total system size (in terms of `N`, `B` and `V`, respectively). For instance,

$NPM(ph) = \partial NP(ph)/\partial N$ Mole number of a phase per mole of the system (*mole fraction*)

$NPW(ph) = \partial NP(ph)/\partial BP(ph)$ Mole number of a phase per mass of the phase in the system (mol/g)

$NPV(ph) = \partial NP(ph)/\partial VP(ph)$ Mole number of a phase per volume of the phase in the system (mol/m³)

$BPM(ph) = \partial BP(ph)/\partial NP(ph)$ Mass (gram) of a phase per mole of the phase in the system (g/mol)

$BPW(ph) = \partial BP(ph)/\partial B$ Mass (gram) of a phase per mass of the system (*mass fraction*)

$BPV(ph) = \partial BP(ph)/\partial VP(ph)$ Mass (gram) of a phase per volume of the phase in the system (g/m³)

$VPM(ph) = \partial VP(ph)/\partial NP(ph)$ Volume (m³) of a phase per mole of the phase in the system (m³/mol)

$VPW(ph) = \partial VP(ph)/\partial BP(ph)$ Volume (m³) of a phase per mass of the phase in the system (m³/g)

$VPV(ph) = \partial VP(ph)/\partial V$ Volume (m³) of a phase per volume of the system (*volume fraction*)

Note that the `VP(ph)` variable is exactly the `V(ph)` property, but their `M/W/V/F`-suffixed quantities are different; `VP(ph)` can be `V`-suffixed (but not `F`-suffixed) while `V(ph)` can be `F`-suffixed (but not `V`-suffixed).

Also note that: if a phase is unstable in the equilibrium system, the `NP(ph)`, `BP(ph)` and `VP(ph)` values equals to zero, and do so their `M/W/V`-suffixed quantities.

One should also keep in mind that: **the phase amount variables, `NP(ph)`, `BP(ph)` and `VP(ph)`, as well as all their `M/W/V`-suffixed quantities, should not be used as conditions. Instead, one can use the `CHANGE_STATUS` command to set a relevant condition, *e.g.*, `CHANGE_STATUS phase <phase>=fix <amount>` where the fixed `<amount>` is roughly the same as the `F`-suffixed quantity `NPF(ph)` [*i.e.*, mole number of a phase per mole formula unit of the phase] which can not be directly evaluated or listed/shown.**

7) <u>Normalizing suffixes **M**, **W** and **V** for *compositional extensive variables* of **a component in a phase**</u>:

Normalizing suffixes like `M` (per mole), `W` (per mass in gram) or `V` (per volume in m^3) *of a phase* can be supplied on all following compositional extensive variables *for a component in the phase*:

    `Z = N(ph,comp), B(ph,comp)`   → `ZM, ZW, ZV`

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable `Z` with regard to the phase amount [in terms of `NP(ph)`, `BP(ph)` or `VP(ph)`] of the phase. For instance,

`NM(ph,comp) =` ∂`N(ph,comp)/`∂`NP(ph)`	Mole number of a component per mole of a phase (*mole fraction*)
`NW(ph,comp) =` ∂`N(ph,comp)/`∂`BP(ph)`	Mole number of a component per mass of a phase (mol/g)
`NV(ph,comp) =` ∂`N(ph,comp)/`∂`VP(ph)`	Mole number of a component per volume of a phase (mol/m^3)
`BM(ph,comp) =` ∂`B(ph,comp)/`∂`NP(ph)`	Mass (gram) of a component per mole of a phase (g/mol)
`BW(ph,comp) =` ∂`B(ph,comp)/`∂`BP(ph)`	Mass (gram) of a component per mass of a phase (*mass fraction*)
`BV(ph,comp) =` ∂`B(ph,comp)/`∂`VP(ph)`	Mass (gram) of a component per volume of a phase (g/m^3)

Note that some suffixed extensive variables stand for certain special quantities, as listed below:

➢ `NM(ph,comp) = X(ph,comp)`   for mole fraction of a component in a phase;
➢ `BW(ph,comp) = W(ph,comp)`   for mass fraction of a component in a phase;

8) <u>Special compositional (extensive) variables of **a component** or **a species**</u>:

The derived compositional variables, `X%(comp)` and `W%(comp)` for a system component, as well as `IN(sp)` and `IM(sp)` for a species (phase constituent), are only available in the TQ and TCAPI programming interfaces.

However, the quantities with the meaning of `X%(comp)` and `W%(comp)` can be used as axis variables in the POST module but they must be instead specified as the followings, respectively:

➢ `Mole-Percent <comp>`   for mole-percent of a component in the system, `X%(comp)`;
➢ `Weight-Percent <comp>`   for mass-percent of a component in the system, `W%(comp)`.

Note that neither of these variables or relevant syntaxes can be used as conditions in the POLY module.

Moreover, when plotting mole-fraction or mass-fraction of a component in the system as an axis available in the POST module, it is recommended to use the following syntaxes, respectively:

➢ `Mole-Fraction <comp>`   for mole-fraction of a component in the system, `X(comp)`;
➢ `Weight-Fraction <comp>`   for mass-fraction of a component in the system, `W(comp)`.
rather than directly using their relevant state variables, `X(comp)` or `W(comp)`.

As another extensive composition variable, the concept of so-called **u-fraction** concept represents an important quantity that is often shown up during special single-point or stepping paraequilibrium calculations within the POLY module of the Thermo-Calc software [or during local/para-equilibrium calculations within the DICTRA monitor of the DICTRA software]. The u-fraction, denoted as u$_i$ for the *i*-th system component (it can be applied to the substitutional matrix component or substitutional alloying components, or to the interstitial component) in a whole system or in a specific phase under some various equilibrium states (such as full-equilibria, partial-equilibria, para-equilibria, local-equilibria, *etc*.), is generally defined as: $\dfrac{x_i}{\sum_{j \in S} x_j}$, where the sum of x_j (*in the denominator*) is taken

for the substitutional matrix element and all substitutional alloying elements in the whole system or in the specific phase, and x_i (*in the numerator*) stands for the mole-fraction of the *i*-th component itself in the whole system or in the specific phase. Please remember that: the u-fraction is not really a standard state variable, and thus can not be directly used inside the POLY module (as no POLY syntax stands for it); however, in the POST module of the Thermo-Calc (and DICTRA) software, the u-fraction quantity is always assigned with the special syntax of `u-f` which can also be directly used as axis variables.

For instance, in the Fe-M-C ternary alloy system, it very frequently happens that one of the elements (the interstitial solute C) diffuses very much faster than the other two (the substitutional matrix element Fe and the substitutional alloying element M). It is often possible that a new phase forms with a different content of the mobile element (C) but without a change of the relative contents of the other two (Fe and M). Therefore, partial equilibria will remain in two phases, and a phase transformation will be partly partitionless through the locally equilibrated two-phase interface. At the interface, there is no driving force. The chemical potential of the mobile element (μ_C) has the same value on both sides, but the chemical potential for the non-mobile elements (μ_{Fe} and μ_M) have different values. Instead, the products of the chemical potentials and the u-fractions of the non-mobile elements [u_{Fe} and u_M, defined as $N_i/(N_{Fe}+N_M)$ or $x_i/(x_{Fe}+x_M)$] have the same values. Under the paraequilibrium state, $dT = dP = d\mu_C = du_{Fe} = du_M = 0$, the driving force should be zero, and T, P, μ_C and $u_{Fe}\mu_{Fe} + u_M\mu_M$ (the combined chemical potentials of Fe and M) must have the same values on both sides. In a molar Gibbs energy diagram (as illustrated in *Figure 8-1*), the tie-line between the two phases in paraequilibrium is directed towards the C corner, which falls on a common tangent line to the two Gibbs energy surfaces but not on the common tangent plane.

9)   Special quantity **QF** of **a phase**:

The Thermo-Calc software system also calculates a special quantity, the ***phase stability function* QF(ph)**, for all kinds of phases in an equilibrium state. A phase stability function for a phase is negative when the phase composition is inside a spinodal, and positive everywhere else. Like an intensive variable, it cannot have any normalization suffix (M, W, V or F). This special quantity cannot be used as a condition.

It is very useful for finding out if a calculated equilibrium state is possibly within the miscibility gap for a solution phase.

10)   Special quantities **TC** and **BMAG** of **a phase with magnetic contribution**:

The Thermo-Calc software system also calculates other two special quantities, the ***Curie temperature* TC(ph)** and *Bohr magneton number* **BMAG(ph)**, for all kinds of phases possibly with magnetic contributions in an equilibrium state. Such a quantity is calculated using a certain model to handle magnetic contributions (***e.g.,*** the Inden's Model for treating pure ferro-/antiferro-/para-magnetic phases, and for modelling solution phases with magnetic ordering/transformations where Curie temperature and Bohr magneton number are dependent upon the composition of the phase). These two special quantities cannot be used as conditions.

11)   Reference State suffix **R** for state variables of **a system** or **a component** or **a phase** or **a constituent**:

The so-called *reference state suffix* R can be added on intensive variables MU, AC, or LNAC in order to get a value that is calculated with respect to a chosen reference state, *e.g.,* MUR(comp), ACR(comp) and LNACR(comp) for a component in the system, and MUR(sp,ph), ACR(sp,ph) and LNACR(sp,ph) for a species *relative* a specific *single-substitutional-lattice* solution phase.

When the reference state for a system component is the default reference state (usually the SER – *Stable Reference State*; that is default defined in a Thermo-Calc database), MUR(comp)=MU(comp), ACR(comp)=AC(comp) and LNACR(comp)=LNAC(comp). However, if another reference state has been set for a system component [by using the SET_REFERENCE_STATE command in the POLY module or through hard-coded routines in a special module such as POURBAIX module, where a reference phase (in which the component exists as a phase constituent) must be specified, and the reference temperature (normally the current temperature presented by the start sign *) and pressure (normally 1 bar, *i.e.,* 100000 Pascal) be entered], the above relations do not hold true any longer.

The chemical potentials and activities of species *relative to* some *single-substitutional-lattice solution phases* (such as aqueous solution, gaseous mixture, metallic liquid solution, slag mixture, MO solid solution, *etc.*) are specially-treated state variables, denoted as MU(sp,ph), MUR(sp,ph), AC(sp,ph), ACR(sp,ph), LNAC(sp,ph) and LNACR(sp,ph). For some such solution phases in their specific databases (*e.g.,* AQUEOUS solution phase in the TCAQ or AQS databases, FE_LIQUID solution phase in the SLAG database), the reference states and standard states of various solution species have been properly pre-defined by their corresponding thermodynamic models. Please keep in mind that for all solution species treated by any solution model in any database, there are always the relations: MUR(sp,ph)=MU(sp,ph), ACR(sp,ph)=AC(sp,ph), and LNACR(sp,ph)=LNAC(sp,ph). For more details on reference state, please refer to *Section 2.13 (Reference State and Standard State)*.

The suffix R can also be added on the special variables QF(ph), TC(ph) and BMAG(ph), but a R-suffixed quantity is always identical to its original variable, *e.g.,* QFR(ph) = QF(ph), under a specific condition in a defined system. In other words, the phase stability functions, Curie temperature and Bohr magneton number of various phases do not change along with any possibly re-defined reference states of system components, when the definitions of the system conditions remain unchanged. Additionally, they cannot be used as conditions, as they can only be calculated under a certain type of equilibrium state.

Actually, the suffix R is also legal to be added on most of the extensive (energetic or compositional) variables and their M/W/V/F−suffixed variables of an entire system, of a component, of a phase, or of a phase constituent, However, one should first understand the meaning of such R-suffixed state variables before using them. An R-suffixed compositional variable is always identical to its original variable (implying that the suffix R may not make any different on a compositional variable), *e.g.,*

`NR = N`	Total size (moles of all components) of the whole system
`NMR(comp)= NM(comp) = X(comp)`	Mole fraction of a component in the whole system
`NPR(ph) = NP(ph)`	Mole number of a phase
`YR(ph,cons#sub) = Y(ph,cons#sub)`	Site fractions of a constituent on a site in a phase

On the contrary, an R-suffixed energetic variable (for the whole system or for a phase) may differ from its original state variable, depending upon the setting of reference states for all components in the defined system. The general expressions for calculating R-suffixed energetic state variable are as follows:

$$ZR = Z - X(comp)\sum_{i=1}^{n} Z(comp)^{REF} \qquad \text{(for the whole system)}$$

$$ZR(ph) = Z(ph) - X(ph,comp)\sum_{i=1}^{n} Z(comp)^{REF} \qquad \text{(for a phase)}$$

For instance, after the redefinition of the reference state of the system component C (changed from `SER` to "`GRAPHITE * 1E5`") in the Fe-Cr-Ni-C-O system, one will notice the following unequal relations:

`GR`	$\neq$ `G`	(for the whole system)
`GMR`	$\neq$ `GM`	
`HWR`	$\neq$ `HW`	
`SVR`	$\neq$ `SV`	
`GR(ph)`	$\neq$ `G(ph)`	(for a phase)
`GVR(ph)`	$\neq$ `GV(ph)`	
`HMR(ph`	$\neq$ `HM(ph`	
`SWR(ph`	$\neq$ `SW(ph`	

12) Heat capacity of **a system** or **a phase**:

Heat capacity (at constant pressure or volume) of a system or of a specific phase in the system are partial derivatives of state variable enthalpy with respect to temperature, by using the dot "`.`" notation between the two state variables (see more descriptions in *Section 2.6, Derived variables*):

`HM.T = `∂`HM/`∂`T`	heat capacity for the system *at either constant P (if pressure is a condition)* *or constant V (if volume is a condition)*
`HM(ph).T = `∂`HM(ph)/`∂`T`	heat capacity for a phase *at either constant P (if pressure is a condition)* *or constant V (if volume is a condition)*

13) Usage of state variables and derived variables:

Please keep the following important facts in mind, regarding how to use various state variables and derived variables inside the Thermo-Calc software system (particularly in its various modules):

☞ The state variables and derived variables (which are described in this and next sections) are the quantities at an equilibrium state that can be directly used in the POLY (Equilibrium Calculation) Module for listing their equilibrium values after an equilibrium calculation (by the `SHOW_VALUE` command).

☞ All the state variables can be used for defining equilibrium conditions in the POLY module, and so do most of their suffixed quantities identified by the normalization suffix `M/W/V/F` or by the reference state suffix `R` (but there are some exceptions; for details, see descriptions given in this table and the above annotations).

☞ All the derived variables can neither be used for defining equilibrium conditions in the POLY module, and nor be directly called for defining diagram axis variables in the POST module or for listing properties in the TAB module. When one wants to plot a diagram with derived variables as axis variables in the POST module or to list out derived variables in the TAB module, one must first define such derived variables as appropriately-entered symbols (as functions/variables/tables, in either the POLY or POST or TAB module).

☞ In other basic modules (*e.g.,* TDB, GES and PARROT), the state variables and derived variables (as well as their suffixed quantities) can be used in the way that is more or less the same in the POLY/ED_EXP/POST/TAB modules. However, there are more properties (regarding model-related parameters in describing certain phases) can be used in the TDB, GES and PARROT modules. Some examples are given below:

`G(ph,sp;0)`	for standard Gibbs energy of a species in a phase
`TC(ph,sp;0)`	for curie temperature of a species in a phase
`BMAGN(ph,sp;0)`	for Bohr magneton number of a species in a phase
`V0(ph,sp;0)`	for molar volume at 1 bar and reference T_0 of a species in a phase
`VA(ph,sp;0)`	for integrated thermal expansivity of a species in a phase
`VC(ph,sp;0)`	for isothermal compressibility of a species in a phase

`VK(ph,sp;0)`	for high-pressure fitting parameter of a species in a phase
`WR(AQ,sp;0)`	for Born function for electro-static contribution $\omega_{j,Pr,Tr}$ of an aqueous species in aqueous solution phase
`G(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order interaction energy between interacting species in a phase
`L(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order interaction energy between interacting species in a phase
`TC(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order composition dependence of curie temperature in a phase
`BMAGN(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order composition dependence of Bohr magneton number in a phase
`V0(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order composition dependence of molar volume in a phase
`VA(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order composition dependence of thermal expansivity in a phase
`VC(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order composition dependence of isothermal compressibility in a phase
`VK(ph,sp1,sp2,...;i)`	for ith binary, ternary, or higher-order composition dependence of high-pressure fitting parameter in a phase

Please note that a species in such a parameter is always corresponding to a defined constitution (with certain constituents on specified sublattice sites) in the phase. For details please refer to *Chapter 3 (Database Manager's Guide) in the document Thermo-Calc Database Guide*.

14) <u>Units for various state variables and derived variables:</u>

The "Possible Unit" column in *Table 1 (State Variables that can be used in the Thermo-Calc Package)* lists some possibly-applied units for various intensive and extensive state variables. However, it is always true that the first one (if there is more one unit listed in the table) is the default unit for the corresponding state variable.

In order to use a desired unit other than the default one for a state variable (or for a derived variable), one should first define a function or variable (using the `ENTER_SYMBOL` command) for appropriately converting the unit. For instance,

Temperature	`T_C`	`= T-273.15`	Celsius (C) *(in the POST module)*
	`TempC`	`= T-273.15`	Celsius (C)
	`TempF`	`= 1.8*T-459.67`	Fahrenheit (F)
		`= 1.8*TempC+32`	
Pressure	`PB`	`= P/1E5`	bars (bar)
	`PKb`	`= P/1E8`	kilobars (kbar)
	`PAtm`	`= P/101325`	atmosphere (atm)
	`PSI`	`= P/6894.76`	pounds/sq. inch (psi)
	`PIHg`	`= P/3342.11`	inches of Hg
	`PTor`	`= P/133.322`	Tors (millimeters of Hg)
Gibbs Energy	`GCal`	`= G/4.1858`	cal
	`GmCal`	`= Gm/4.1858`	cal/mol
	`GphCal`	`= G(ph)/4.1858`	cal
	`GmphCal`	`= Gm(ph)/4.1858`	cal/mol
Heat Capacity	`Cp`	`= HM.T/4.1858`	cal/mol/K
	`Cpph`	`= HM(ph).T/4.1858`	cal/mol/K
Chemical Potential	`MUi`	`= MU(comp)/4.1858`	cal/mol
	`MURi`	`= MUR(comp)/4.1858`	cal/mol

Therefore, you can possibly use various types of units for a certain state variables (or derived variable) by using additionally-entered functions or variables that are pre-defined in special modules (such as SCHEIL and POURBAIX module) or by a user. For an extensive overview, please refer to *Appendix C (Units for State Variables and Derived Variables) in the Thermo-Calc Console Mode User's Guide*.

2.6　Derived Variables (Partial Derivatives)

For some material systems (such as heterogeneous interactions involving aqueous solutions, gaseous mixtures, liquids, etc.), it is necessary to utilize some additional derived variables which are defined as functions of state variables. The Thermo-Calc software (especially some advanced, easy-to-use modules) predefines some derived variables as assigned symbols (variables, functions and tables) for some phases. A user can also define any derived variable, as he prefers for his systems.

The state variables can be used to define additional functions or variables, through some mathematical expressions of state variables or other functions. Such functions or variables are referred as partial derivatives or derived variables.

Many derived variables *of a defined system*, or *of a certain system component*, or *of a given phase*, or *of a specific component or species in (related to) a given phase*, can be easily obtained using appropriate partial derivatives of state variables, such as heat capacity, thermal expansivity, isothermal compressibility, among others.

Derivatives of state variables can be evaluated using a dot ".", between two state variables , for example:
　　　　`HM.T`　*for heat capacity of the system.*

Important Note: **The variable after the dot sign "." MUST be a condition that has already set in the equilibrium calculation of the defined system.**

Actually, some variables listed in *Table 1* are derived variables, *e.g.,* `HM.T` and `HM(ph).T`, where a dot "." notation is used. As an important feature of the Thermo-Calc and DICTRA software, any partial derivatives of one state variable with respect to another can be defined/evaluated as a derived variable, by using the dot "." notation between the two state variables.

One may use many more elaborate derivatives, *e.g.,* `T.W(LIQUID,C)` means the slope of the phase boundary of the liquid with respect to carbon; after the liquidus temperature or solidus temperature (under a certain composition condition) has been calculated, the `T.W(C)` value implies the changing direction/scale of the liquidus temperature or solidus temperature along with each unit of the varying carbon composition condition `W(C)` in the defined system.

Some typical examples are listed below:

$\text{HM.T} = (\partial \text{HM}/\partial \text{T})_{\text{condition}}$　　heat capacity for the system *at either constant P, C_p (if pressure is a condition)*
　　　　　　　　　　　　　　　　　　　　　　　　　　or constant V, C_v (if volume is a condition)

$\text{HM(ph).T} = (\partial \text{HM(ph)}/\partial \text{T})_{\text{condition}}$　heat capacity for a phase *at either constant P, C_p(ph) (if pressure is a condition)*
　　　　　　　　　　　　　　　　　　　　　　　　　　or constant V, C_v(ph) (if volume is a condition)

$\text{H.T} = \partial \text{H}/\partial \text{T}$　　heat capacity for the system *multiplied by total mole number of components*
　　　　　　　　　　　　i.e., $\partial \text{H}/\partial \text{T} = C_p * \text{N}$ (if pressure is a condition in a close system)
　　　　　　　　　　　　$\partial \text{H}/\partial \text{T} = C_v * \text{N}$ (if volume is a condition in a close system)

$\text{H(ph).T} = \partial \text{H(ph)}/\partial \text{T}$　　heat capacity for a phase *multiplied by* NP(ph) *plus* HM(ph)*$* \partial$NP(ph)$/\partial$T
　　　　　　　　　　　　i.e., C_p(ph)*NP(ph)+HM(ph)*∂NP(ph)$/\partial$T (if pressure is a condition)
　　　　　　　　　　　　C_v(ph)*NP(ph)+HM(ph)*∂NP(ph)$/\partial$T (if volume is a condition)

$\text{VM.T} = \partial \text{VM}/\partial \text{T}$　　thermal expansivity of the system *(already multiplied by the total molar volume)*
　　　　　　　　　　　　i.e., $\partial \text{VM}/\partial \text{T} = \alpha * \text{VM}$

$\text{VM(ph).T} = \partial \text{VM(ph)}/\partial \text{T}$　　thermal expansivity of a phase *(already multiplied by its molar volume)*
　　　　　　　　　　　　i.e., $\partial \text{VM(ph)}/\partial \text{T} = \alpha$(ph)*VM(ph)

$\text{V.T} = \partial \text{V}/\partial \text{T}$　　thermal expansivity of the system *(already multiplied by the total volume)*
　　　　　　　　　　　　i.e., $\partial \text{V}/\partial \text{T} = \alpha * \text{V}$

$\text{V(ph).T} = \partial \text{V(ph)}/\partial \text{T}$　　thermal expansivity of a phase *(already multiplied by the phase volume)* plus the
　　　　　　　　　　　　VM(ph)*∂NP(ph)$/\partial$T term.
　　　　　　　　　　　　i.e., ∂V(ph)$/\partial \text{T} = \alpha$(ph)*V(ph)
　　　　　　　　　　　　　　　　= α(ph)*VM(ph)*NP(ph)+VM(ph)*∂NP(ph)$/\partial$T

$\mathrm{VM.P} = -\partial\mathrm{VM}/\partial\mathrm{P}$	isothermal compressibility of the system *(already multiplied by the total molar volume)* i.e., $\partial\mathrm{VM}/\partial\mathrm{P} = -\kappa*\mathrm{VM}$
$\mathrm{VM(ph).P} = -\partial\mathrm{VM(ph)}/\partial\mathrm{P}$	isothermal compressibility of a phase *(already multiplied by its molar volume)* i.e., $\partial\mathrm{VM(ph)}/\partial\mathrm{P} = -\kappa\mathrm{(ph)}*\mathrm{VM(ph)}$
$\mathrm{V.P} = -\partial\mathrm{V}/\partial\mathrm{P}$	isothermal compressibility of the system *(already multiplied by the total volume)* i.e., $\partial\mathrm{V}/\partial\mathrm{P} = -\kappa*\mathrm{V}$
$\mathrm{V(ph).P} = -\partial\mathrm{V(ph)}/\partial\mathrm{P}$	isothermal compressibility of a phase *(already multiplied by the phase volume)* plus the $\mathrm{VM(ph)}*\partial\mathrm{NP(ph)}/\partial\mathrm{P}$ term. i.e., $\partial\mathrm{V(ph)}/\partial\mathrm{P} = -\kappa\mathrm{(ph)}*\mathrm{V(ph)}$ $= -\kappa\mathrm{(ph)}*\mathrm{VM(ph)}*\mathrm{NP(ph)}+\mathrm{VM(ph)}*\partial\mathrm{NP(ph)}/\partial\mathrm{P}$
$\mathrm{T.X(comp)} = \partial\mathrm{T}/\partial\mathrm{X(comp)}$	slope of a phase boundary on a *T-X(comp)* phase diagram with respect to mole fraction of the component in the system
$\mathrm{T.W(comp)} = \partial\mathrm{T}/\partial\mathrm{W(comp)}$	slope of a phase boundary on a *T-W(comp)* phase diagram with respect to mass of the component in the system
$\mathrm{T.X(ph,comp)} = \partial\mathrm{T}/\partial\mathrm{X(ph,comp)}$	slope of a phase boundary on a *T-X(ph,comp)* phase diagram with respect to mole fraction of the component in the phase
$\mathrm{T.W(ph,comp)} = \partial\mathrm{T}/\partial\mathrm{W(ph,comp)}$	slope of a phase boundary on a *T-W(ph,comp)* phase diagram with respect to mole fraction of the component in the phase
$\mathrm{P.T} = \partial\mathrm{P}/\partial\mathrm{T}$	slope of a phase boundary on a *P-T* phase diagram *(Note that the equilibrium with phase assemblage must be calculated first)*

Restrictedly speaking, any of energetic extensive variables o of *the entire system,* of *a specific system component in the whole system,* of *a given phase*, or of *a specific system component (or species) in (or related to) a given phase,* with normalizing suffixes like M (per mole of component), W (per mass in grams), V (per volume in m^3) or F (per mole formula unit) as specified above and listed in *Table 1*, are derived variables, which have been explicitly defined inside the program by using expressions as either first or second derivatives of some state variables with respect to other independent state variables. In case a phase is not stable in the system, many standard variables and derived quantities for the phase will be still calculated by the program and saved in the workspace. However, when showing a partial derivative (after an equilibrium calculation), the state variable used after the dot sign "." must have been defined as a condition prior to the calculation. For instance, the derived variable G.B is exactly the same as the W-suffixed state variable GW when B (total mass of all components in the system) has been defined as an equilibrium condition in the system.

Moreover, those compositional extensive variables with normalizing suffixes like M (per mole), W (per mass in gram), V (per volume in m^3), F (per mole formula unit), or % (percent) of *the entire system, any specific or all system components in the whole system,* or *a given phase*, or *any specific or all system components in a given phase,* as listed in *Table 1*, are also derived variables, which are defined by expressions of some independent state variables. Therefore, the derived variable N(comp).N is exactly the same as the M-suffixed state variable NM(comp) or X(comp) when N (total moles of all components in the system) has been defined as an equilibrium condition in the system. For instance,

$\mathrm{N.N} = \mathrm{NM} = \partial\mathrm{N}/\partial\mathrm{N}$	*(always as unity so it is unnecessary!)*
$\mathrm{N.B} = \mathrm{NW} = \partial\mathrm{N}/\partial\mathrm{B}$	moles per mass of the system (mol/g)
$\mathrm{N.V} = \mathrm{NV} = \partial\mathrm{N}/\partial\mathrm{V}$	moles per volume of the system (mol/m^3)
$\mathrm{B.N} = \mathrm{BM} = \partial\mathrm{B}/\partial\mathrm{N}$	mass per mole of the system (g/mol)
$\mathrm{B.B} = \mathrm{BW} = \partial\mathrm{B}/\partial\mathrm{B}$	*(always as unity so it is unnecessary!)*
$\mathrm{B.V} = \mathrm{BV} = \partial\mathrm{B}/\partial\mathrm{V}$	density of the entire system (g/m^3)
$\mathrm{N(comp).N} = \mathrm{NM(comp)} = \mathrm{X(comp)}$ $= \partial\mathrm{N(comp)}/\partial\mathrm{N}$	mole fraction of a component in the system
$\mathrm{N(ph,comp).NP(ph)} = \mathrm{NM(ph,comp)} = \mathrm{X(ph,comp)}$ $= \partial\mathrm{N(ph,comp)}/\partial\mathrm{NP(ph)}$	mole fraction of a component in a phase
$\mathrm{X\%(comp)} = \mathrm{X(comp)}*100$	mole percent of a component in the system
$\mathrm{B(comp).B} = \mathrm{BW(comp)} = \mathrm{W(comp)}$ $= \partial\mathrm{B(comp)}/\partial\mathrm{B}$	mass fraction of a component in the system
$\mathrm{B(ph,comp).BP(ph)} = \mathrm{BW(ph,comp)} = \mathrm{W(ph,comp)}$ $= \partial\mathrm{B(ph,comp)}/\partial\mathrm{BP(ph)}$	mass fraction of a component in a phase
$\mathrm{W\%(comp)} = \mathrm{W(comp)}*100$	mass percent of a component in the system

```
NP(ph).N = NPM(ph) = ∂NP(ph)/∂N          moles of a phase per mole of the system (mole fraction)
NP(ph).B = NPW(ph) = ∂NP(ph)/∂B          moles of a phase per mass of the system (mol/g)
NP(ph).V = NPV(ph) = ∂NP(ph)/∂V          moles of a phase per volume of the system (mol/m³)
      NPF(ph) =   NP(ph)/NA              moles of a phase per mole formula unit

BP(ph).N = BPM(ph) = ∂BP(ph)/∂N          mass of a phase per mole of the system (g/mol)
BP(ph).B = BPW(ph) = ∂BP(ph)/∂B          mass of a phase per mass of the system (mass fraction)
BP(ph).V = BPV(ph) = ∂BP(ph)/∂V          mass of a phase per volume of the system (g/m³)
      BPF(ph) =   BP(ph)/NA              mass of a phase per mole formula unit

VP(ph).N = VPM(ph) = ∂VP(ph)/∂N          volume of a phase per mole of the system (m³/mol)
VP(ph).B = VPW(ph) = ∂VP(ph)/∂B          volume of a phase per mass of the system (m³/g)
VP(ph).V = VPV(ph) = ∂VP(ph)/∂V          volume of a phase per volume of the system (volume fraction)
      VPF(ph) =   VP(ph)/NA              volume of a phase per mole formula unit
```

All the state variables listed in *Table 1* can be used to define additional functions or variables for quantities that the user may be interested in, by utilizing the `ENTER_SYMBOL` command. Functions are saved in the Thermo-Calc workspaces, and at any time a function value is requested all functions will be evaluated (for the reason that they may depend on each other). Variables are evaluated only when they are entered or if they are explicitly named in an `EVALUATE` command, and it is possible to enter a variable with a new expression anytime. Variables can be used as values of conditions in an `SET_CONDITION` command. Please also note that such derived variables, either predefined by the GES, PLOY or PARROT modules, or by an advanced module (*e.g.,* POURBAIX and SCHEIL), or entered by the users, are saved as special symbols (variables, functions or tables). Each symbol has a unique name that must start with a letter and can have maximum 8 legal characters [including letters (either UPPER or lower case), digits and underscore "_", but not any other special character such as parentheses " (" and ") ", plus "+", minus "−", slash "/" or "\", period "."].

There are many different ways to define additional derived variables and functions depending on users' purposes. For instance, the *activity coefficient of a component* in the system, and the *partition coefficient of a component* between two phases, can be defined as follows:

```
Rc<name>  = ACR(component)/X(component)
Pc<name>  = X(phase1,component)/X(phase2,component)
```

It is important to note that the activity coefficient of a species in a solution phase depends upon the model definitions on the reference states and standard states for the species (see more descriptions in the *Section 2.13, Reference state and standard state*). When the standard state of a species is defined as the same as the "*pure species*" in a substitutional phase (such as gas and liquid, where all the dissolved species in the phase can substitute for each other and occupy equivalent sites, and the phase is possible to exist as pure with only the species), the *activity coefficient of the species* can then be calculated by:

```
RC<name> = ACR(species,phase)/Y(phase,species)
```

If there are more than one sublattice in the phase and thus the reference states for the phase species can not be presented by the "*pure species*", *e.g.,* C in FCC [`(Fe)₁(C,N,VA)₁`] as the model may end at 50% C plus 50% Fe, the chemical potential and activity of all phase constituents will not be well defined. Therefore, one can not properly define the activity coefficients of the species in the phase.

For an aqueous solution phase, no matter what model (*e.g.,* SIT, HKF, PITZ or another) is used, the reference state and standard state for both the solvent and solutes are properly defined in a special way in the Thermo-Calc software. The reference state for the solvent is set as "***pure water***", the same as its standard state (according to the **Raoults's Law**). The standard state for a solute species is set the "*hypothetical solute* ***species***", whilst its reference state is defined as the *"hypothetical state at unit molality (one mole dissolved into 1.0 kg of solvent) but in which the environment of each molecular is the same as at infinite dilution"* (according to the **Henry's Law**). Under these definitions, the *activity coefficients for both solvent and solute species* can be calculated, as follows:

```
RC<H2O>  = ACR(H2O,aqueous)/Y(aqueous,H2O)                    (for solvent)
RC<spec> = AI(species,aqueous)/ML(aqueous,species)            (for solute)
         = ACR(species,aqueous)/Y(aqueous,species)*Y(aqueous,H2O)
```

where `AI` is the activity of solute species calculated from the model, and `ML` is the molality of the species.

The aqueous solution phase is treated in a comprehensive way within the Thermo-Calc software, due to its special requirements on presenting the calculated quantities that are of particular interest for aqueous chemistry, materials corrosion, chemical engineering, geochemistry, environmental engineering, *etc*. All the standard state variables used for other phases (see *Table 1*) can be directly applied to the aqueous solution phase. Moreover, some additional derived variables that are defined as functions of state variables are necessary for the phase. The software (especially in the POURBAIX module) predefines some derived variables as assigned symbols (variables, functions and tables) for the aqueous solution phase.

Some examples of the Thermo-Calc predefined derived variables for the aqueous solution phase are listed and briefly described in *Table 2*. Because the EOS (Equation of State) expressions, standard thermodynamic properties and transport properties for the pure solvent H_2O must be identical to those for the pure gaseous species H_2O, some derived variables for a gaseous mixture phase are also listed in the table. Under a certain temperature-pressure-composition condition, an aqueous solution phase may be in equilibrium with a stable gaseous mixture phase or a saturated vapour.

Another frequently-used concept regarding the constitution of a phase is **solubility**, that is applied where one or several of the constituents are dominant (dissolving, highly concentrated) while the rest species remain at minor levels of contents (dissolved, less concentrated or even dilute). Please note that the solubility concept is usually used when there exists a heterogeneous equilibrium between a dissolving (terminal) solution/mixture phase (*e.g.,* liquid, gas, aqueous or solid; which has a dissolving capacity) and another stoichiometric/solution phase (*e.g.,* metallic/non-metallic solids/liquids/gases, carbide/carbonate/nitride/nitrate/hydride/oxide/hydroxide/silicate/ sulphide/sulphate/… solids; from which some constituents tend to be dissolved into the dissolving solution/mixture phase). One should also keep in mind that the application of the solubility concept is usually related to a saturation status between the dissolving (terminal) solution phase and dissolved phase (which is not completely-dissolvable for the terminal phase). For instance,

  ➢ A Fe-/Cr-dominant BCC phase may dissolve certain amounts of *e.g.* Ni and C from a carbide phase (such as M23C6, M7C3 and M3C) under a specific condition of temperature-pressure and defined Fe-Cr composition; so the Ni and C elements in the carbides will have their defined solubility in the BCC phase;

  ➢ An aqueous solution phase is always dominant by the solvent water H_2O, and any other element (such as Fe and C) or substance [such as a pure SO2 gas, stoichiometric phase Cu_2S and solution phase `(Fe,Ni)`$_1$`(O,Va)`$_1$] may have a solubility limit under a specific condition of temperature-pressure and other aqueous compositions;

  ➢ An O_2-dominant gaseous mixture phase may dissolve certain amounts of Fe^{+2}/Fe^{+3} species from magnetite (Fe_3O_4) under a given condition of temperature-pressure and concentrations of other dissolved species in the mixture; therefore, the magnetite solid will have a defined solubility in the gaseous mixture under the given condition;

  ➢ A Fe-dominant liquid mixture phase may dissolve certain amounts of *e.g.* Cr and O under a specific condition of temperature-pressure and concentrations of other dissolved species in the liquid phase; this is why that the Cr and O components will have their defined solubility in the liquid mixture.

Table 2.   Derived Variables Predefined for Aqueous Solution and Gaseous Mixture Phases

Name	*Mnemonic*	*Possibly Units*	*Meaning*	*Comments*
For Aqueous Solution Phase				
pH	PH	*dimensionless*	Acidity	of the aqueous solution phase, `pH = -log10(AC(H+)) = -log10(ACR(H+,AQ))`
Eh	EH	V, mV	Hypothetical electric potential	of the aqueous solution phase, `Eh = u(ZE)/96485.309`
pe	PE	*dimensionless*	Logarithm of the hypothetical electron activity	of the aqueous solution phase, `pe = u(ZE)/(2.3025851*RT)`
Ah	AH	kJ, kcal	Thermodynamic affinity per electron	of a redox couple *wrt* the standard hydrogen electrode in the aqueous solution phase, `Ah = u(ZE)`
y_w	YH2O	*dimensionless*	Mole fraction	of the solvent H_2O in the aqueous solution phase, `YH2O = Y(AQ,H2O)`
N_w	AH2O	mole	Mole number	of 1.0 kg of solvent H_2O, `AH2O = 55.508435`
N_{sp}	NSH2O	mole	Mole number, `NS(AQ,H2O)`	of the solvent (H_2O) in the aqueous solution phase, `NS(AQ,H2O) = YH2O*NP(AQ)`
	NS#		Mole number, `NS(AQ,sp)`	of a solute species in the aqueous solution phase, `NS(AQ,sp) = Y(AQ,sp)*NP(AQ)`
m	ML#	mol/kg_H_2O	Molality, `ML(AQ,sp)`	of a solute species in the aqueous phase, `ML(AQ,sp) = Y(AQ,sp)*AH2O/YH2O`
m*	TIM	equivalent molality	Total molality	of all solute species in the aqueous solution phase `TIM = sum[ML(AQ,sp)]`ᵢₒₙₛ `        + sum[ML(AQ,sp)]`complexes
m_t	TIC#	equivalent molality	Total ionic concentration, `TIC(AQ,sp)`	of a cation I in the aqueous phase, `TIC(AQ,spI) = sum[ML(AQ,spJ)*V(`*spI-in-spJ*`)]`
I	ISTR	*dimensionless*	Ionic strength	of the aqueous solution phase, `ISTR=1/2*sum[ML(AQ,sp)*Z(AQ,sp)**2]`
γ	RCH2O	*dimensionless*	Activity coefficient, `RC(H2O,AQ)`	of the solvent (H_2O), `RC(H2O,AQ) = ACR(H2O,AQ)/YH2O`
	RC#		Activity coefficient, `RC(sp,AQ)`	of a solute species, `RC(sp,AQ) = ACR(sp,AQ)/Y(AQ,sp)*YH2O`
α_i	AIH2O	*dimensionless*	Activity, `AI(H2O,AQ)`	of the solvent (H_2O), `AI(H2O,AQ) = ACR(H2O,AQ)`
	AI#		Activity, `AI(sp,AQ)`	of a solute species *related to* the aqueous solution phase, `AI(sp,AQ) = ACR(sp,AQ)*AH2O`

	LogAI#		Log10 Activity,
			`LogAI(H2O,AQ)`,
			`LogAI(sp,AQ)`
				of the solvent or a solute species *related to* the aqueous solution phase in common logarithm,
				`LogAI(H2O,AQ) = log10[AI(H2O,AQ)]`
				`LogAI(sp,AQ)  = log10[AI(sp,AQ)]`

α_w	AW	*dimensionless*	Activity	of H_2O in the aqueous solution phase, `AW = ACR(H2O,AQ)`
ϕ	OS	*dimensionless*	Osmotic coefficient	of aqueous solution phase, `OS = -55.508435*lnAW/TIM`
At1	AT1	equil_mol/kg_H_2O	Titration alkalinity *(definition 1)*	of the aqueous solution phase, generally defined as the equivalent molality of carbonate and bicarbonate at the methyl orange endpoint (pH=4.5)
At2	AT2	equil_mol/kg_H_2O	Titration alkalinity *(definition 2)*	of the aqueous solution phase, generally defined as the equivalent molality of carbonate and bicarbonate, plus sulfide, at the methyl orange endpoint (pH=4.5)
For Gaseous Mixture Phase				
γ	RA#	*dimensionless*	Activity coefficient, `RA(sp,GAS)`	of a gaseous species in the gaseous mixture, `RA(sp,GAS) = `*function*`(Y,T,P)`
γ^*	RF#	*dimensionless*	Fugacity coefficient, `RF(sp,GAS)`	of a pure gaseous species under *TP*, `RF(sp,GAS) = `*function*`(T,P/V)`

f	FUG#	pa, bar, psi	Fugacity,
			`FUG(sp,GAS)`
				of a gaseous species in the gaseous mixture,
				`FUG(sp,GAS) = RA(sp,GAS)*RF(sp,GAS)`
				`                    *Y(GAS,sp)*P`

f_t	TFUG	pa, bar, psi	Total gas fugacity	of the gaseous mixture phase, `TFUG = sum[FUG(sp,GAS)]`

All such derived variables for an aqueous solution phase as listed in the above table have been automatically predefined by the POURBAIX module. However, due to the syntax regulations in the software, those quantities for various individual aqueous species (and gaseous species) are defined as a name followed by a digital number, *e.g.,* `NS#`, `ML#`, `TIC#`, `RC#`, `logAI#` and `AI#` (the same applies to `RA#`, `RF#` and `FUG#`).

2.7   Gibbs Phase Rule

The *Gibbs Phase Rule* describes a system in equilibrium so that

$$f = N - M + 2$$

where *f* is the number of **degrees of freedom**, *N* is the number of system components, and *M* is the maximum number of stable phases.

If no stable phase is prescribed, the Gibbs Phase Rule requires that the user set *N+2* conditions in order to calculate an equilibrium. The maximum number of stable phases is *N+2* in an equilibrium system.

The rule also means that, in a region with *M* stable phases, one can change the values of *N−M+2* state variables independently and still have the same set of stable phases. In other words, if there are *M'* stable phase presented and the number of intensive variables (*I = M-M'*) are set as constants in the region, the values of *N+2−M'* state variables can be changed independently.

If *M' = N+2−I [i.e., f = N+2-M'−I = 0]*, there are *zero degree of freedom* which defines an **invariant equilibrium** because it can be attained only for a single set of values of all the state variables. Examples of this are the three-phase equilibrium assemblage in either a unary system with variable temperature and pressure [*i.e.,* 0=1+2−3−0] or a binary system at constant pressure [*i.e.,* 0=2+2−3−1].

If *M' = N+2−I−1 [i.e., f = N+2−M'−I = 1]*, there is *one degree of freedom*, and the case presents a **univariant equilibrium** where the set of stable phases depends solely on the value of one state variable. Examples are the two-phase equilibrium assemblage in either a unary system with variable temperature and pressure [*i.e.,* 1=1+2−2−0] or a binary system at constant pressure [*i.e.,* 1=2+2−2−1].

A phase diagram is made up of lines of univariant equilibria and cross-points of invariant equilibria. An area surrounded by lines and points on the two-dimensional phase diagram or a surface on three-dimensional phase diagram describes equilibria with two or more intensive variables.

2.8   Thermodynamic Functions of State

A number of thermodynamic functions of state (characteristic state functions) have been introduced, in accordance with the first and second laws of thermodynamics:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i - Dd\xi$$

$$dA = -SdT - PdV + \sum_i \mu_i dN_i - Dd\xi$$

$$dU = TdS - PdV + \sum_i \mu_i dN_i - Dd\xi$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i - Dd\xi$$

These characteristic state functions can simplify the description of the equilibrium state, at which the driving force *D* = 0 and thus *Ddξ* = 0. The advantage of using one characteristic state function, as opposed to any other, depends on how the system under consideration is controlled:

- Controlling the temperature, pressure and composition of a system makes the **Gibbs energy** (*G*) the most useful function since *G* has its minimum at the equilibrium.
- Controlling the temperature, volume and composition of a system forces the **Helmholtz energy** (*A*) to be at its minimum when the system is at equilibrium.
- Controlling the entropy, volume and composition of a system ensures the **Internal energy** (*U*) will be at its minimum when the system is at equilibrium.
- Controlling the entropy, pressure and composition of a system leads the **enthalpy** (*H*, which is related to the heat content of the system) to be at its minimum when the system is at equilibrium.

2.9   Systems with Many Phases

Thermodynamics can be applied to systems with just one phase (***homogeneous systems***) or systems with many phases (***heterogeneous systems***). The Gibbs Phase Rule gives the maximum number of phases that can be stable in a defined system with a given number of components. It is important to realize that the properties of one phase are completely independent of the properties of any other phase in the system. Thus, one can define the Gibbs energy for each phase individually. The Gibbs energy of the whole system is the sum of each of the stable phases multiplied by the amount of that phase.

The Thermo-Calc software employs the ***Gibbs Energy Minimization*** technique (see *Section 2.17*) to calculate the most stable phase assemblage in a multicomponent and multiphase equilibrium (*i.e.,* heterogeneous equilibrium), in which the equations of mass balance, mass action, and conservation of electrons are automatically satisfied through both mathematical and thermodynamic solutions.

Table 3 lists various types of phases that can be handled by the Thermo-Calc software/database/programming-interface package, and currently available models and related databases.

Table 3.   **Various Phases Handled by the Thermo-Calc Package**

Phase Type	*Phase Examples*	*Available Models*	*Database Examples*
Pure stoichiometric phase	Pure metals	appropriate EOS	PURE, SSUB
	Pure stoichiometric oxides, sulfides, hydroxides, silicates, *etc.*	appropriate EOS	SSUB, SLAG, TCMP, TCES
	Pure stoichiometric condensed substances under high pressure and high temperature	Murnagham, Birch-Murnagham, GPVT	TCFE, TCNI, TCAL, TCMG, SSOL , GCE, PGEO
	Pure gaseous species in their standard states	Ideal Gas	SSUB, SLAG, TCMP, TCES
	Simple organic substances	appropriate EOS	
Pure ferro-, antiferro- or para-magnetic phase	Magnetic elements	CEF with Inden MO	TCFE, NUCLEA, SSOL
	Magnetic oxides	CEF with Inden MO	TCFE, NUCLEA, SSOL
Condensed substitutional solution	Alloys with metallic components on one or more substitutional sublattices	CEF, GPVT	TCFE, TCNI, TCAL, TCMG, TCSLD, SSOL
	Metallic liquid mixture without sublattice	CEF, GPVT	TCFE, TCNI, TCAL, TCMG, TCSLD, SSOL
	Complex oxides, silicates, *etc.*	CEF, GPVT	ION/TCOX, TCSC, TCFC, STBC, NOX, GCE
Interstitial solution	Alloys with metallic components on one or more substitutional sublattices, and with carbon, nitrogen, *etc.* on an interstitial site	CEF, GPVT	TCFE, TCNI, TCAL, TCMG, TCSLD, SSOL, TCMP, TCES
Solution phase with several sublattices	Alloys with metallic component occupying different sublattice sites	CEF, GPVT	TCFE, TCNI, TCAL, TCMG, TCSLD, SSOL, TCMP
	Solid salts with charged ions	CEF, AM, QCM	SALT, TCMP
Solution phase with chemical defects on certain sublattices	Non-stoichiometric oxides with charged ions	CEF, GPVT, AM, QCM	ION/TCOX, STBC, NUOX, NOX, TCMP
	Non-stoichiometric salts with charged ions	CEF, AM, QCM	SALT, TCMP
	Ionic liquid with two sublattices	ITSLM, GPVT	ION/TCOX, STBC, NUOX, SLAT, TCFE
Solution phase with ordering transformations	Chemically and/or magnetically ordered alloys, oxides, silicates, *etc.*	CEM with CVM, with Inden MO	TCFE, TCNI, TCAL, TCMG, TCSLD, SSOL, TCMP
Amorphous phase	Bulk non-crystallized phases	G2SLM	
Solution phase with forming species	Gaseous mixtures	SUPERFLUID	SUPERFLUID
	Aqueous solutions	SIT, HKF, PITZ	TCAQ, AQS
	Melts/Liquids	ITSLM, AM, QCM	TCFE, ION/TCOX, SSOL
	Molten salts	ITSLM, AM, QCM	SALT
	Glasses		
Solution phase with covalence bonding	Complex organic substances		
	Metal-organic complexes		
	Polymers	FHM	

Notes: For details of models and databases available for different phases, please refer to the related chapters/sections in this Thermo-Calc Software System document, Thermo-Calc Console Mode User's Guide and Thermo-Calc Database Manager's Guide, as well as to the information given on TCS web site (www.thermocalc.com).

2.10   Irreversible Thermodynamics

All concepts introduced in this presentation of classical thermodynamics are actually only defined for systems in equilibrium, *i.e.,* when there are no changes. The concepts can also be extended to situations where the rate of change is very low; such processes are called reversible because at any moment reverse the direction of the process is allowed to proceed. However, most processes in nature are irreversible and many systems are in states that have not yet reached equilibrium. The question then becomes whether one can apply thermodynamics to these problems. The answer is that it can sometimes be done if one is careful. However, discussing what is meant by careful is outside the scope of this presentation.

2.11   Thermodynamic Models

It is important to comprehensively describe the EOS (Equation of State) and all thermodynamic functions of both pure substances and solution phases in the system to make a reliable thermodynamic calculation. The Thermo-Calc software/database/programming-interface package requires such thermodynamic descriptions to formulate the Gibbs energy expressions, as well as the second derivatives, to perform an equilibrium calculation using the Gibbs energy minimization technique (Sundman, 1981, 1990; Jansson, 1984; Lukas *et al.,* 2007). Any model which gives explicit Helmholtz or Internal energy rather than Gibbs energy shall be *analytically or numerically* converted to a Gibbs energy expression by implementing some special algorithm in the Thermo-Calc GES module (for details and examples, see *Chapter 11 - Gibbs Energy System Module (GES)* in the *Thermo-Calc Console Mode User's Guide*.

The EOS and basic thermodynamic description of a pure substance should give specific and well-defined physical and chemical data. A good model for pure substances should be able to present the *P-V-T* relations, thermodynamic functions (*G, H, S, C_p/C_v, α* and *β/κ*), as well all possible additional contributions from magnetic ordering, chemical ordering, electrostatic reactions, *etc*. Such data are very important to calculate the standard thermodynamic properties of the pure substance in either a stoichiometric phase or a certain reference state in a solution phase). For instance,

➢ *Inden Model* (Inden, 1975) is utilized to calculate the magnetic contribution;

➢ *CVM (Cluster-Variation-Method) Tetrahedron Method* (Kikuchi, 1951; Sundman and Mohri, 1990) is applied to calculate the configuration entropy contribution resulting from chemical ordering;

➢ *Comprehensive Water and Steam EOS Model* (Johnson and Norton, 1991; Haar *et al.,* 1984) and the *Complete Revised Helgeson-Kirkham-Flowers Model* (Johnson *et al.,* 1991) have been implemented into Thermo-Calc to calculate the standard thermodynamic and transport properties of H_2O (water, vapor and ice) and aqueous solution species over a wide temperature and pressure range;

➢ *Murnaghan Model* and *Birch-Murnaghan Model* (Saxena *et al.,* 1995) and *Generalized PVT Model* (Chen *et al.,* 2006) can be used to calculate the *P-V-T* relations and thermodynamic properties of materials under very high temperatures and pressures.

The common models for solution phases used by Thermo-Calc for the composition dependence of the phases are:

➢ *Regular Solution Model* with one symmetrical binary interaction parameter, or *Subregular Solution Model* with the symmetrical and asymmetrical binary *Redlich-Kister* interaction parameters plus several extensions for composition-dependent ternary parameters [*e.g., Redlich-Kister_Muggianu, Redlich-Kister_Kohler* and *Redlich-Kister_Toop*; please refer to Hillert (1980) and Sundman (2004) for more details] or with asymmetrical binary excess models in either simple or legendre polynomials,

➢ *Sublattice Model* or the so-called *Compound-Energy Formalism* (Sundman and Ågren, 1981; Andersson *et al.,* 1986) for either substitutional solution phases (without sublattice) or interstitial solution phases (with one or more substitutional sublattices and one interstitial site). This model can also take ionic constraints (charged cation/anion species) into account. For chemical ordering (in *e.g.* ordered BCC, FCC and HCP phases), either *Two-Substitutional-Sublattice Ordering Model* or *Four-Substitutional-Sublattice Ordering Model* can be applied (one additional interstitial site can also be considered).

Specific solution models are used in Thermo-Calc software for some particular solution phases, for instance,

➢ *Ionic Two-Sublattice Liquid Model* (Hillert *et al.,* 1985), *Associated Model* (Jordan, 1979), and three varieties of the *Quasi-Chemical Model* [they are the *Quasi-Chemical_IRSID Model* (*i.e., Kapoor-Frohberg-Gaye Cell Model* developed by Gay and Welfringer, 1984), *Quasi-Chemical_Ionic Model*

(according to Prof. Mats Hillert, 2001), and ***Quasi-Chemical_FACT00 Model*** (developed by Kongoli *et al.,* 2002)] for complex oxide liquids (liquid slag);

➢ ***Generalized Two-State Model*** for handing amorphous phenomena (changing between solid and liquid);

➢ ***Flory-Huggins Model*** for polymers;

➢ ***SUPERFLUID Model*** (Shi and Saxena, 1992; Belenoshko *et al.,* 1992) for sub-/super-crtitcal C-H-O-S-N-Ar gaseous/fluid mixtures; and

➢ **SIT** (***Specific Ionic Interaction Theory***; Ciavatta, 1990), **HKF** (***Complete Revised Helgeson-Kirkham-Flowers Model***; Helgeson *et al.,* 1981; Shock *et al.,* 1992; Shi *et al.,* 1992) and **PITZ** (***Generalized Pitzer's Formalism***; Pitzer, 1991) models for aqueous solutions.

Besides these two parts of ordinary contributions (for pure substances and solutions, respectively) to Gibbs energy of a material system, Thermo-Calc also provides the possibility for users to append any types of extra contributions to the Gibbs energy of the interaction system, such as the surface tension energy.

All of the thermodynamic models for pure substances and solution phases are extensively explained in detail in <u>*Chapter 11 - Gibbs Energy System (GES)*</u> in the <u>*Thermo-Calc Console Mode User's Guide*</u>.

There are two main occasions where a user especially needs to understand modelling parameters; the first is that start values for a calculation must be provided by the user, and the second is that miscibility gaps or ordering phenomena are calculated.

2.12   Dependence of Gibbs Energy on Various State Variables

As already mentioned above, the Gibbs energy of a phase depends on various different state variables. In most alloy systems, the thermodynamic properties of a phase can be modelled by using an expression showing how the Gibbs energy depends on temperature and composition (usually the fractions of the constituents in the phase). Other state variables, such as pressure, volume or entropy, may also serve as parameters in the Gibbs energy expression.

However, for some phases at certain states where the volume can not be directly and explicitly described as a function of pressure (*e.g.,* minerals under very high pressures), or the classical thermodynamics can not be applied (*e.g.,* H_2O in its critical region). Under such circumstances, the Gibbs energy for the phases should be analytically or numerically converted from either Helmholtz energy or Internal energy, or be numerically obtained from inside of GES calculating routines.

Table 1 in *Section 2.5* lists the basic intensive and extensive variables that are suitable in the Thermo-Calc software system.

2.13   Reference State and Standard State

Gibbs energy is always given relative to some references. For an example, if one inquires Gibbs energy for various forms of iron, one may find information on all the other forms relative to the *BCC* form.

There are normally more than one ways to choose the reference state for a stoichiometric or solution phase. When representing Gibbs energy for a substance with a certain composition as a function of temperature and pressure, one can use as reference either the same substance with the same composition at some constant temperature and pressure (*e.g.,* 0 K and 1 bar, or 298.15 K and 1 bar, or 970 K and 1 bar), or the same substance with the same composition but the most stable structure for each component in the substance at current temperature and 1 bar. However, the reference states for various components in a multicomponent heterogeneous system must be the same for each component in different phases in the system.

The Thermo-Calc software allows the user to choose appropriate reference states for various components in a phase. The most usual way is to set the reference state for all components if in element forms as the so-called *Stable Element Reference (SER)*, which is defined as default in all Thermo-Calc databases. However, one can choose other reference states for any component in the system, especially when the components are not in element forms (*e.g.,* CaO and O2 for the Ca-O system; H2O and H+1 for H-O system; UO2+2 and O-2 in U-O system).

The reference state for a component (if differing from the SER state) in the system can be specified by the `SET_REFERENCE_STATE` command, in which a reference phase must be specified, and the reference temperature (normally the current temperature) and pressure (normally 1 bar) be entered.

In case of that the SER reference is used, the molar Gibbs energy of formation of a stoichiometric compound Θ from pure elements at any temperature and pressure is expressed by:

$$^{o}G_{m}^{\Theta} - H^{SER} = \Delta_{f}\,^{o}G_{m}^{\Theta} + \sum_{i} v_{i}(^{o}G_{i}^{\alpha} - H_{i}^{SER})$$

When the substance is a solution phase α with a certain composition x_i, it is also necessary to choose appropriate standard states for all components in the phase at the same temperature and pressure, which are usually set as the pure components in the same structure as the solution, *i.e.,* the so-called end-members in the solution phase. The molar Gibbs energy of formation of the phase, added with the excess Gibbs energy term, can be expressed by:

$$G_{m}^{\alpha}(x_i) - H^{SER} = {}^{EX}G_{m}^{\alpha}(x_i) + \sum_{i} x_{i}(^{o}G_{i}^{\alpha} - H_{i}^{SER})$$

Practically, the reference state of a species in a specific phase is the "*pure*" species in the phase at current temperature and 1 bar. Note that the chemical potential or activity for a species can be obtained for any substitutional phase (*i.e.,* all the dissolved species in the phase can substitute for each other and occupy equivalent sites), but not for cases where there are more than one sublattice in the phase as it is even not well defined. In other word, the necessary condition to calculate such properties is that, from the viewpoint of the model, the phase must be possible to exist as pure with only the species. That is always true for substitutional phases which dissolve the species, but not true for non-substitutional phases, *e.g.,* C in FCC [`(Fe)₁(C,N,VA)₁`] as the model may end at 50% C plus 50% Fe. For instance, for a gas mixture phase where there is only one sublattice and any of the gaseous species is possible to exist as a pure phase, the state variables `MUR(species,gas)` and `ACR(species,gas)` can be used, with the later one always corresponds to the partial pressure (partial fugacity) of the gaseous species. For a liquid phase, it is normally considered (in the Thermo-Calc software) to have a single sublattice and all species can substitute each other in the phase, and then the state variables `MUR(species,liquid)` and `ACR(species,liquid)` can be obtained.

Appendix D (On Reference States and Standard States) in the Thermo-Calc Console Mode User's Guide gives an extensive overview and comprehensive examples on how to set reference states for various system components inside the Thermo-Calc software system and how to explain the calculated results.

The reference state and standard state for an aqueous solution phase are treated in a special way in the Thermo-Calc software. Generally, the single-sublattice approach is also applied to the aqueous solution phase. The constitutional structure of the phase may allow a "*pure species*" (the solvent `H2O` or a specific solute); however, thermodynamic models (*e.g.,* SIT, HKF or PITZ) will normally enforce some concentration limits for the solute species dissolved into the solvent. Therefore, the uses of appropriate standard states of both solvent and solute species become very important for an aqueous solution phase. The reference state for the solvent is set as "*pure water*", the same as its standard state (according to the Raoults's Law). The reference state for a solute species is set the "*pure species*", whilst its standard state is defined as the "*hypothetical state at unit molality (one mole dissolved into 1.0 kg of solvent) but in which the environment of each molecular is the same as at infinite dilution*" (according to the Henry's Law). Under these definitions, the state variables `MUR(species,aqueous)` and `ACR(species,aqueous)` can also be used. However, one should remember that the activities of aqueous species (solvent and solute) with respect to the standard states [normally entered as `AI(sp,aqueous)`, or `AW` for solvent and `AI#` for solute with a specific number # for each species] and with respect to the reference states [always denoted as `ACR(sp,aqueous)`] have the following relations:

```
AW  = AI(H2O,aqueous) = ACR(HeO,aqueous)                (for solvent)
AI# = AI(sp,aqueous)   = ACR(sp,aqueous)*55.5084        (for solute)
```

2.14 Miscibility Gaps

In a unary system, a liquid+vapour two-phase coexistence line in the P-T phase diagram ends at a critical point, above which one can move continuously from the higher-density liquid phase to the lower-density vapour phase; in a binary, ternary, quaternary or higher-order system, it is sometimes possible that two phases with the same structure but different compositions are in equilibrium under constant pressure. Such a two-phase field are usually described as a **miscibility gap**, which can be of characteristic of either a solid, or a liquid or a vapour.

A stable miscibility gap in a binary A–B system shows a top point on a phase diagram, which presents the stability limit of the two-phase field. This point is called **critical point** (because the two coexisting states become identical there) or **consolute point**, where $\left\{ \partial^2 G_m / \partial x_B^2 \right\}_{T,P} = 0$. The line representing the stability limit in a miscibility gap is called a **spinodal curve** or simply a **spinodal** or a **spinode** [because it falls on a sharp point (*spine* meaning *thorn*) in property diagrams with potential axes], and the phase boundary of a miscibility gap is called a **binodal**. The critical point of a stable miscibility gap extends into a line in a ternary system, into a surface in a quaternary system, and so forth. For more comprehensive descriptions on miscibility gaps in multicomponent systems, please refer to pages 376-381 in Hillert M. (1998): *Phase Equilibria, Phase Diagrams and Phase Transformations – Their Thermodynamic Basis.* Cambridge University Press.
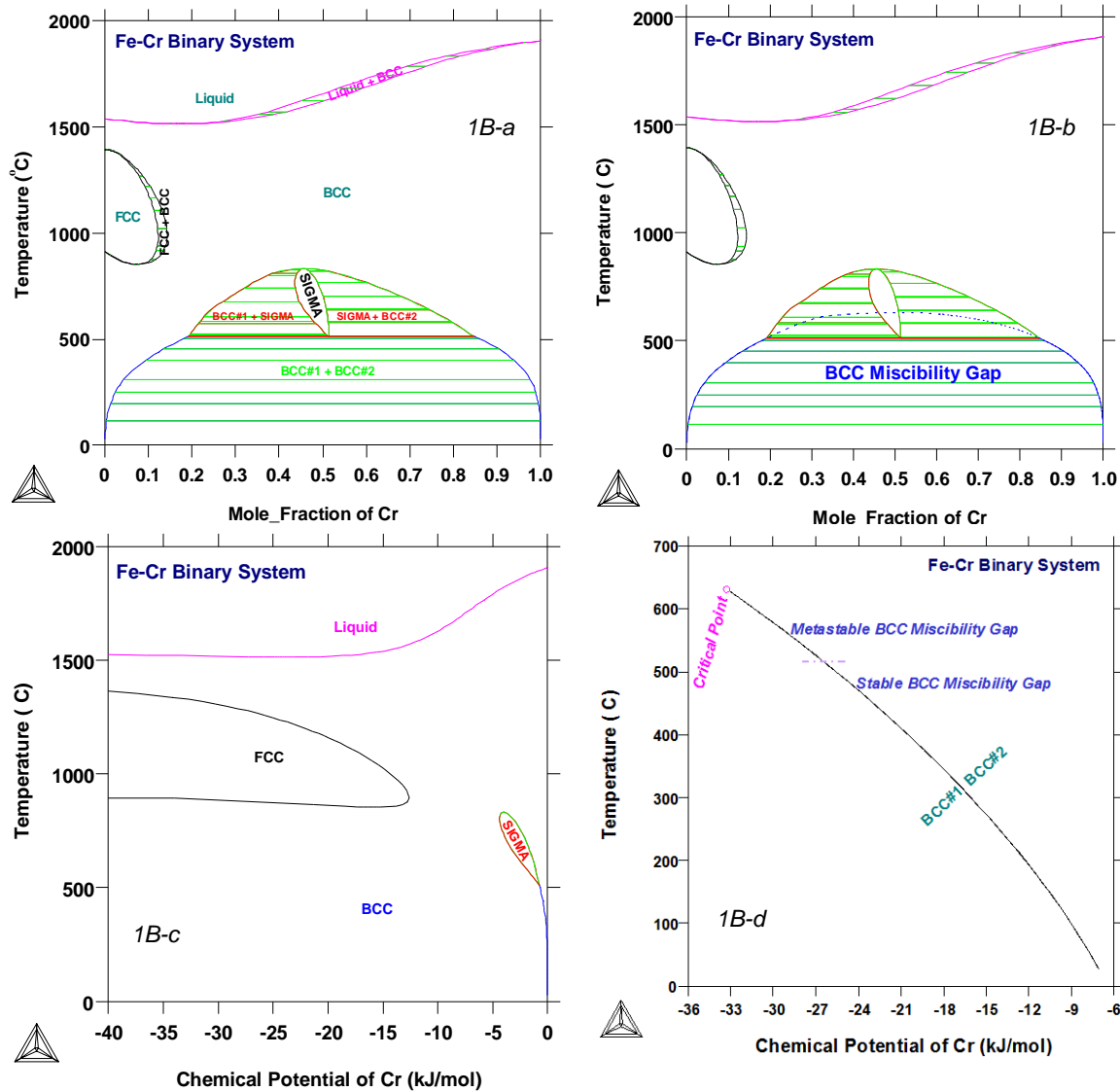
Figure 1A shows the phase diagram of the Cr-Mo binary system at a constant pressure of 1 bar [in both the x_{Mo}-T and μ_{Mo}-T plots], where a solid miscibility gap of the BCC solution phase is stable. The critical point of the miscibility gap is around T=941°C and x_{Mo}=0.40.
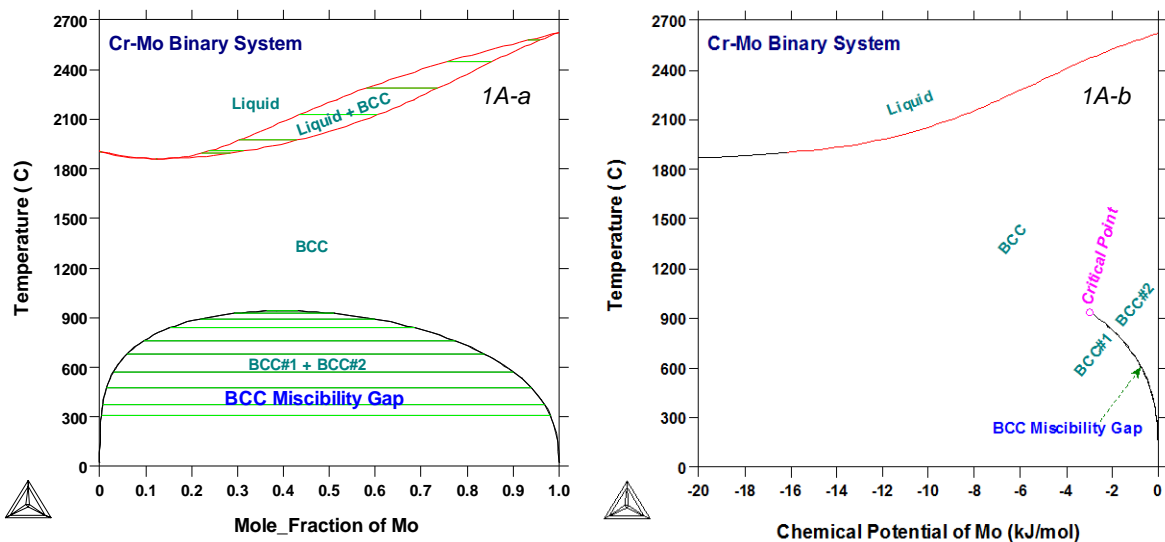
Figure 1A.   Phase Diagram of the Cr-Mo Binary System: Miscibility Gap.

The diagram *1A-a* illustrates the phase relations (single-phase and two-phase regions) among BCC and Liquid solution phases in the Cr-Mo binary system, in the temperature *vs* x_{Mo} space. The diagram *1A-b* shows the μ_{Mo} variation (with the default reference of state SER) in two-phase regions BCC#1+BCC#2 and Liquid+BCC (please note that the lower μ_{Mo} part of the Liquid+BCC region has been cut out on the diagram), illustrating that there is top point on the curve representing the BCC#1+BCC#2 two-phase region which is the critical point of the BCC miscibility gap.

Figure 1B shows the phase diagram of the Fe-Cr binary system at a constant pressure of 1 bar [in both the x_{Cr}-T and μ_{Cr}-T plots]. A solid miscibility gap of the BCC solution phase is stable at low temperatures (below 512°C) and metastable at intermediate temperature range where the SIGMA (σ) solution phase is stable and coexists with the BCC phase (as illustrated in the diagram *2A-a*). By calculating the metastable BCC miscibility gap above 512°C (as plotted in *2A-b*), one can find the critical point of the BCC miscibility gap as being around T=631.25^{o}C and x_{Cr}=0.507.
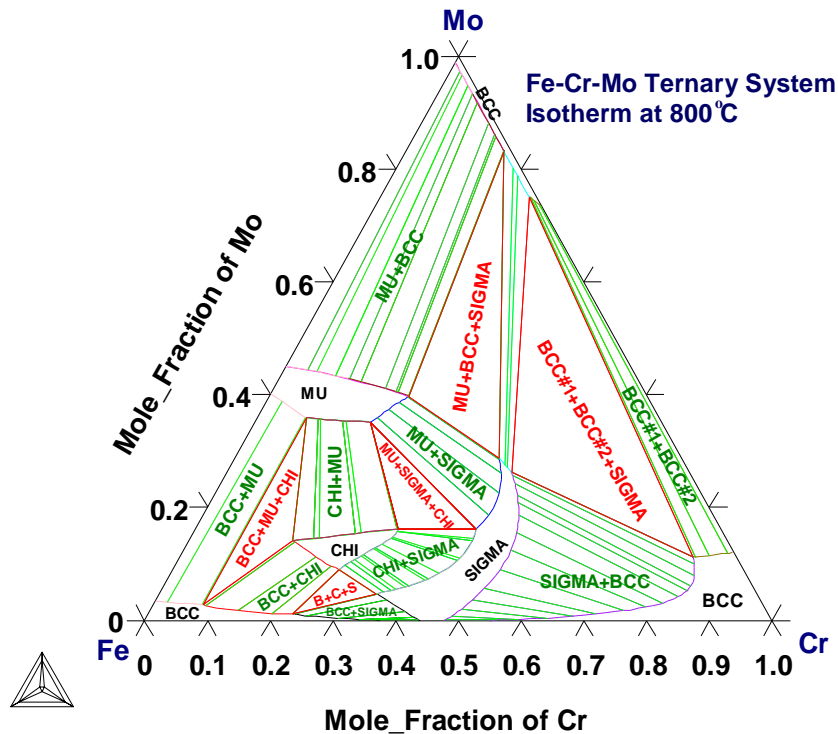
Figure 1B.   Phase Diagram of the Fe-Cr Binary System: Miscibility Gap.

The diagram *1B-a* illustrates the stable phase relations (single-phase and two-phase regions) among BCC, FCC and SIGMA (σ) and Liquid solution phases in the Fe-Cr binary system, in the temperature *vs* x_{Cr} space. The miscibility gap for the BCC solution phase is stable below around 512°C in the intermediate bulk composition range [*i.e.,* the stable BCC phase exhibits demixing behavior (a homogeneous BCC is not the most stable state) and is separated as to two co-existing BCC with different compositions: *e.g.,* at 450°C, BCC#1 with approximate x_{Cr}=0.13 on one side and BCC#2 with approximate x_{Cr}=0.91 on the other]. Above 512°C (while below 832 ^{o}C), the BCC miscibility gap becomes metastable, whereas the SIGMA phase is in equilibrium with BCC on both sides of the SIGMA single-phase region. By imposing the metastable part of the BCC miscibility gap on the stable phase diagram (*1B-b*), it shows the BCC miscibility gap has a critical point around T=631.25^{o}C and x_{Cr}=0.507. The graph *1B-c* plots the μ_{Cr} variation (with the default reference of state SER) in two-phase regions BCC#1+BCC#2, BCC#1+SIGMA, BCC#2+SIGMA, BCC+FCC, and Liquid+BCC (please note that the lower μ_{Cr} parts of the Liquid+BCC and BCC+FCC regions have been cut out on the diagram), illustrating that there is top point on the curve representing the BCC#1+BCC#2 two-phase region which is the critical point of the BCC miscibility gap; and the graph *1B-d* only plots the μ_{Cr} variation (with the default reference of state SER) for the BCC miscibility gag in both it stable and metastable regions (up to its critical point). Please refer to *Figure 2* for the Gibbs energy relations and driving forces within the Fe-Cr binary system at some selected temperatures.

Figure 1C shows the isothermal section of the Fe-Cr-Mo ternary system at a constant pressure of 1 bar [in the x_{Fe}-x_{Cr}-x_{Mo} plot]. A solid miscibility gap of the BCC solution phase is stable at low temperatures (below 512°C) and metastable at intermediate temperature range where the SIGMA (σ) solution phase is stable and coexists with the BCC phase (as illustrated in the diagram *2A-a*). By calculating the metastable BCC miscibility gap above 512°C (as plotted in *2A-b*), one can find the critical point of the BCC miscibility gap as being around T=631.25°C and x_{Cr}=0.507.

Figure 1C. Phase Diagram of the Fe-Cr-Mo Ternary System: Miscibility Gap.

The isothermal section illustrates the stable phase relations (single-phase, two-phase and three-phase regions) in the Fe-Cr-Mo ternary system under 800°C and 1 bar. The BCC miscibility gap (BCC#1+BCC#2 coexistence) is stable at the low-x_{Fe} and intermediate x_{Cr}-x_{Mo} region.

In order to calculate such an equilibrium, it is necessary to introduce the same number of composition sets for the solution phase as simultaneously stable compositions. This is normally done optionally by the command `ADVANCED_OPTION` (with the `NEW_COMPOSITION_SET` option) in the POLY module or `AMEND_PHASE_DESCRIPTION` in the GES module, or permanently by the type-definition `AMEND_PHASE_DESCRIPTION` in the TDB module. By default, each solution phase normally has only one composition set; while in some databases, there are some type-definitions that generate some pre-defined composition sets for some solution phases.

However, the Global Minimization Technique (introduced since TCCR version) can always automatically create necessary composition sets for some solution phases during a POLY-module calculation (for single-point or stepping or mapping). For more details, please refer to *Section 2.18 – Global Minimization* in this document and *Chapter 8 in the Thermo-Calc Console Mode User's Guide*.

2.15　Driving Force and Common Tangent

Driving force (*D*) is the affinity between reacting chemical species in a certain internal process, for which the process extent is usually represented by the internal variable ξ. According to the second law of thermodynamics, it is proportional to the internal entropy production $d_{ip}S$ and can be expressed as the relation $D = T\, d_{ip}S/d\xi$. If a system is not in a state of equilibrium, there may be a spontaneous internal process for which the second law gives $d_{ip}S > 0$ and thus $Dd\xi > 0$ that drives the process to approach the equilibrium.

Equilibrium thermodynamics deals with systems where $d_{ip}S = 0$ and $D = 0$, regardless the natures of internal processes. In a chemical equilibrium state, there is no variation of all characteristic state functions at the equilibrium value of the internal variable ξ. Thus the driving force at the equilibrium state can be expressed as:

$$D = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,N_i} = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N_i} = -\left(\frac{\partial A}{\partial \xi}\right)_{T,V,N_i} = -\left(\frac{\partial H}{\partial \xi}\right)_{S,P,N_i}$$

In the Thermo-Calc software system which is based on Gibbs energy minimization for equilibrium systems, the driving force of a phase α is always evaluated by:

$$D^\alpha = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,N_i} = -\left(\frac{\partial G}{\partial N^\alpha}\right)_{T,P,N_i} = -\Delta G_m^\alpha$$

The driving force (*i.e.,* the so-called **thermodynamic factor**) for a phase is the shortest distance between the Gibbs energy surface of the phase and the plane made up by joining the chemical potentials for all components in the system at the equilibrium state. This plane is called the **stable common tangent plane** because it is a common tangent to the Gibbs energy surfaces of all stable phases in the defined system. It is clear that the driving force for a stable phase is always equal to zero, whilst for an unstable phase is negative (the more unstable the more negative!). Any phase with a positive driving force is thermodynamically impossible to exist in an equilibrated system.

Please note: when a phase has a tendency to become possibly stable in a defined multicomponent system while has been set with a so-called `DORMANT` or `SUSPENDED` phase status, it can have a positive driving force (in case of the `DORMANT` phase status) or a zero driving force (in case of the `SUSPENDED` phase status).

The Thermo-Calc software assigns the driving force of a phase to the state variable `DGM(phase)` [as well as `DGW(phase)`, `DGV(phase)` and `DGF(phase)`], but please keep in mind that such a `DG(phase)` quantity are *always* presented as a value that *has already divided by RT and is thus dimensionless.*

For simplicity, let's analysis a binary system, where the Gibbs energy surface is a curve and the stable tangent plane is a line, and the driving force for each phase in the system is thus the distance between the stable common tangent line and the phase's tangent line which is parallel to the stable common tangent line. *Figure 2* can be used as a perfect example on how the driving forces are calculated based on the Gibbs energy curves and phase relations in the Fe-Cr binary system at 450, 700, 1000 and 1600°C; please also refer to *Figure 1* which is the phase diagram from the Fe-Cr binary system.

> The graph *2-a* shows Gibbs energy curves for the BCC, FCC, SIGMA (σ) and Liquid solution phases in the Fe-Cr system at 450°C. The thick line represents the stable common tangent plane in the equilibrium state of the system when its system bulk composition varies between approximately 0.133 and 0.906 mole fraction of Cr where the miscibility gap for the BCC phase is stable. The points marked on the Gibbs energy curves for SIGMA, FCC and Liquid solution phases are those closest to the stable common tangent plane. The tangent for each Gibbs energy curves at these compositions shown as a dashed line, must be parallel to the stable common tangent plane. Please also note that: as long as the bulk composition range of the Fe-Cr binary system changes within the stable region of the BCC miscibility gap [*i.e.,* $x_{Cr} \approx 0.133 \sim 0.906$ at 450°C], the driving forces ΔG_m^{ph} (as marked to right of the graph) and phase stability functions `QF(phase)` of all the other metastable phases (*e.g.,* FCC, SIGMA and Liquid) remain the exactly same; while as the bulk composition range of the binary system is out of this two-phase region, the stable common tangent is shifted (not shown on the graph), depending upon which phase (BCC#1 or BCC#2 in this case) is stable in the system, and driving forces ΔG_m^{ph} (not shown on the graph) and phase stability functions `QF(phase)` of all the other metastable phases (*e.g.,* FCC, SIGMA and Liquid) will alter accordingly.
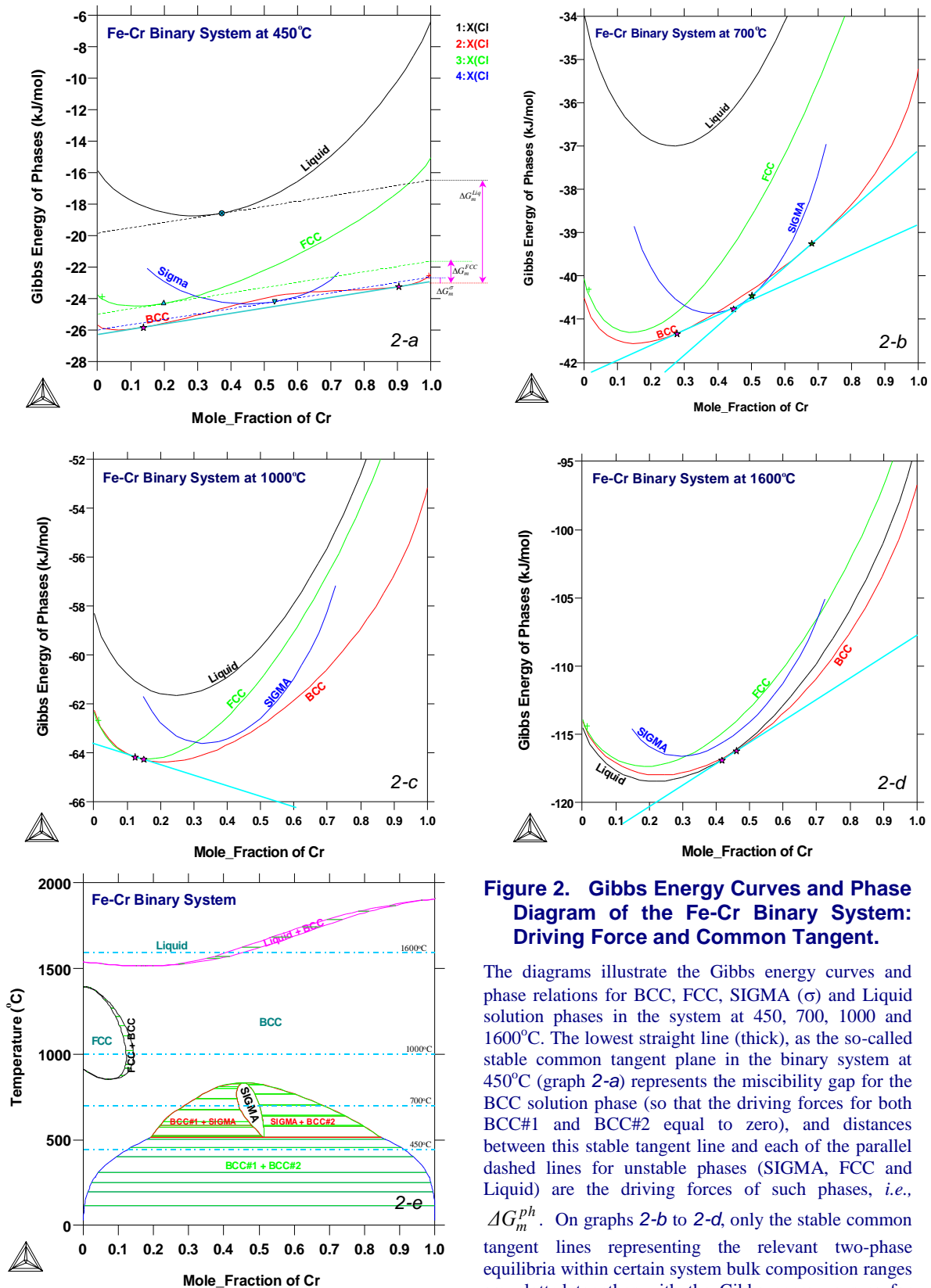
Figure 2. Gibbs Energy Curves and Phase Diagram of the Fe-Cr Binary System: Driving Force and Common Tangent.

The diagrams illustrate the Gibbs energy curves and phase relations for BCC, FCC, SIGMA (σ) and Liquid solution phases in the system at 450, 700, 1000 and 1600°C. The lowest straight line (thick), as the so-called stable common tangent plane in the binary system at 450°C (graph *2-a*) represents the miscibility gap for the BCC solution phase (so that the driving forces for both BCC#1 and BCC#2 equal to zero), and distances between this stable tangent line and each of the parallel dashed lines for unstable phases (SIGMA, FCC and Liquid) are the driving forces of such phases, *i.e.,* ΔG_m^{ph}. On graphs *2-b* to *2-d*, only the stable common tangent lines representing the relevant two-phase equilibria within certain system bulk composition ranges are plotted together with the Gibbs energy curves for various phases. The graph *2-e* is the stable phase diagram of the binary system, with the iso-temperature lines for 450, 700, 1000 and 1600°C plotted.

The graphs *2-b through 2-d* shows Gibbs energy curves for the BCC, FCC, SIGMA (σ) and Liquid solution phases in the Fe-Cr system at 700, 1000 and 1600°C, respectively. Please note that: on these graphs, only the stable common tangent lines representing the stable two-phase regions (related to certain system bulk composition ranges) at such temperature conditions are plotted, and not tangent lines and driving force marks for metastable phases are given. At 700°C, there are two stable two-phase regions (*i.e.,* BCC#1+SIGMA and SIGMA+BCC#2), and thus the plotted stable common tangent lines connects the stable phases at the system bulk compositions $x_{Cr} \approx 0.290 \sim 0.442$ for the BCC#1+SIGMA two-phase region and $x_{Cr} \approx 0.501 \sim 0.681$ for the SIGMA+BCC#2. At 1000°C, the FCC+BCC two-phase coexistence is stable over the system bulk composition $x_{Cr} \approx 0.122 \sim 0.143$, and the plotted stable common tangent line. At 1600°C, the stable common tangent line is plotted for the Liquid+BCC two-phase coexistence is stable over the system bulk composition range $x_{Cr} \approx 0.419 \sim 0.468$, and the plotted stable common tangent line.

The graph *2-e* is the stable phase diagram of the Fe-Cr binary system, with the iso-temperature lines for 450, 700, 1000 and 1600°C plotted, to view the stable phase relations which are corresponding to the Gibbs energy curves drawn on the graphs *2-a through 2-d*.

2.16   Chemical Reactions

The common method in chemistry is to describe a system by giving a chemical reaction between species and calculating or tabulating the thermodynamic properties for this reaction. A useful application may be the calculation of the heat balance for a reaction, from which the final temperature of an adiabatic interaction system may be found. When many reactions are involved, it may be advantageous to calculate the equilibrium in the system by an automatic minimization procedure (see *Section 2.17* in this document).

2.17   Gibbs Energy Minimization Technique versus Equilibrium Constant Approach

In principle, the Gibbs Energy Minimization Technique (GEM) will give identical results as the Equilibrium Constant Approach (ECA) in an equilibrium calculation. This similarity presumes that the latter approach considers all the important chemical reactions in the heterogeneous interaction system are considered and all the equilibrium constants for such reactions must be internally consistent with each other.

From a practical point of view, it is often true that the GEM Technique provides an easier and more efficient way to ensure, *mathematically and thermodynamically*, the internal consistency of thermodynamic data in a specific materials system (thanks to its direct use of a basic thermodynamic function, the Gibbs energy) and the highly efficiency of thermodynamic calculations for multicomponent heterogeneous systems/processes.

The GEM technique employed in the Thermo-Calc package has been proved to be one of the best available for thermochemical calculations, due to the high efficiency and convenience in interactively accessing to the Gibbs energy expressions in the Gibbs Energy System (GES), to the calculated phase stability, assemblage and speciation in the Heterogeneous Equilibrium Calculation Module (POLY), to the derived thermodynamic functions (including reaction constants) in the Tabulation Module (TAB), and to the assessed thermodynamic variables in the Parameter Optimization Module (PARROT). The following chapters will further demonstrate the power of the Thermo-Calc GEM technique in solving various kinds of problems.

2.18   Global Minimization

One of the major improvements in the Thermo-Calc software is that the recently-implemented Global Minimization Technique is used to assure that the present minimum in an equilibrium calculation is the most stable minima for the specified conditions. In other words, this will prevent that you end up with an undesired metastable or unstable (local) equilibrium. Additional composition sets are automatically created in a solution phase if needed (for handling single or multiple miscibility gaps), *i.e.* there will no longer be necessary for the user to specify these in advance.

The technique used may be demonstrated with the example present in *Figure 3*. In this example, the Fe-Cr-Ni system is considered, and we seek a stable minima for an alloy with the bulk composition of $x_{Fe} = 0.5$, $x_{Cr} = 0.4$

and x_{Ni}=`0.1` (shown as the red star), under the conditions of `T=700` K and `P=1` bar (100000 Pascal). When the `COMPUTE-EQUILIBRIUM` command in the POLY module is executed in the new versions, a set of meshes is first computed; these meshes consist of discretized Gibbs energy functions for all the individual phases present in the system. Using these meshes and the defined equilibrium conditions, we find an approximate solution for the common tangent plane that has the lowest Gibbs energy. This plane is in this example defined by three different points which are indicated by yellow squares (which present BCC#1+BCC#2 miscibility gap and FCC phase). These points and also the amounts calculated for each of the phases are used as a start point in a subsequential POLY optimization in order to reach a truly global minimum (the most stable equilibrium state in the defined alloy).

Since TCCR/TCW4, fully-supported equilibrium conditions in the Global Minimization Technique are: `N`, `N(component)`, `B`, `B(component)`, `W(component)` and `X(component)`. If other types of conditions are used, a Global Minimization test and corrections are performed until the lowest minimum is found after the initial POLY optimization.

Please note that the price to pay for assuring a global minimum in a calculation is an increase in the computational time. Global Minimization is normally used as default in a single-point equilibrium calculation, as well as in a stepping or mapping calculation, but can of course be turned off by the user.
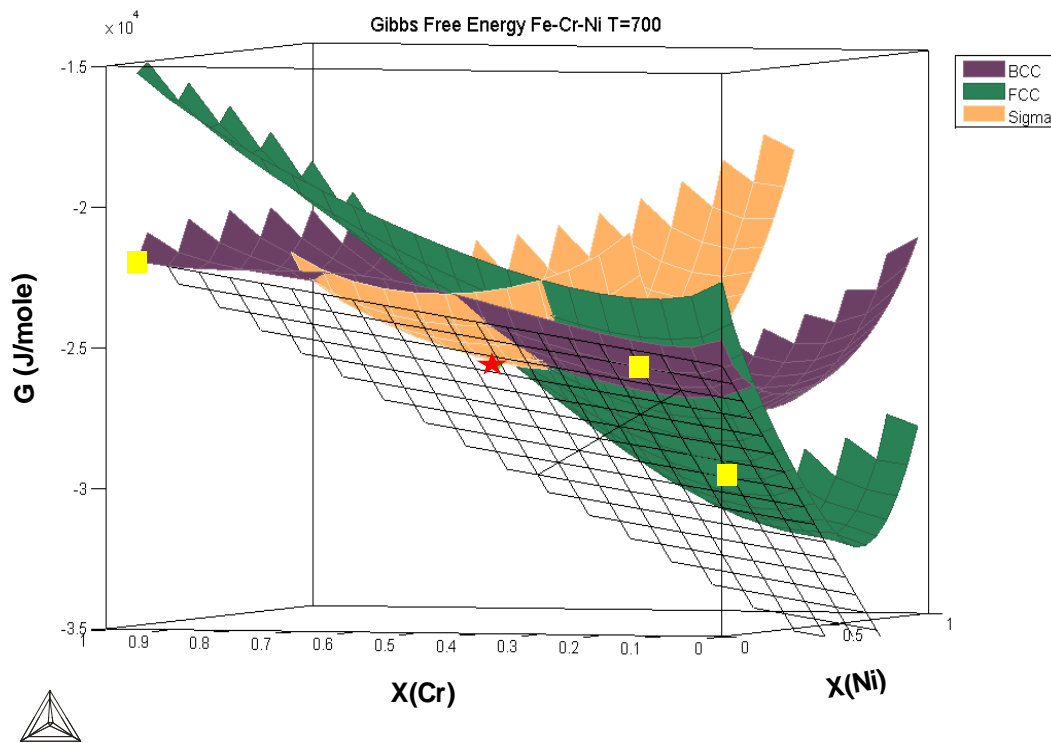
Figure 3.   Global Minimum *vs* Local Minimum

The diagram illustrates the Gibbs energy surfaces for BCC (α), FCC (β) and SIGMA (σ) phases in the Fe-Cr-Ni system (with a bulk composition of X(Fe)=0.5, X(Cr)=0.4 and X(Ni)=0.1, shown as the red star), under the conditions of 700 K and 1 bar.

The Global Minimization Technique finds the lowest Gibbs energy plane that is defined by three different points (that are indicated by yellow squares which present BCC#1-BCC#2 miscibility gap and FCC phase). This phase and the amounts calculated for each of phases are used as a start point in a further POLY optimization in order to finally find a truly global minimum (the most stable equilibrium state in the alloy). Without a global minimization, a calculation may end up a local minimum where the SIGMA (σ) phase is possibly in meta-stable equilibrium with BCC and FCC phases.

Please also note that the Global Minimization Technique is not used, and should not be used, in the PARROT module for data assessment/evaluation. This is simply because that data points used during a PARROT optimisation procedure are normally for specific phases (stoichiometric or solution phases), for well-defined phase

boundaries, and for certain phase assemblages in a given low-order subsystem (which is often a unary, binary, ternary, quaternary or another subsystem within a multicomponent system), and due to that some experimental data used in an assessment/evaluation are probably for some local/partial equilibrium states (that are not always necessarily at the global Gibbs energy minima state for a larger-scaled system).

2.19   Equilibrium Calculations

Before calculating of the state of equilibrium for a homogeneous or heterogeneous system, the user must first retrieve thermodynamic data from a database, and then specify the equilibrium conditions.

Generally, the Thermo-Calc software allows complete freedom to use any combination of conditions for specifying the calculation. It is sufficient to specify the stable phases when calculating an invariant equilibrium; amounts of the components or their chemical potential or activity may also be used. Other specifications may include: equality of composition of two components in two phases at the equilibrium in order to calculate a congruent transformation, or a given value of enthalpy of a system in order to calculate the final temperature after an adiabatic reaction.

There are many different and flexible ways inside the Thermo-Calc software system, for defining equilibrium conditions. For details please refer to *Section 2.5* and *Chapter 8 in the Thermo-Calc Console Mode User's Guide*.

2.20   Metastable Equilibrium Calculations

A metastable equilibrium can also be calculated by setting the phase status of the primarily most stable phases as either SUSPEND or DORMANT (rather than the ENTERED or FIXED phase status). The calculated equilibrium with a stable phase suspended will represent a metastable equilibrium. This is necessary for calculations of phase/property diagrams and simulations of materials processes for *e.g.* C-bearing steels where the graphite phase should be suspended so that various forms of carbides would form instead (more from a kinetic point of view). For details on how to set phase status please refer to *Section 8.10.1in the Thermo-Calc Console Mode User's Guide*.

2.21   Local and Partial Equilibrium Calculations

Thermo-Calc software is intended only for equilibrium calculations, and thus time-/space-dependent transformation processes cannot be simulated. However, several simple types of phase transformations, in which local and partial equilibrium states develop, can be simulated with the Thermo-Calc (and its previous versions TCC/TCW) software/database/programming-inrterface package*, i.e.,* (1) ***solidification processes*** where the diffusion in the liquid phase is very fast, while the diffusion in the solid phases are so slow that in some cases it can be ignored or in other cases back-diffusion phenomena of fast-diffusing components in formed solids can be considered, (2) so-called T_0**-temperature** under which two specific phases have the same Gibbs energy, and (3) ***paraequilibrium conditions*** when the chemical potentials of one or more interstitial components (*e.g.,* C, N, O, S, *etc*.) are the same in two specific phases in a multicomponent system while the **combined chemical potentials** (*i.e*., the products of the chemical potentials and the so-called **u-fractions**) of the non-mobile substitutional elements are equal.

In a simplified **solidification process** (using the *Scheil-Gulliver Model*), the situation at the liquid/solid interface can be described with a local equilibrium. By stepping with small decrements of the temperature (or enthalpy or amount liquid phase), one can determine the new composition of the liquid and then remove the amount solid phase formed by resetting the overall composition to the new liquid composition before taking the next step. This is achieved with the special option EVALUATE, of the POLY command STEP, *i.e.,* the through command sequence STEP EVALUATE. In order to conduct such a solidification simulation in a more user-friendly way, a special module, *i.e.,* the **SCHEIL Module**, was implemented in the Thermo-Calc (and its previous versions TCC/TCW) software. Since TCCQ and TCW3, this module had been improved and modified (as called **Modified SCHEIL Module** or **SCHEIC Module**), which makes it possible (1) to consider one or more fast-diffusing components (usually interstitials, but unnecessarily always interstitials) so that their back diffusion in solid phases can be automatically taken into account during the Scheil-Gulliver simulation, (2) to allow phase transformation

BCC→FCC in already-formed solid phases during solidification process in the simulation, and of course (3) to perform traditional Scheil-Gulliver simulations (as via the ordinary SCHEIL Module). More detailed description of the Modified SCHEIL Module can be found in *Sections 10.8* in the *Thermo-Calc Console Mode User's Guide*, and two cases using the module are included in the ***Thermo-Calc Console Mode Examples Book*** (*i.e., Examples 15* and *30*).

A **T_0-temperature** (**T-zero**) is defined as the temperature where two phases have the same Gibbs energy for a certain composition in a multicomponent system. The T_0-temperature is located within the two-phase field between the phases and it is the theoretical limit for a diffusionless transformation. Calculations of T_0-temperatures are thus of interest *e.g.* when studying diffusionless transformations. The T_0 temperature in a multicomponent system with a fixed composition is a single point which locates at the common tangent line where the Gibbs energies of two phases in the partial equilibrium of a diffusionless transformation are equal, rather than chemical potentials of components. If the composition of one or two components varies, the common Gibbs energy (as illustrated in *Figure 8-2* in the *Thermo-Calc Console Mode User's Guide*) for the two phases in partial equilibrium of a diffusionless transformation becomes a plane or surface, and T_0 becomes a line or plane, accordingly.

A **paraequilibrium** means a partial equilibrium where one or more interstitial components (such as carbon C, nitrogen N, O oxygen, S sulfur; *individual* or *combined*) in a multicomponent alloy can diffuse much faster than the other components (the substitutional elements, including the matrix element and alloying elements), and consequently the chemical potential for the interstitial component but not for the other components in two partially equilibrated phases are equal. Under such a paraequilibrium state, it is possible to have a partly partitionless transformation where a new phase can form with different content of the mobile component but with the same composition of the slow diffusing components. A paraequilibrium calculation is useful *e.g.* when studying phase transformations in systems with large differences in the diffusivities of different elements. Transformations occurring under paraequilibrium states can be much more rapid than if full local equilibrium holds at the phase interface. For instance, in a ternary alloy system (*e.g., Fe-M-C*), it very frequently happens that one of the elements (the interstitial solute C) diffuses very much faster than the other two (the substitutional matrix element Fe and the substitutional alloying element M). It is often possible that a new phase forms with a different content of the mobile element (C) but without a change of the relative contents of the other two (Fe and M). Therefore, partial equilibria will remain in two phases, and a phase transformation will be partly partitionless through the locally equilibrated two-phase interface. At the interface, there is no driving force. The chemical potential of the mobile element (μ_C) has the same value on both sides, but the chemical potential for the non-mobile elements (μ_{Fe} and μ_M) have different values. Instead, the products of the chemical potentials and the so-called **u-fractions** of the non-mobile elements [u_{Fe} and u_M, defined as $N_i /(N_{Fe} + N_M)$ or $x_i /(x_{Fe} + x_M)$] have the same values. Under the paraequilibrium state, $dT = dP = d\mu_C = du_{Fe} = du_M = 0$, the driving force should be zero, and T, P, μ_C and $u_{Fe}\mu_{Fe} + u_M\mu_M$ (the combined chemical potentials of Fe and M) must have the same values on both sides. In a molar Gibbs energy diagram (as illustrated in *Figure 8-1* in the *Thermo-Calc User's Guide*), the tie-line between the two phases in paraequilibrium is directed towards the C corner, which falls on a common tangent line to the two Gibbs energy surfaces but not on the common tangent plane.

Since TCCP, two advanced options (T-ZERO TEMPERATURE and PARAEQUILIRBIUM) have been made available in the POLY commands SPECIAL_OPTIONS and STEP_WITH_OPTIONS, respectively, which automatically calculate the so-called T_0 temperature and paraequilibrium conditions, where partial equilibria establish in complex multicomponent systems. For more details, please refer to *Sections 8.4.4*, *8.10.16* (the ADVANCED_OPTIONS command) and *8.9.4* (the STEP_WITH_OPTIONS command) in the *Thermo-Calc Console Mode User's Guide*, as well as *Examples 42* and *43* in the *Thermo-Calc Console Mode Examples Book.*

2.22 Phase Diagrams

Almost every type of diagram for presenting primary or derived thermodynamic properties has its own name. The term *phase diagram* often means a *T-x* type of diagram for binary systems but the term is used here for any type of diagram with two or more independent state variables used as axis variables. From a phase diagram one can obtain information about the state of a system for any value of the state variables used as axis variables. The Thermo-Calc software allows plotting of various types of multicomponent phase diagrams with up to 5 axis variables.

Phase diagram examples include predominance area diagrams with activities as axis variables, Kellogg diagrams with *1/T* as one axis, isothermal sections, isopleths, and iso-activity diagrams. A phase diagram is calculated with the POLY module using the MAP command. At least two axis variables should be set in the POLY module. In the POST processor, one may specify different independent quantities to be plotted as axis variables for various types of phase diagrams.

2.23 Property Diagrams

A *property diagram* plots the value of a dependent property against an independent variable, such as the carbon activity versus temperature in steels. In multicomponent systems, property diagrams are often more useful than phase diagrams, as they give information within the phase region whereas phase diagrams give only when the set of stable phases changes. The Thermo-Calc software allows plot various types of property diagrams for multicomponent systems with up to 40 components.

A property diagram is calculated with the POLY module using the STEP command. Only one axis variable should be set in the POLY module. In the POST processor, one may specify different dependent quantities to be plotted as the Y-axis while normally keeping the stepping variable as the X-axis.

3   Thermodynamic Data

High quality thermodynamic data is essential for conducting reliable thermochemical calculations. Without accurate and validated databases, any thermodynamic software is useless or misleading.

Thermodynamic data existed prior to thermochemical software. Such data were derived from available various experimental results (*e.g.,* phase diagram determinations, calorimetric measurements on heat of formations or reactions, EMF measurement of stability, *P-V-T* relation and structure determinations, solubility and speciation monitoring, *etc*.). The Thermo-Calc software/database/programming-interface package has provided academic and industrial societies with useful tools in many different ways in studying physico-chemical properties of various substances, in investigating various complex industrial and natural processes, and in assisting materials design and engineering.

The **Thermo-Calc Software** system is a sophisticated software/database/programming-interface package for performing all kinds of thermodynamic calculations of complex homogeneous/heterogeneous phase equilibria, and of phase transformation, property diagrams and phase diagrams in multicomponent heterogeneous interaction systems. It uses the method of the ***Global Gibbs Energy Minimization*** for a given set of equilibrium conditions in a defined multicomponent homogeneous/heterogeneous system. The thermodynamic quantities needed for calculations are provided by the **Gibbs Energy System Module** (**GES**) and equilibrium calculations are conducted by the **Equilibrium Calculation Module (POLY)** inside the Thermo-Calc software system. However, the actual thermodynamic data that describe the thermochemical and thermophysical properties of various types of phases for different material systems are stored in many specific **Thermo-Calc Databases**, which are retrieved through the **Database Module (TDB)** and loaded into the GES and POLY workspaces.

The **Thermo-Calc Databases** are created and maintained in the so-called **Thermo-Calc Database Format (TDB)** which has been used worldwide as an international standard for the CALPHAD-type calculations and simulations.

Emphasis has always been put on simultaneous establishment of good quality thermodynamic data for various materials through enormous critical assessments, during the development of the Thermo-Calc software. Great achievements have been made over the last four decades, and many critically-assessed and internally-consistent databases and datasets have been developed, at Thermo-Calc Software (TCS) and KTH-MSES, through many international and national collaborations [such as SGTE society, CALPHAD community, STT foundation, CAMPADA consortium, NIST institution, ThermoTech company, NPL laboratory, TGG program, CSU-MSES, USTB-MSES, AEA corporation, and so on].

This section introduces data structure, data formats, data assessment, data quality and data sources in the Thermo-Calc software/database/programming-interface package. The documents Thermo-Calc Database User's Guide, Thermo-Calc Database Manager's Guide and Chapter 5 (Database Module, TDB) of the Thermo-Calc Console Mode User's Guide, more information will be given on currently available databases and on how to interactively use and manage a thermodynamic database, dataset or data-file.

3.1   Data Structures

An application-oriented dataset or data-file for a specific system can be extracted from a general database, or be created by a user. The use of such a dataset or data-file is straightforward, but its application is accordingly limited. Moreover, its implementation into various software might be restricted due to its special data structure and data contents. A good thermochemical software/database system must be constructed in a general way, in terms of both data structure and data contents. The system must contain and manage data for a number of traditionally separate fields, *e.g.,* metallurgy, alloys, ceramics, semi-/super-conductors, polymers, high temperature/pressure gas phase equilibria, aqueous chemistry, geochemistry, and environmental systems.

The Thermo-Calc software/database system uses some general databases, and as many as possible specific application-oriented datasets/data-files in a single software/database system, which is easy to learn and use for all kinds of thermochemical calculations in various applications.

Ideally, the data structures of a general database or an application-oriented dataset/data-file should be the same or similar in the Thermo-Calc software/database system. In the *Thermo-Calc Database Manager's Guide* document, more details will be given. The following paragraphs will provide some brief descriptions on the general **Thermo-Calc Data Structure** (or **Thermo-Calc Database Format**), focusing on how and why such a structure is designed, and if any special consideration is necessary for modelling some complicated phases.

A database must have at least a setup file normally with an extension of "`***setup.TDB`", that contains appropriate **system definitions** on *available elements, all kinds of species, possible phases and their phase constituents*.

There are normally additional **default definitions** in a database, such as:

> ➢ global temperature limits
> ➢ common constants
> ➢ default system definition on `DEFINE_SYSTEM` value (`ELEMENT` or `SPECIES`) and the GES-reference type index
> ➢ default phase definitions on major constituent, phase type codes, data type codes, compound phases, allotropic phases, applicable models on various excess energy terms, *etc*.
> ➢ default TDB-module commands (for defining or rejecting basic elements/species/constituents, and rejecting and restoring phases)
> ➢ default type-definitions:
>> ❖ TDB-module command `GET_DATA` to retrieve data from either sequential or random files (and their paths)
>> ❖ GES-model commands on the phase level (*e.g.,* `AMEND_PHASE_DESCRIPTION` command to predefine phase status bits, composition sets, excess models, magnetic contributions, electrostatic contribution, chemical ordering or other extra energy contributions; `CHANGE_PHASE_STATUS` command as to predefine phase status)
>> ❖ a condition (`IF/THEN`) on executing a certain type-definition.
> ➢ database information
> ➢ database version and release date

Additionally, the database files may contain comment lines (always beginning with a "`$`" mark) to explain specific portions, in either very simple or comprehensive details, for general users and database manager.

The thermodynamic functions, parameters, tables and references can be directly included in the database setup file or stored in separate sequential/random files (with arbitrary names with any extension). The names and paths for all sequential/random files must be properly defined in the setup file. Sometimes, an FTP file (a special function random access file) is used to store many functions with their record numbers if a database is too big; such an FTP file can usually dramatically speed up the data retrieving procedure.

The database contains the expressions relating the Gibbs energy of each phase to the temperature, pressure and constitution of the phase. The database can also be used to calculate metastable equilibria since the data can be extrapolated from regions where the involved phases are stable. As discussed earlier, it is possible to obtain the value of any thermodynamic property once the Gibbs energy function is known. Thus, equilibrium calculations for an entire system or local/partial subsystem, phase diagrams, property diagrams, *etc.,* are simply performed.

A Thermo-Calc database normally covers data that are available for temperatures above 298.15 K and up to a maximum 6000 K although the upper temperature limit is lower in many cases. The expression for the temperature-pressure dependence is basically a power series of *T* and *P*, but logarithms and (sometimes) exponential functions have also been used.

Most data for inorganic and metallurgical systems is assessed for the pressure of one bar, and the gas phase applies the *Ideal Gas Law* is assumed for pressure dependence. However, there are some available databases, which contain phases modelled with non-ideal pressure-dependent parameters, and both EOS for pure substances and interaction terms for solution phases are used. For examples, an aqueous solution phase modelled by the Complete Revised Helgeson-Kirkham-Flowers Model will have stored data on non-ideal pressure dependence data for pure solute species, which can be applied at pressures up to 5 kbar. Alloy/mineral phases modelled by the Murgnahan Model, Birch-Murgnahan Model and Generalized PVT Model will have data on molar volume, thermal expansion, compressibility and their derivatives with respect to temperature and pressure, which can describe the *P-V-T*

relations for various alloys/minerals over a very wide range of temperature (298.15 to 6000 K) and pressure (1 bar to 1000 kbar).

The compositional dependency of Gibbs energy of a solution phase is stored as interaction parameters assigned to certain interacting constituent combinations (binary, ternary or high-order), which might be further described as functions of temperature and pressure.

The Gibbs energy contributions from specific physical and chemical effects for some particular phases can be recorded in a database; such data can partially or entirely describe their Gibbs energy relations. For instance, magnetic ordering phases store the magnetic constants and Curie temperatures in the database; an aqueous solution phase caches the Born functions (to calculate the electrostatic contribution, Debye-Hückel Limiting Law term and ionic solvation) in the database.

As mentioned above, for some complex phases, the data stored in a database may not be sufficient to describe the Gibbs energy relation in either pure substance or solution phase states. These complicated parts of Gibbs energy contributions should be programmed as special subroutines into the Thermo-Calc GES system, or should be coded as a special data file that consists of all extensive expressions for the phase. This exception is especially true when the equilibrium state of a phase cannot be implicitly expressed by Gibbs energy, so that its implicit Helmholtz energy or Internal energy description has to be converted into Gibbs energy. Another common problem is when the classical thermodynamics cannot be applied to a phase under a certain circumstance, thus a suitable non-classical thermodynamic approach has to normally be coded inside the Thermo-Calc GES system directly. An excellent example for such extreme cases is the thermodynamic description of H_2O and aqueous solutions over a wide temperature-pressure-composition range (*e.g.,* modelled by whether the complete Revised Helgeson-Kirkham-Flowers Model or the Generalized Pitzer's Formalism).

Using the calls on the type-definition (AMEND_PHASE_DESCRIPTION) inside the database will bridge the stored data, special data files and/or extra program parts to handle the non-ideal characteristics of concerned phase. This is especially important whenever a Gibbs energy expression is more complicated than the ordinary temperature and composition dependence terms, and whenever such a difficult phase is involved and/or such a complicated model is considered.

3.2   Data Formats

As mentioned above, a general database, an application-oriented dataset and a problem-oriented data-file, whether provided by Thermo-Calc Software AB or created by a user, normally have the same Thermo-Calc Data Structure (or the so-called Thermo-Calc Database Format) regarding various definitions and Gibbs energy expressions. However, for the latter two types, it is unnecessary to store functions and parameters in sequential and random files, due to their limited sizes. For convenience, all of them will be referred as databases.

All available databases used inside the Thermo-Calc software system must have been built in the ***Thermo-Calc Database Format*** that is described in *Section 3.1*. Any other database (from any source) with a different data structure has to be converted to the Thermo-Calc Database Format. Some separate conversion programs are available for performing such data conversion. For example, the ACCESS program (Jacobs, 1996) can convert all the SGTE databases from one to another among various formats of Thermo-Calc, MTDATA and ChemSage (and MALT). The SKSCONV program (Sundman and Shi, 1992-2012) and AQSCONV program (Shi and Sundman, 1999-2012) can convert the GCE and AQS databases to the Thermo-Calc database format.

A database used inside Thermo-Calc will be first retrieved within the Database Module (TDB). The retrieved data, and some additional definitions or possible modifications, could be saved in several other formats of Thermo-Calc files. In the Gibbs Energy System Module (GES), such retrieved data or additions or modifications for an individual phase or an entire defined system may be optionally listed on screen or written into a single file with a structured format similar to the original database.

The Gibbs Energy System Module (GES), the Equilibrium Calculation Module (POLY) or the Optimization Module (PARROT) can save all such retrieved data, and some additional definitions or possible modifications, into the relevant GES5, POLY3 or PARROT workspaces. However, the data structure will be accordingly adjusted, and the data format will not be visible.

All these types of Thermo-Calc data formats will be extensively described and demonstrated in the corresponding chapters later on.

3.3   Data Assessment

Despite that a large quantity of data for thermochemical quantities and chemical equilibria has been determined experimentally, it may be difficult to find sufficient experimental information for solving a particular problem. This frustration is a consequence of that the limited experimental work can only cover a small fraction of all combinations. The missing data must therefore be estimated by some kind of extrapolation from the experimentally determined values. Such extrapolation requires high skill.

The Thermo-Calc database system has been designed to be useful for persons without the time or skill to make extrapolations from experimental data. This is achieved by applying the "***CALPHAD Method***" (Kaufman and Bernstein, 1970; Sunders and Miodownik, 1998; Sundman *et al.,* 2000; Sundman *et al.,* 2006; Lukas *et al.,* 2007), that is the experimental data available in the literature are assessed by experts using mathematical models founded upon physical bases. From these models many relationships can be derived between experimental data for various quantities and this makes it possible to put to effective use even scattered and incomplete experimental data. The results of such assessments are obtained as parameter values, which are stored in the database together with a description of the mathematical model. Not only do these parameters describe the experimental data used in the assessment but they can be also used for reliable interpolations and even extrapolations.

It therefore makes no difference whether a user asks for a value, which has been determined experimentally or not. The value calculated from the parameters stored in the database system is the best value available, according to the judgement of the assessor, provided it falls within the recommended range of validity of the assessment. From the models one may calculate many different quantities and their values are always mutually consistent.

Thermo-Calc also provides the user with a unique tool (the PARROT module) for critical assessment based upon varied experimental data such as EOS, phase equilibria, phase diagrams and so on. By means of this module the user can efficiently expand some databases or reliably create various datasets or databases for some specific materials and applications. The extended CALPHAD method has been implemented in the PARROT module that is available in both the Thermo-Calc and DICTRA packages (*Figure 4*).
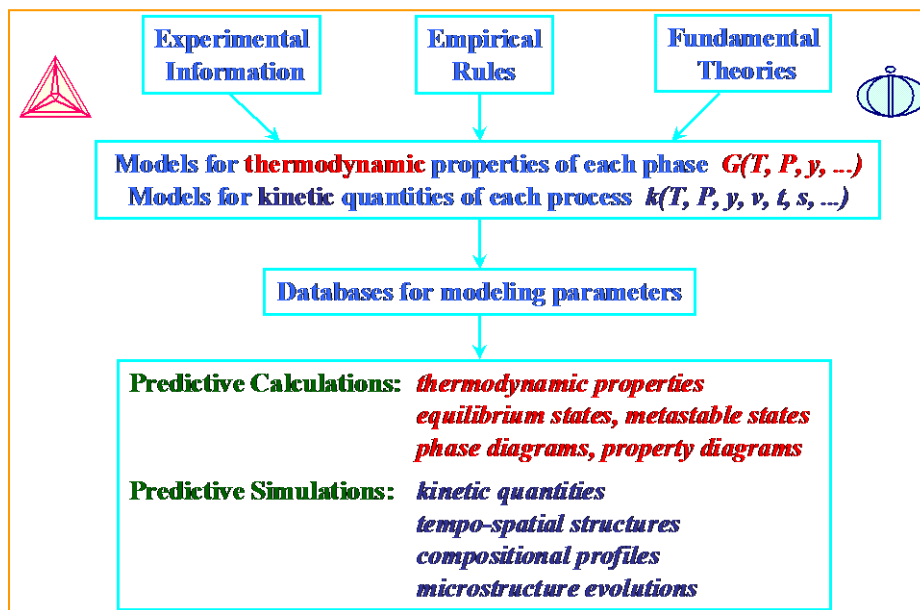

Figure 4.   Extended CALPHAD Method in the Thermo-Calc and DICTRA Packages.

3.4   Data Quality

Of course, the reliability of the calculations depends upon the efficiency of the models and the quality of the assessments. Thermo-Calc Software AB and its collaborators all over the world provide many general and specified databases in high quality for many applications (see *Thermo-Calc Database Description Forms* which are available at www.thermocalc.com/Databases.htm or www.thermocalc.com/TCDATA.htm). Devoted and on-going efforts will enlarge the scope of thermodynamic data in currently existing and future potential applications.

It is very important that the user fully understands and appreciates all the bases upon which the database is established. This comprehension includes the potential application systems and processes, as well as possible limitations on composition, temperature and pressure. Furthermore, some other factors may also have contributed to the quality of a specific database. These include the choices on efficient thermodynamic models for various phases, the tools used in parameter optimization procedure, the criteria of selecting reliable experimental and literature information, the experience and skill levels of the individuals in the assessments, *etc*. It is equally important to be aware that no database can be used universally for all kinds of applications; a so-called "general" database will only be possible to a rather wide but limited systems and processes. A specified database (whether application-oriented dataset or problem-oriented data-file) will usually have a limited application range (of materials type, composition, temperature or pressure). A database with good quality might be possible to interpolate or extrapolate the data reasonably well to the ranges where there is little or no experimental information.

With the unique and powerful optimization module PARROT included in the Thermo-Calc software system, users are encouraged to generate highly professional standard data of their own, through critical assessments based on various sound, experimental investigations and reliable, literature information.

The most successful and beneficial developments in such applications are the TCFE (specialized for steels and Fe-alloys) and the SGTE databases (general for pure elements, inorganic and metallurgic substances and solution phases). These high quality databases have been continuously updated by many international collaborations between expert researchers with high assessment skills.

A general database (such as the SGTE PURE/SSUB/SSOL databases) is designed to contain many elements, varied types of phases, and cover different materials as many as possible (Ansara and Sundman, 1986; Dinsdale, 1991). Consequently, it may be applied to simulate many systems and processes. On the other hand, it may need some additional data to achieve more accurate calculated results for some particular subsystems. More specified databases (such as TCFE, TCNI, TCAL, TCMG, TCNF, TTNI/TTTI/TTTA/TTAL/TTMG/TTZR, TCSLD/NSLD/USLD, SLAG, SALT, ION/TCOX, TCSC, TCFC, STBC, NUCLEA/MEHPISTA/NUOX/SNUX, SEMC, among others) are oriented to particular applications or problems, which have limitations regarding composition, temperature or pressure.

In a Thermo-Calc database, such limitations could be stored as special records in appropriate portions. For instance, the temperature limits is always set for a Gibbs energy expression. The compositional ranges are stored in some databases. The Database Information and Reference sections in any of the Thermo-Calc databases may also contain some descriptions on the application limitations. Within some databases (such as the SGTE SSUB/SSOL databases) some quality designation codes for classifying the quality level are stored. The Thermo-Calc software/database system can, in some cases, promptly indicate if the calculation has gone outside the proper application ranges.

3.5   Data Sources

Along with the Thermo-Calc software system, various critically assessed thermodynamic databases using certain thermodynamic models are usually provided for various applications. Examples include the SGTE SSUB/SSOL general databases for substances and solutions in inorganic and metallurgic systems, TCS TCFE/TCNI/TCAL/ TCMG/TCSLD specialized databases for steels and alloys, TCAQ/AQS database for aqueous solution systems, *etc*. The SGTE database is a general thermodynamic database which describes the thermochemical properties of substances and phases with variable composition for temperatures from 298.15 K up to those where only the gaseous state is stable. In the *Thermo-Calc Console Mode User's Guide* (*Chapter 5 – Database Module TDB*) and *Thermo-Calc Database Description Forms* (that are available at our web site www.thermocalc.com), more detailed description will be given on various available databases, and how they are used and managed in the Thermo-Calc package.

Within the Thermo-Calc package, databases from many sources (such as SGTE, ThermoTech, TGG, NPL, NIST, USTB, *etc*.) can use different models for each phase in a system. Such databases cover a wide spectrum of materials ranging from steels, alloys, ceramics, slag, melts, semi-/super-conductors, solders, hard materials, nuclear materials, gas/fluids, aqueous solutions, organic substances, to geochemical and environmental systems, which can be applied to research and development in both industrial engineering and natural systems. For more details on various available databases, please see *Thermo-Calc Database Description Forms* (that are available at www.thermocalc.com/Databases.htm or www.thermocalc.com/TCDATA.htm).

For many years, TCS has been actively devoted to developments of more application-oriented databases of various industrial interests. Our R&D partners, such as the Thermo-Calc Group at KTH-MSE, have also initiated and participated in many international projects in order to create general and validated databases.

There are also many users in various academic societies and industrial companies all over the world who have been establishing their own databases or datasets with assistance from the Thermo-Calc package.

3.6   Data Encryption

All commercial databases are distributed in an encrypted format in order to avoid illegal copying, while for all free databases the unencrypted format is still used. Such an encrypted database can be used only together with a specific database license key that is obtained from TCS or its agent.

An encrypted database always consists of binary data files with extension `*.TDC` (both for Thermo-Calc thermodynamic databases and for DICTRA mobility databases), while an unencrypted database may contain various types of textual data files (unblocked, blocked or sorted) with different extensions (*e.g.,* `*.TDB`, `*.DAT`, `*.REF.`, *etc*.).

An `*.TDC` data file cannot be viewed or edited by any editor, and is only usable inside the Thermo-Calc, DICTRA and TC-PRISMA software, as well as in the TQ/TCAPI programming interfaces and TC-MATLAB Toolbox, with an appropriate database key file, which is solely made by TCS for a specific computer/server based on the unique identification number(s) obtained from the end-user(s).

A blocked or sorted data file (*e.g.,* `*.TDB`, `*.DAT`, `*.REF`, *etc*.) can be viewed by a simple textual editor, but a user should never try to edit it due to its restricted structure (otherwise, it can not be used by the Thermo-Calc, DICTRA and TC-PRISMA software anymore). An unblocked data file can be viewed and edited with a great carefulness by a simple textual editor. A user-specified database is normally built as unblocked data file(s).

The database files are occasionally CPU-dependent, implying the files for UNIX/Linux system and for MS-Windows are incompatible, due to different data structures. A standard routine for automatically converting database files has been implemented, making it possible to read database files from both systems. The routine gives a warning message if conversion is necessary.

The retrieval of thermodynamic data in the TDB module, and the storage of data in the `GES5` and `POLY3` workspaces, from such encrypted databases remain the same as for unencrypted ones. But thermodynamic parameters and related functions retrieved from an encrypted commercial database, for any defined system or any phase in the system, cannot be shown/listed up on screen or into textual files (`*.TDB` or `*.DAT`) in the GES module, while the definitions of phase constitutions can be shown by using appropriate TDB and GES commands. Detailed references for original data assessments for a defined system retrieved from an encrypted database can also be listed out in the GES module.

4 Thermo-Calc User Interface and Modules

The Thermo-Calc software system has several levels of user interfaces and programming interfaces, and has a well-defined modular structure.

Continuous improvements on user-friendly features have been the top priority in the R&D strategies of the Thermo-Calc, DICTRA and TC-PRISMA software/database/programming-interface package. Thanks not only to the fast development of hardware and software environments, but also the constructive and stimulating suggestions from many Thermo-Calc/DICTRA/TC-PRISMA users, TCS has greatly improved user interfaces of our various products.

Keeping in mind that a good user interface must bring benefits to users by enhancing their efficiency of using the software/database/programming-interface package in various applications, the improvement of the Thermo-Calc user interface has been focused on five levels, as summarized in *Table 4*.

Table 4.   Different Levels of the Improvement of the Thermo-Calc User Interface

Levels	*Purposes*	*Availability*
1) Command-Line User Interface	Provide the users with a textual command line interface.	Thermo-Calc Console Mode
2) Modular Interface	Provide the users with simple inputs (only answers to few questions) to perform certain calculations like solidification simulations.	Thermo-Calc Console Mode
3) Graphical User Interface	Provide a graphical user interface in various OS environments.	Thermo-Calc Graphical Mode *and (partially)* Thermo-Calc Console Mode
4) User Programming Interface	Provide programmers with the possibility to include the Thermo-Calc Engine into their own application programs.	TQ, TCAPI
5) Software Toolbox Interface	Provide the Thermo-Calc Engine as a merged toolbox in some third-party software packages (such as MATLAB®, Fluent® and Phoenix®).	TC-MATLAB Toolbox

The first two levels of the user interface are borne within the Thermo-Calc (Console Mode) and DICTRA software. This chapter primarily describes the current situation of the command-line user interface, modular structure and graphical interaction (*i.e.,* partially on the third level) within the Thermo-Calc (Console Mode) and DICTRA software. Detailed information on the command-line user interface and on some special modules are given in the *Chapters 2 and 10* of the ***Thermo-Calc Console Mode User's Guide***.

The third level is found in the ***Thermo-Calc (Graphical Mode) User's Guide***, the fourth level is described in the ***TQ Programmer's Guide and Examples*** and ***TCAPI Programmer's Guide and Examples***, and the fifth level (within the integrated software package MATLAB) is subject to ***TC-MATLAB Toolbox Programmer's Guide and Examples***. Meanwhile, some basic information on these three levels will be briefly given in the following sections of this document.

4.1 Thermo-Calc (Console Mode) User Interface

The Thermo-Calc (Console Mode) software (and its previous versions TCC) is an interactive system controlled by giving textual commands from a menu; so does the DICTRA software.

Great efforts are continuously being made to improve the user-friendliness of the system's user interface, by using the following design rules:

- *Complicated actions have been split up into several independent commands.*

- *Commands are often a full sentence to make them easily understood.*

- *The amount of typing required by the user has been minimized by allowing abbreviations and providing default values to questions.*

- *The informative output has been kept to a minimum in order to allow for slow terminals and low-speed connections.*

- *Extended informative output or help is available in all situations whenever the user simply types a question mark "?".*

- *A calculation can be saved and resumed at some later time.*

- *MACRO files, which make records of all kinds of on-line commands, can be directly used for later calculations on the same system or similar systems with slightly different conditions.*

- *Some special, easy-to-use modules for automatically calculating and plotting certain types of phase or property diagrams (e.g., binary, ternary, potential, Pourbaix, etc.) or simulating materials processes (e.g., Scheil-Gulliver solidification) are available. In such modules, a user just needs to answer some simple questions, and the program automatically handles all the necessary steps for the calculation and post-processing.*

By following these guidelines on improving the command-line user interface, it has been possible to construct a system which is easy to learn but not cumbersome to use, even for a beginner. However, it must be understood that a software/database system to be used for calculations cannot be constructed in the same way as a retrieval system for bibliographic data. The user must know how to define his problem within the framework of the software/database system.

Figure 5 gives an example of the menu-driven user interface of the Thermo-Calc (Console Mode).

For various kinds of details on how the menu-driven user interface of the Thermo-Calc (Console Mode) works, please refer to *Section 2.4.1* of the ***Thermo-Calc Console Mode User's Guide***.
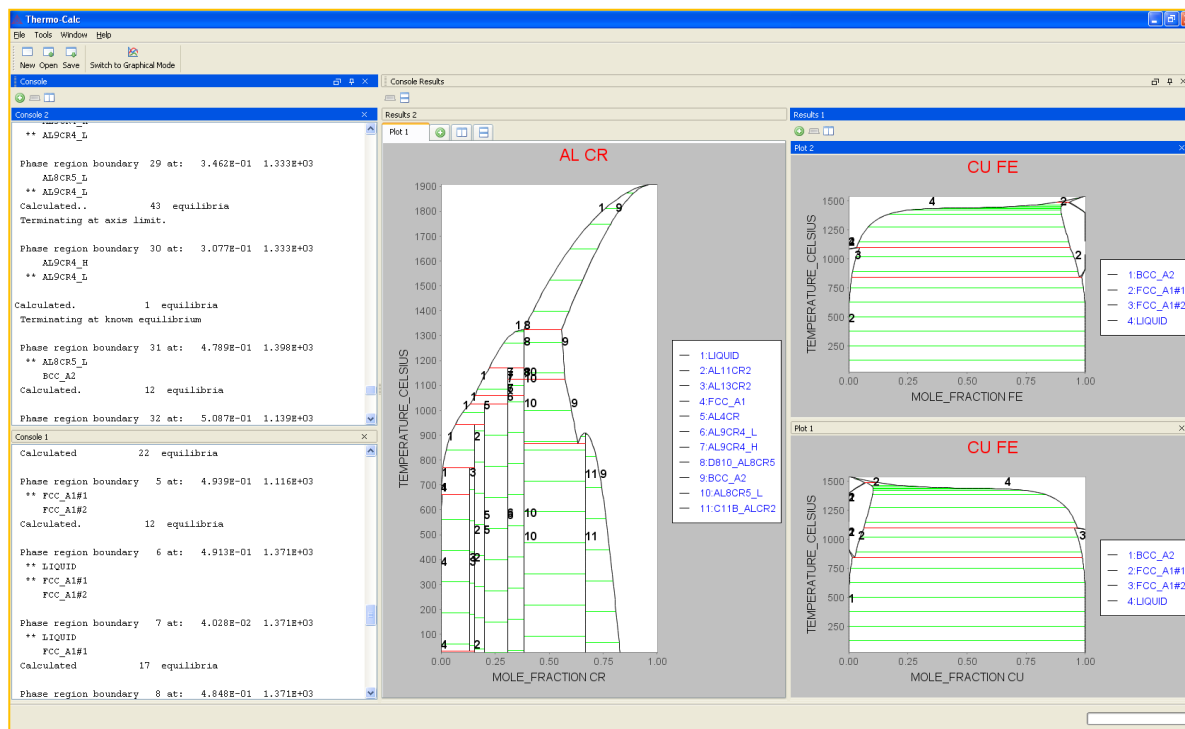

Figure 5. Menu-Driven Command-Line User Interface in the Thermo-Calc (Console Mode)

4.2   Modules in Thermo-Calc (Console Mode)

The basic and special modules in the menu-driven Thermo-Calc (Console Mode) software (and its previous versions TCC – Thermo-Calc Classic) are summarized in the *Table 5*.

Table 5.   Modules and Application Programming Interfaces of the Thermo-Calc Package

Level	*Abbr. Name*	*Full Name*	*Primary Functions*
Basic Module	SYS	SYSTEM_UTILITIES	General system utilities for working environmental settings and MACRO creation and opening
	TDB	DATABASE_RETRIEVAL	Database selection/combination, system definition, and data retrieval
	GES	GIBBS_ENERGY_SYSTEM	Handling of thermodynamic models and thermodynamic quantities
	TAB	TABULATION	Tabulation of thermodynamic properties for substances and reactions
	POLY	POLY	Calculations of complex heterogeneous equilibrium, metastable, local/partial equilibrium states (for single points, one-dimensional stepping and two-dimensional mapping)
	POST	POST_PROCESSOR	Post processing of all kinds of calculation results and comparison with experimental data
	PARROT	PARROT	Assessment of experimental data, and establishment of thermodynamic data
	ED-EXP	EDIT_EXPERIMENTS	Edit and pre-treatment of experimental data for optimization
Special Module	BIN	BINARY_DIAGRAM	Automatic calculation and plotting of binary phase diagram
	TERN	TERNARY_DIAGRAM	Automatic calculation and plotting of ternary phase diagram
	POT	POTENTIAL_DIAGRAM	Automatic calculation and plotting of gas potential diagram in a ternary system
	SCHEIL	SCHEIL_SIMULATION	Automatic simulation and plotting of solidification profile and property diagrams, based on the modified Scheil-Gulliver model; since TCCQ/TCW3, it also allows more than one interstitial species with back diffusion
	POURBAIX	POURBAIX_DIAGRAM	Automatic calculation and plotting of Pourbaix diagram and property diagrams for aqueous-bearing interaction systems
	REACTOR	REACTOR	Simulation of chemical reactions in not only steady-state reactors but also dynamic reactors that change with time (for example decarbrization of liquid steel)
API	TQ	TQ	User programming interface (in FORTRAN) for application-oriented programming (under Windows Vista/XP/2000/NT4, Linux and UNIX)
	TCAPI	TCAPI	User programming interface (in FORTRAN, C/C++/VC, VB, Delphi, Java or any other modern programming language) for application-oriented programming (under Windows and Linux).
	TC Toolbox	TC-MATLAB Toolbox	User programming interface (in the MATLAB® specified language/environment) for application-oriented programming (under Windows)

The Thermo-Calc (Graphical Mode) software (and its previous versions TCW – Thermo-Calc Windows) has a GUI-driven user interface, while some of the Thermo-Calc basic and special modules (*e.g.,* TDB, GES, POLY, BIN, TERN, SCHEIL, POST) have also been implemented into the Graphical Mode, in an implicit way that certain Thermo-Calc basic/special modules are connected with specific sequential graphical windows (modules)

for various definitions in calculations/simulations. For the details of Thermo-Calc (Graphical Model) sequential graphical-window/module structure, please refer to the *Thermo-Calc (Graphical Mode) User's Guide*.

The Thermo-Calc application programming interfaces, which are not normally regarded as modules, are also listed in the *Table 5,* for the reasons that: (1) such a programming interface uses a structured routine that is linked with various special (and even special) modules for system initialisations, system definitions, data manipulations, condition settings, calculation performances and result treatments; and (2) through such a programming interface one can build up some other special modules (which are similar to the existing special modules) for certain types of calculations/simulations.

Note that since TCCR, the FOP Module (`FUNC_OPT_PLOT`, the simple function optimizer and plotting facility; for function/parameter mathematic-fitting and plotting) has been completely eliminated from the Thermo-Calc (Console Mode) software. One should instead use the PARROT module to perform critical thermodynamic assessments.

Within the Thermo-Calc software, all modules share a global data area with thermodynamic data, and internally connect with each other.

Figure 6 illustrates the interactions between a user and various modules of the Thermo-Calc package.

For all kinds of details on various basic and special modules inside the Thermo-Calc (Console Mode), please refer to *Section 2.4.2* and various chapters of the ***Thermo-Calc Console Mode User's Guide***.
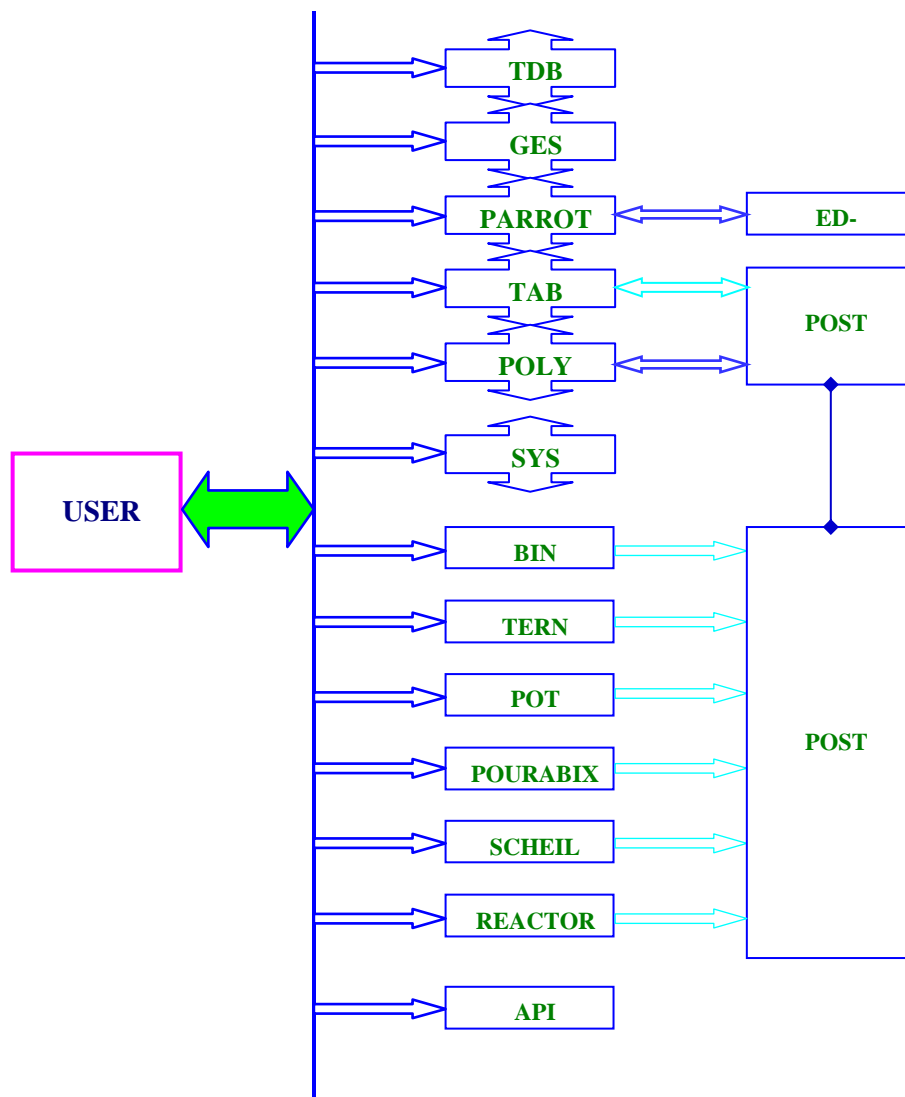

Figure 6.   Interaction between the User and Modules of the Thermo-Calc (Console Mode)

4.3   Graphical User Interface of Thermo-Calc

The Thermo-Calc (Console Mode) software (like its previous version TCC) has an extremely high flexibility, which gives great functionality but (in some senses) is also quite difficult to learn. Remember all commands and getting the most out of the program requires daily uses. For those experienced users, Thermo-Calc (Console Mode) is still highly recommended.

However, continuous developments have been made to improve the graphical user interfaces and application programming interfaces of the Thermo-Calc package, in addition to its ordinary menu-driven command-line user interface. These advances include the much easier graphical user interfaces [*i.e.,* Thermo-Calc (Graphical Mode) software (like its previous version TCW)], the application programming interfaces [*i.e.,* TQ and TCAPI] and the third-party software toolboxes [*e.g.,* TC-MATLAB Toolbox], as described in this section and next part. All these interfaces are connected with a very powerful thermochemical engine (*i.e.,* Thermo-Calc Engine). These developments premise simplified routine but precise methods in materials property calculations and materials process simulations.

### 4.3.1   Thermo-Calc Graphical Mode, the Complete GUI-driven Thermo-Calc

Thermo-Calc 3.0 *Graphical Mode*d has been united with TCC which becomes the ***Thermo-Calc Console Mode***. Beginners find the Thermo-Calc Graphical Mode program very straightforward to use *(Figure 7).* Advanced calculations of complex phase equilibria, phase diagrams and property diagrams in multicomponent systems can be performed, by just clicking on buttons and menus with the mouse without needing to remember the Thermo-Calc Console Mode commands!

4.3.2   Thermo-Calc Graphs in 3D

Since TCCP, it has made possible to view Thermo-Calc diagrams in 3-dimensions with high-quality, through a VRML (Virtual Reality Modelling Language) viewer such as plug-ins to web browsers or standalone programs. Such viewers include the ***Cortona VRML Client*** (which is developed by ParallelGraphics, and downloadable from www.parallelgraphics.com), the ***SIM VRMLView*** (which is developed by SIM - Systems in Motion, and downloadable from www.sim.no) and alternative viewers listed at the VRLM Repository at www.web3d.org (Wed3D Consortium). In some browsers, it is needed to set correct background colour or to turn on the so-called Headlight for best viewing. The headlight always shines directly on the 3D diagram.

This new feature is suitable for presentation of diagrams such as ternary phase diagrams represented by two compositional axis and a third Z-axis for temperature. In such cases, the diagram can be plotted as a triangular diagram or a square diagram. It can also be used for presentation quaternary diagrams where the temperature and pressure has been fixed and lines in the compositional space are drawn. In such cases, the diagram should be plotted as tetrahedron diagram with all three axes set to compositional variables.

For this particular purpose, a new POST command (CREATE_3D_PLOTFILE) has been added, which can automatically convert all the default/predefined graphical definition information and selected data points (expressed and stored in specific tables or *.TAB files, which are taken from the current and/or previous MAP/STEP calculations) into an appropriate format and create an *.WRL (Virtual Reality Modelling Language) file for viewing 3D diagrams by a VRML viewer. *Figure 8* shows an example on how two Thermo-Calc diagrams are viewed in 3D by the two aforementioned VRML web browsers. For more information, please refer to *Section 9.7* in the *Thermo-Calc Console Mode User's Guide*.
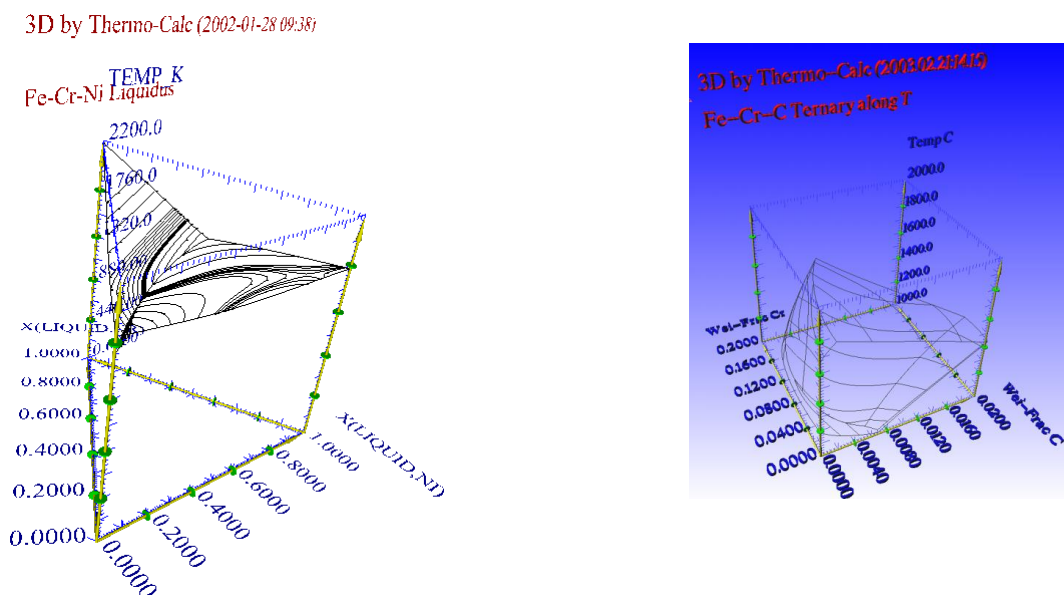
Figure 8.   **Thermo-Calc Graphs in 3D Viewed by two VRML Web Browsers (Cortona VRML Client and SIM VRMLView, respectively).**

5   Thermo-Calc Programming Interfaces

The increased requirements on the general user interface and application programming interface have inspired the development of thermochemical engines in the past several years. Thanks to the powerful, efficient and flexible Thermo-Calc software/database system, many Thermo-Calc users have also been using it as an engine in various application-oriented programs and third-party software packages. With such a combination, one can significantly extend the applications of the Thermo-Calc package to materials property calculations, materials process simulations and even materials engineering controls.

5.1   Thermo-Calc as an Engine

The Thermo-Calc Engine (with DICTRA extensions) is fuelled with all the important functionality of various modules (*Figure* 9). It can be connected to a User's own programs via the application programming interface (TQ and TCAPI), or with third-party software packages (such as MATLAB®) via the thermochemical calculation toolbox (TC-MATLAB Toolbox).

The most successful example of using the Thermo-Calc Engine in materials process simulations is the DICTRA software/database system. Thermo-Calc Engine conducts all kinds of thermodynamic calculations regarding local and partial equilibria, and DICTRA simulates complex diffusion-controlled kinetic processes (*Figure 10*).

The TC-MATLAB Toolbox implemented in the well-known software package MATLAB® is another good example of utilizing the Thermo-Calc Engine. With this toolbox, users can explore the Thermo-Calc applications in many research and development fields.

More sophisticated development of a comprehensive Materials Interface using both the Thermo-Calc and DICTRA software as thermodynamic and kinetic engines may be made available in the future, for materials property calculations, materials process simulations, materials production optimizations and materials utility controls.
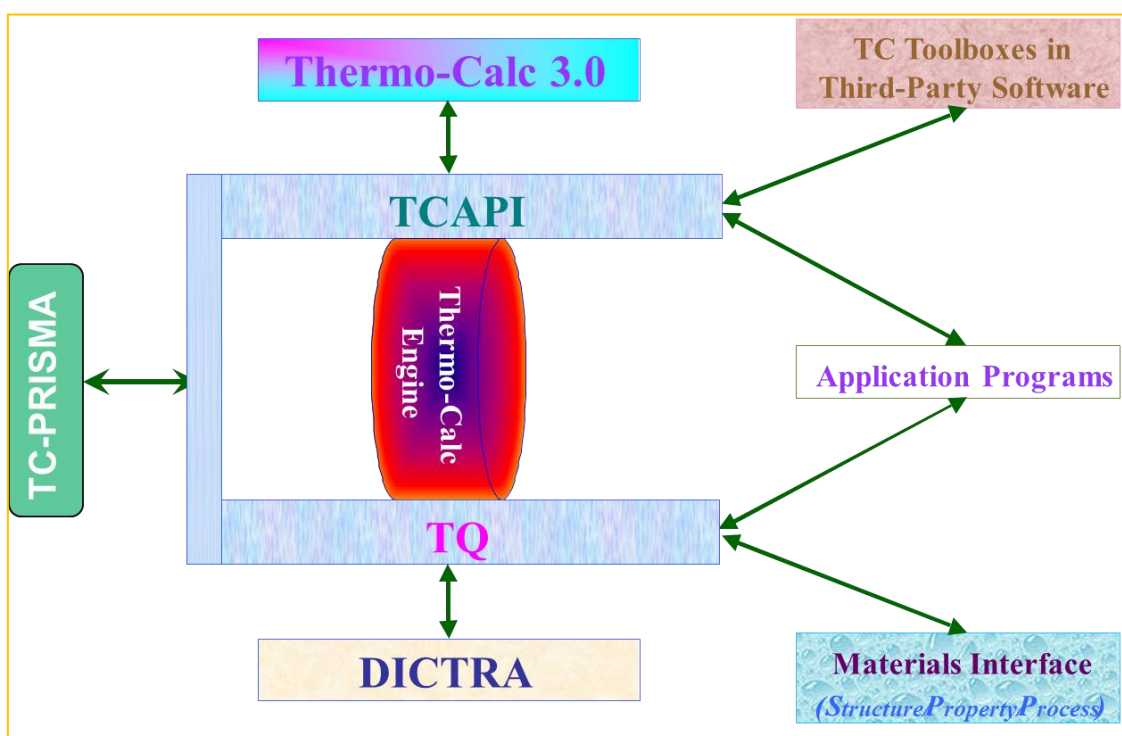

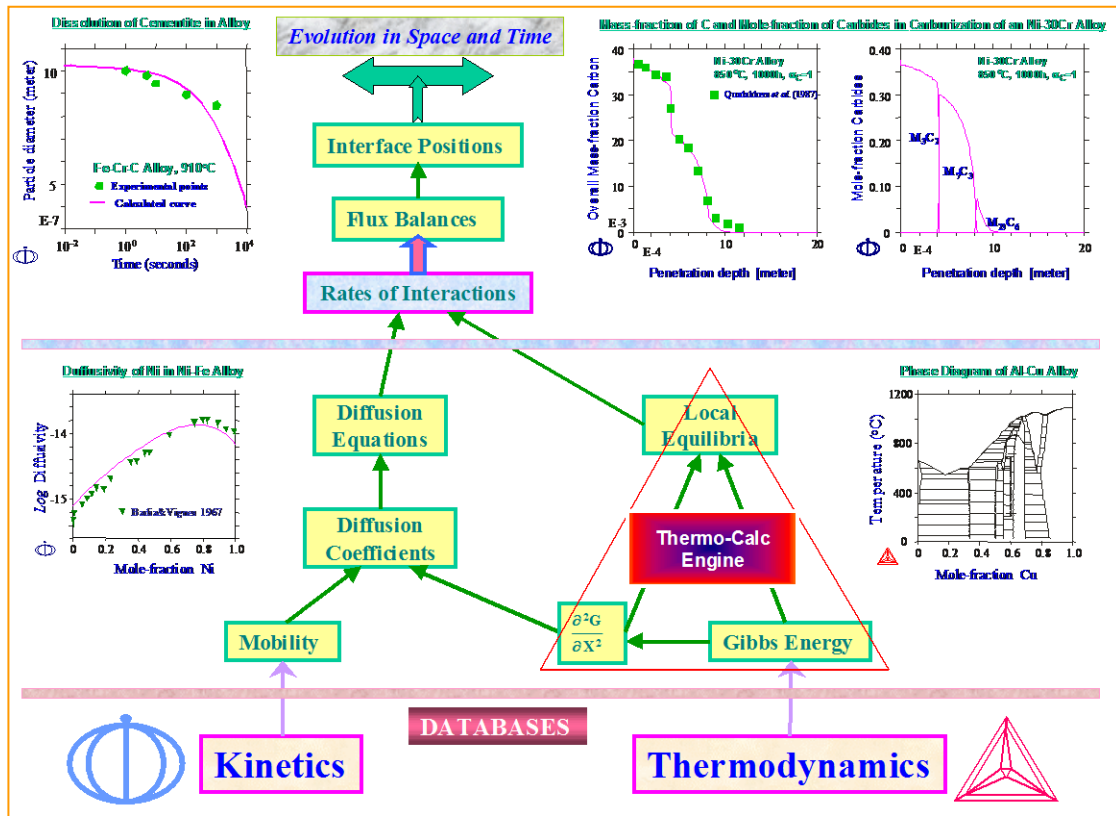**Figure 9.   Programming and Graphical Interfaces of the Thermo-Calc Engine**

Figure 10.   Thermo-Calc Coupled with DICTRA for Diffusion Simulations

5.2 Thermo-Calc Application Programming Interfaces: TQ & TCAPI

The TQ and TCAPI are two independent versions of the Thermo-Calc application program interface. They are intended for application programmers to write applications using the Thermo-Calc Engine as a kernel without needing to appreciate its complexity or follow its continuous improvements and modifications.

With this interface, it is easy to make the Thermo-Calc Engine an integral part of an application program such as for processing simulation or microstructure evolution modelling where thermodynamic or phase equilibrium data are needed. The thermodynamic properties and phase equilibrium data which could be obtained by using the TQ and TCAPI programming interfaces (as well as the TC-MATLAB Toolbox) include: temperature, pressure, volume, thermo-chemical properties (*e.g., G, H, S, U, C_p*; *ΔG, ΔH, ΔS, ΔU, C_p*; and so forth), derivatives of state functions (*e.g.,* $\dfrac{\partial G_m^\theta}{\partial x_i}$, $\dfrac{\partial^2 G_m^\theta}{\partial x_i \partial x_j}$), chemical potential, phase amount, phase composition, partition coefficients, liquidus or solidus points, invariant temperature, heat of reaction, adiabatic combustion temperature, driving forces, diffusion coefficients, thermodynamic limits for partitionless transformations and transformations under paraequilibrium and quasi-paraequilibrium conditions, among many others.

The development strategy of the Thermo-Calc application programming interface is as follows. It should provide the Thermo-Calc users with the possibility to write their own applications with an already existing user interface or similar interface as of the Thermo-Calc software system.

Therefore, the Thermo-Calc application program interface has been designed as two categories *(Figure 7)*:

- ⋗ TQ is written in FORTRAN, for applications (coded in FORTRAN) under almost all available CPU environments, *e.g.,* MS-Windows, PC Linux.

⋗   TCAPI is written in both FORTRAN and C/C++, for applications (coded in FORTRAN, C/C++/VC, VB, Delphi, Java or any other modern programming language) under MS-Windows and Linux environments.

⋗

For the more details and examples of using the TQ and TCAPI, please refer to the ***TQ and TCAPI Manuals***.

A very simple example of source code for calculating the T_0-temperature using the TQ interface is demonstrated below:

```
C ... A number of lines initialising the program
C ... Do the calculation from minimum carbon content (Xmin) to maximum carbon
C       content (Xmax) with the increment dX
C
        Do 2000, XC=Xmin,Xmax,dX
          Tmax=Tmax0
          Tmin=Tmin0
          T=(Tmax0+Tmin0)*0.5
          P=101325
          N=1.0
          its=0
C Suspend both phases
        call tqcsp(iph1,'SUSPENDED',0,iwsg)
        call tqcsp(iph2,'SUSPENDED',0,iwsg)
C Set conditions for temperature (T), pressure (P), System size (N)
C   and Composition (X)
        call tqsetc('P',-1,-1  ,P ,numcon,iwsg)
        call tqsetc('T',-1,-1  ,T ,numcon,iwsg)
        call tqsetc('N',-1,-1  ,N ,numcon,iwsg)
        call tqsetc('X',-1,icmp,XC,numcon,iwsg)

 100    continue
        its=its+1
        call tqsetc('T',-1,-1  ,T ,numcon,iwsg)

C Calculate the Gibbs free energy for the two phases and store them in gm1 and gm2.
          call tqcsp(iph1,'ENTERED',1,iwsg)
          call tqcsp(iph2,'SUSPENDED',0,iwsg)
          call tqce(' ',0,0,0.0,iwsg)
          gm1 = tqggm(iph1,iwsg)
C
          call tqcsp(iph1,'SUSPENDED',0,iwsg)
          call tqcsp(iph2,'ENTERED',1,iwsg)
          call tqce(' ',0,0,0.0,iwsg)
          gm2 = tqggm(iph2,iwsg)
C Calculate the relative difference between gm1 and gm2.
C If it is small enough the temperature is approximately the T0-temperature
          gmd=(gm1-gm2)/gm1
          if (abs(gmd).le.eps) goto 200
C We did not find the solution, adjust the temperature and do one more iteration.
          if (gmd.lt.0) then
             Tmin=T
             T=(T+Tmax)*0.5
          endif
          if (gmd.gt.0) then
             Tmax=T
             T=(T+Tmin)*0.5
          endif
          goto 100
200     continue
C
C We have found the solution for this composition.
C Write out composition, T0-temperature and number of iterations.
        write(*,*)' X(C),T,its ',XC,T,its
C
2000 continue
      end
```
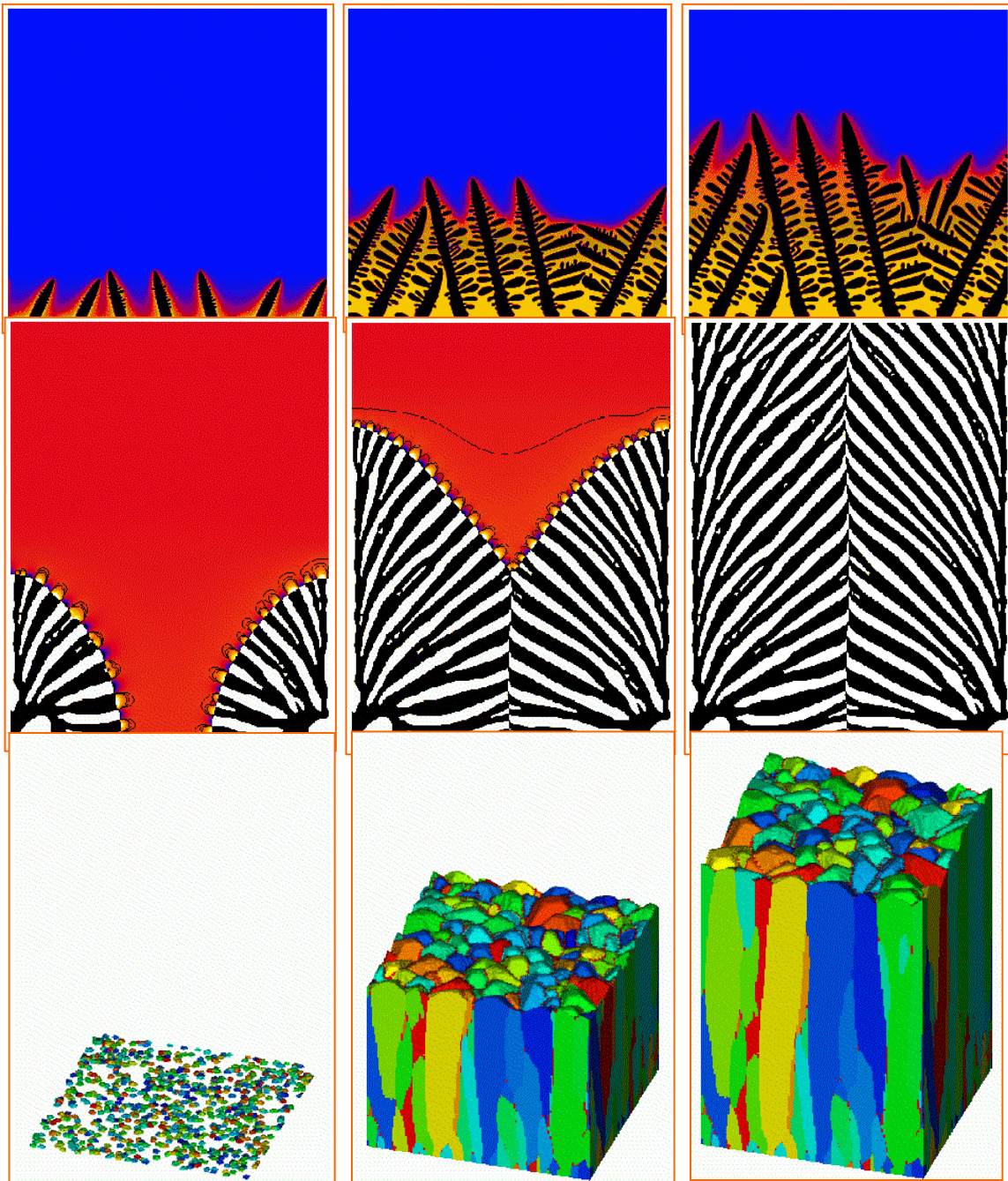
A very much advanced application example using the TQ programming interface (with some DICTRA extensions) is the **MICRESS™** software, a sophisticated computer program developed by our collaboration partner *ACCESS e.V.,* Germany. Several application results are illustrated in *Figure 11*.

Figure 11.   An Advanced Example of Using the TQ Interface: MICRESS

MICRESS, a 2 and 3D phase-field software, is now being launched by our German partner ACCESS e.V. This software has been developed for simulation of microstructure evolution during phase transformations and especially the effect of different microstructures on the phase transformation kinetics can be investigated. Applications such as solidification, solid-state transformations, grain growth and recrystallization can be studied. It has been linked to Thermo-Calc using the latest version of TQ, and thus any thermodynamic or kinetic information as available in Thermo-Calc and/or DICTRA can basically be incorporated into this application software. The TQ interface provides MICRESS with a reliable basis for treating complex thermodynamic and kinetic behaviours in multicomponent alloys. For more information, please visit www.access.rwth-aachen.de.

The TCAPI (Thermo-Calc Application Programming Interface) is a general programming interface for integrating thermodynamics into user applications in MS-Windows and Linux environments. Thermo-Calc Graphical Mode (and its previous versions TCW) and TC-Toolbox are based on this application programming interface.

TCAPI is similar in functionality as compared with the TQ interface. However, it does differ in some important aspects.

- The TCAPI is written in C/C++ and is therefore suited for interfacing with most other programming languages than FORTRAN.
- The TCAPI includes some functionality of the Thermo-Calc software which is not yet available in the TQ interface. It offers access to most of the used commands in the TDB, POLY and POST modules and some important commands in the GES module.

Using TCAPI, it is easy to build tailor made windows applications containing advanced thermodynamic calculation. *Figure 12* gives a simple example of using the TCAPI interface.
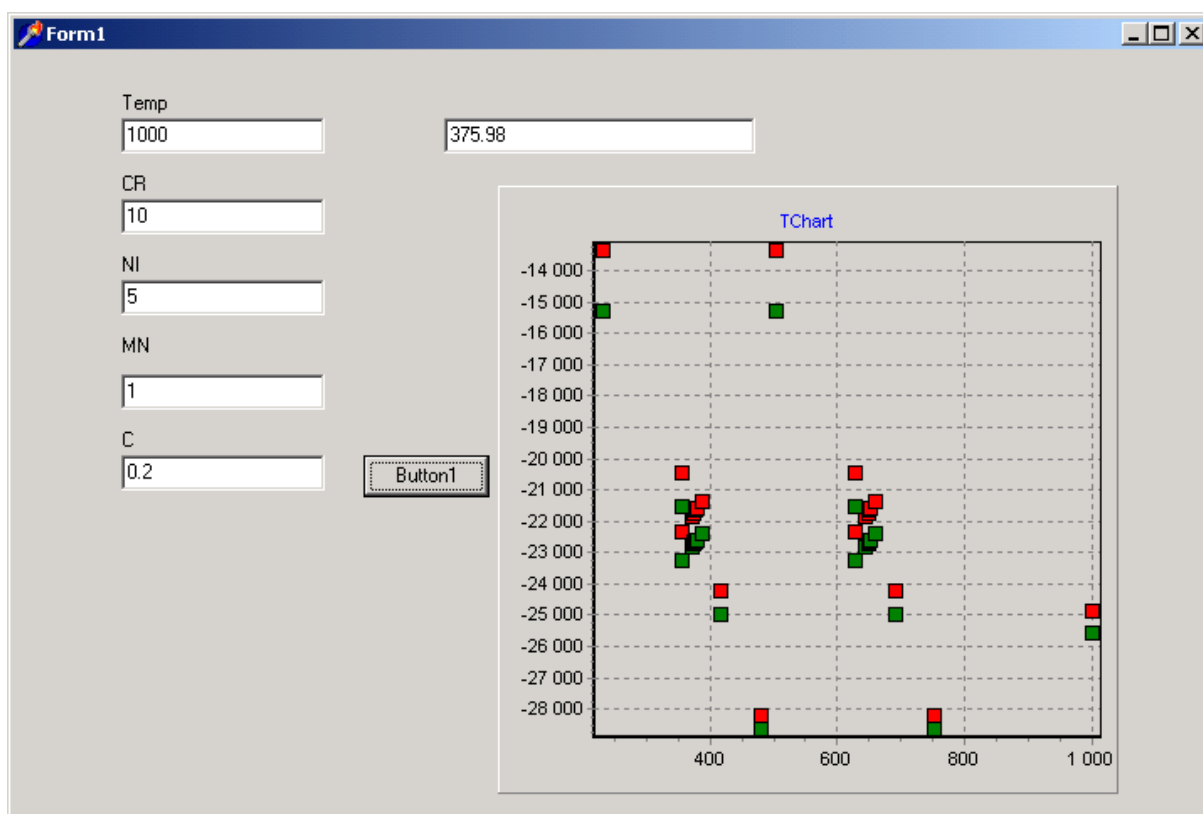
Figure 12.   A Simple Example of Using the TCAPI Interface

Another but very much advanced application example using the TCAPI interface (with some DICTRA extensions) is the **PrecipiCalc™** software, a sophisticated computer program developed by our collaboration partner *QuesTek Innovations LLC*, USA. Two application results are illustrated in *Figure 13*.
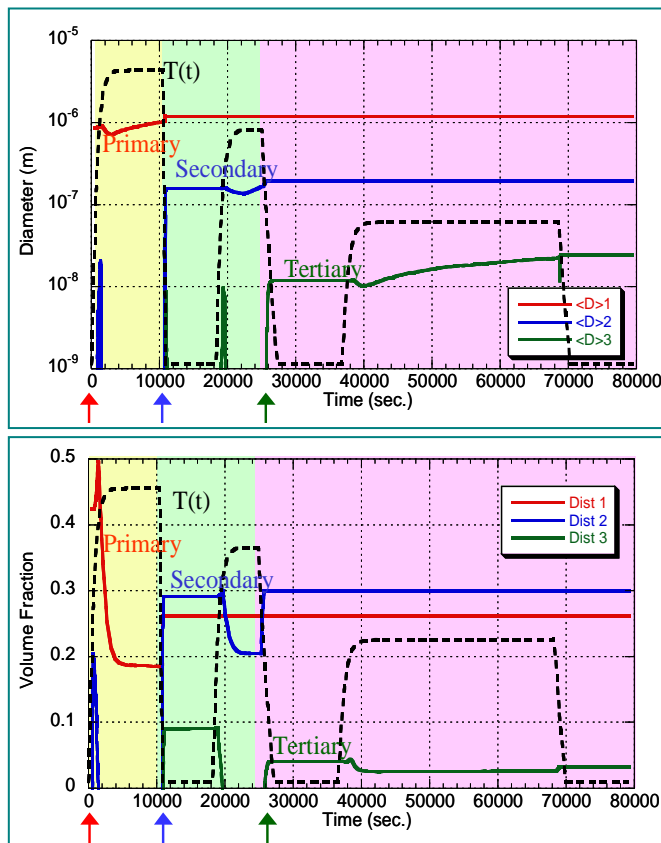
The two plots shown here illustrate an example of *PrecipiCalc* γ' precipitation calculations for an aeroturbine disk Ni-based superalloy, IN100, under a complex commercial heat treatment. Three distinct γ' particle size distributions within a range of size scales (10nm to 1μm) are observed experimentally and validated in this calculation. Integrating the *PrecipiCalc* calculations with a FEM heat transfer simulation and a mechanistic strength model allows the spatial microstructure/property variation in the disk to be determined. This evaluates uncertainly and variation of the alloy properties within the disk, a valuable tool in accelerating the qualification of the alloy in this critical application. Such complex calculations would be significantly more difficult without access to underlying thermochemical and kinetic quantities that the TCAPI provides.

Figure 13.   An Advanced Example of Using the TCAPI Interface: PrecipiCalc Software

PrecipiCalc software is for calculating the 3D multiparticle diffusive precipitation kinetics of multiple phases. It adopts multicomponent thermodynamics and diffusion based on the CALPHAD approach, through the incorporation of TCAPI. This allows realistic and mechanistic modelling of nucleation, growth, and coarsening without resorting to *ad hoc* treatments. The incorporation of TCAPI allows access to the thermodynamic and kinetic quantities of complex alloys boosting the numerical efficiency and accuracy of the software.

The primary input of *PrecipiCalc* software includes:
- **Physical quantities such as material compositions, bulk thermodynamics and mobility (TDB files), interfacial properties (e.g., surface energy), lattice properties (e.g., molar volume);**
- **Thermal cycle, or temperature profile, which defines the thermal history of the material being processed. The thermal cycle can be constant (isothermal), linear cooling (quench), or as complicated as nonlinear and non-monotonic heat treatment (such as multi-step tempering).**

The output of *PrecipiCalc* software includes the time evolution of
- **Precipitate microstructure — precipitate size distribution, number density and fraction;**
- **Compositions of matrix and precipitate;**
- **Driving forces, nucleation rates, and critical radii.**

***PrecipiCalc* has been successfully applied to the design and process optimization of a wide range of metallic systems, including γ' and carbide/boride precipitation in Ni-based superalloys, carbide/nitride/intermetallic precipitation during welding and heat treating in steels, FCC devitrification in amorphous Al-based metals, and Heusler phase in NiTi-based shape memory alloys.**

For more information about the *PrecipiCalc* software and applications, please contact Dr. Herng-Jeng Jou, hjjou@questek.com.

Furthermore, the **PrecipiCalc**™ software has been merged into yet another new software named **TC-PRISMA**®™, which has been developed under a close collaboration between our ***Thermo-Calc Software (TCS) Company*** and ***QuesTek Innovations LLC***, USA. The TC-PRISMA software uses the Thermo-Calc engine for thermodynamic calculations and the DICTRA engine for kinetic/diffusion simulations, and it further extends to some more advanced physical and kinetic simulations of precipitations in multicomponent alloys. It has been built up on top of another Java-based TCAPI layer. One example of the program layout and some application results of the TC-PRISMA software are shown in *Figure 14*. For various details about the developments, data-inputs, result-outputs, applications and other aspects of this software, please refer to the ***TC-PRISMA User's Guide and Examples***.
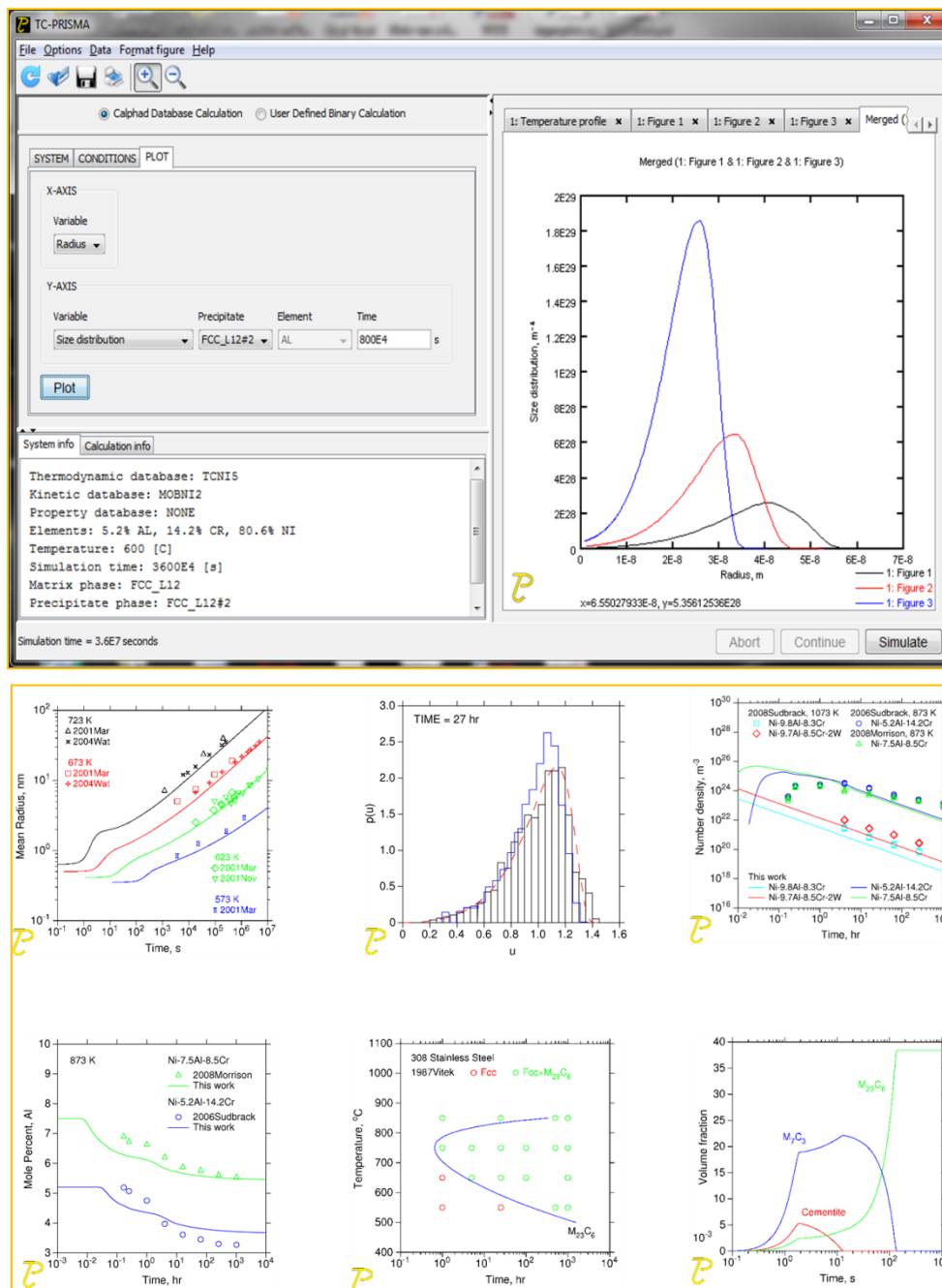
Figure 14.   TC-PRISMA Software

5.3　Development of Thermo-Calc Toolboxes in Other Software

The TC-MATLAB Toolbox is for use in the well-known and widely used MATLAB® software package for specific applications *(Figure 15)*. Using the Thermo-Calc engine the TC-MATLAB Toolbox can be utilized for materials property calculations, materials process simulations and even materials engineering controls.
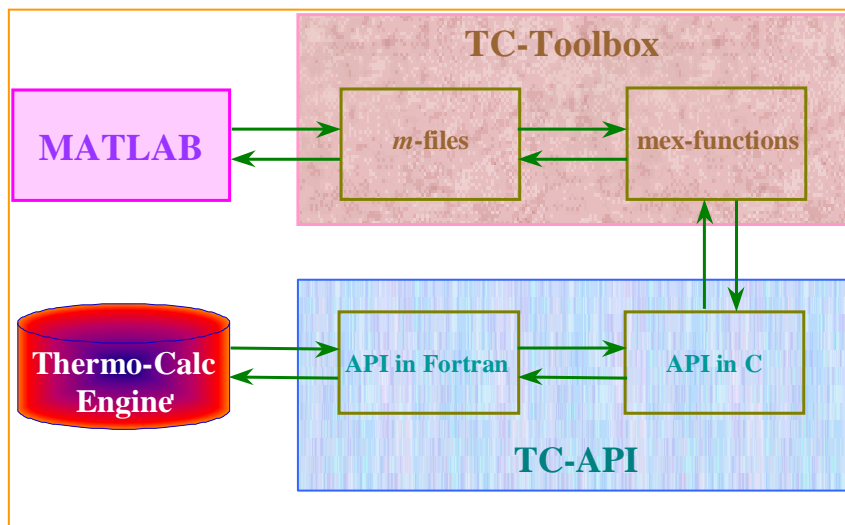
Figure 15.　The TC-MATLAB Toolbox in the MATLAB®™ Software Package

MATLAB®™ is a very flexible software for technical computing and visualization of data. The software comes with more than 600 mathematical, statistical and engineering functions and great graphical capabilities. It can be considered a matrix-oriented programming language and contains compilers, links and libraries for different scientific applications. This flexibility is now enhanced even more with the possibility to retrieve thermodynamic and kinetic quantities through the TC-MATLAB Toolbox. This programming interface is ideal for fast realization of ideas and visualization of results during research and development activities.

The TC-MATLAB Toolbox are available for the application programmer including a set of commands for communicating with the DICTRA software. Thanks to the many predefined functions available in MATLAB the programs get very compact and simple to set up, see *Figure 17-b* for example code and graphical output.

TC-MATLAB Toolbox has been used in a process simulation model developed at SSAB Tunnplåt in Borlänge, Sweden. The model, containing a whole range of sub-models, is used for prediction of mechanical properties in hot rolled products. The thermodynamic data needed in the model calculations are retrieved through the TC-MATLAB Toolbox.

For the general functionality and applications of the MATLAB®™ and its sister software package (such as SIMULINK®™, FEMLAB®™, *etc*.), please refer to the documentation provided by the MathWorks Ltd. (http://www.mathworks.com) and its partners all over the world. TCS also supplies some helpful guides to providers and users; please visit our web site (www.thermocalc.com) for the TC-MATLAB Toolbox documents.

Figure 16 is an example of a calculation performed using TC-MATLAB Toolbox. It is a calculation of the liquidus surface for a ternary A-B-C system which is plotted in 3D effects of the MATLAB environment.
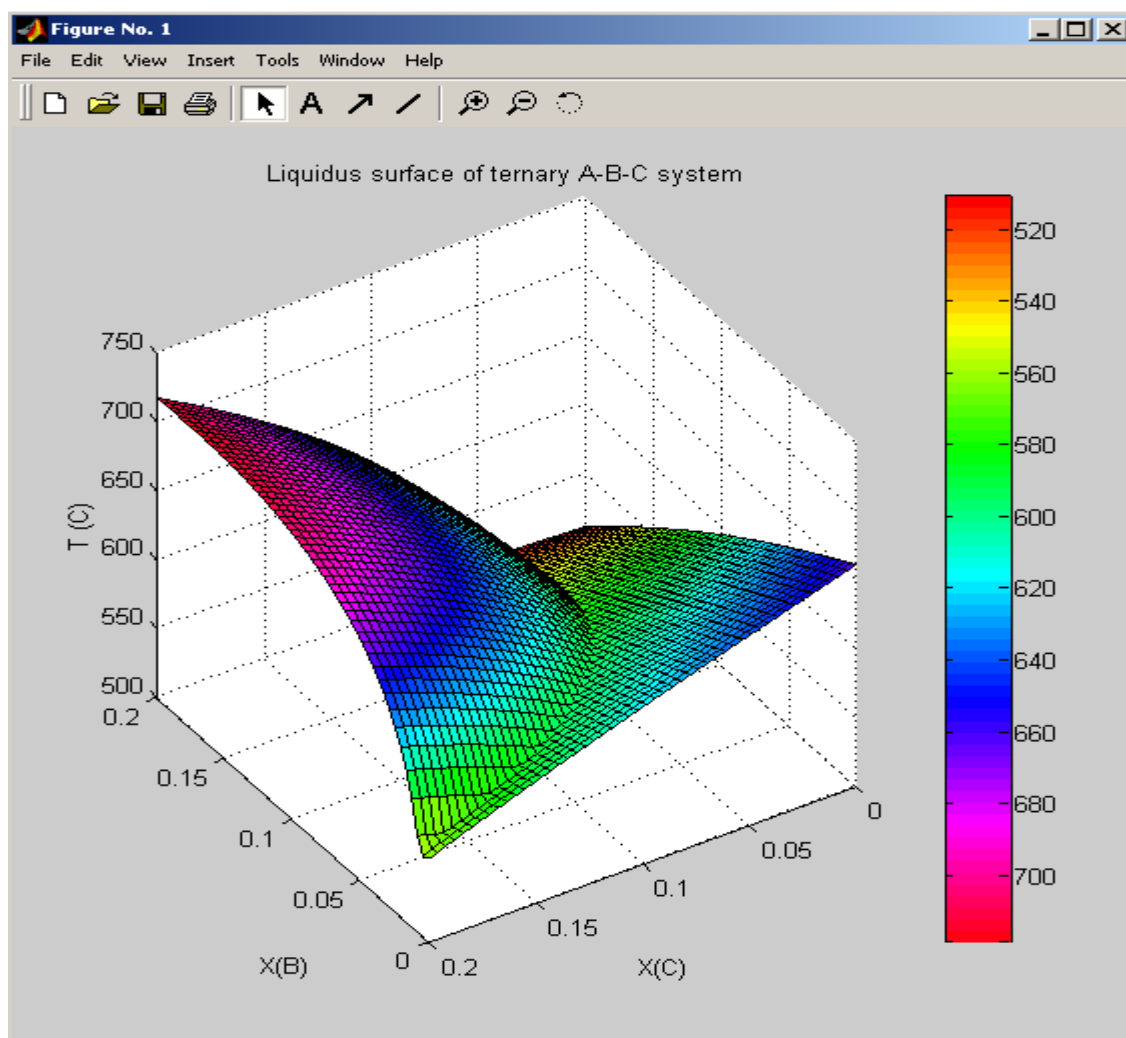

Figure 16.   Liquidus Surface of the A-B-C System Calculated and Plotted Using the TC-MATLAB Toolbox in the MATLAB® Software

Figure 17 shows two more examples of applications utilizing the TC-MATLAB Toolbox, performed by SSAB Tunnplåt in Borlänge, Sweden.

The first application is a software system for prediction of mechanical properties in hot rolled products, Hybroll, is under development. The work started as a multipartner ESCS project ("*The prediction of the mechanical properties of hot rolled strip products using hybrid methods*", ESCS Project #7210-PR-164). The system is designed for materials that cover C-Mn steels, HSLA steels with Nb, Ti and V additions and high carbon steels.
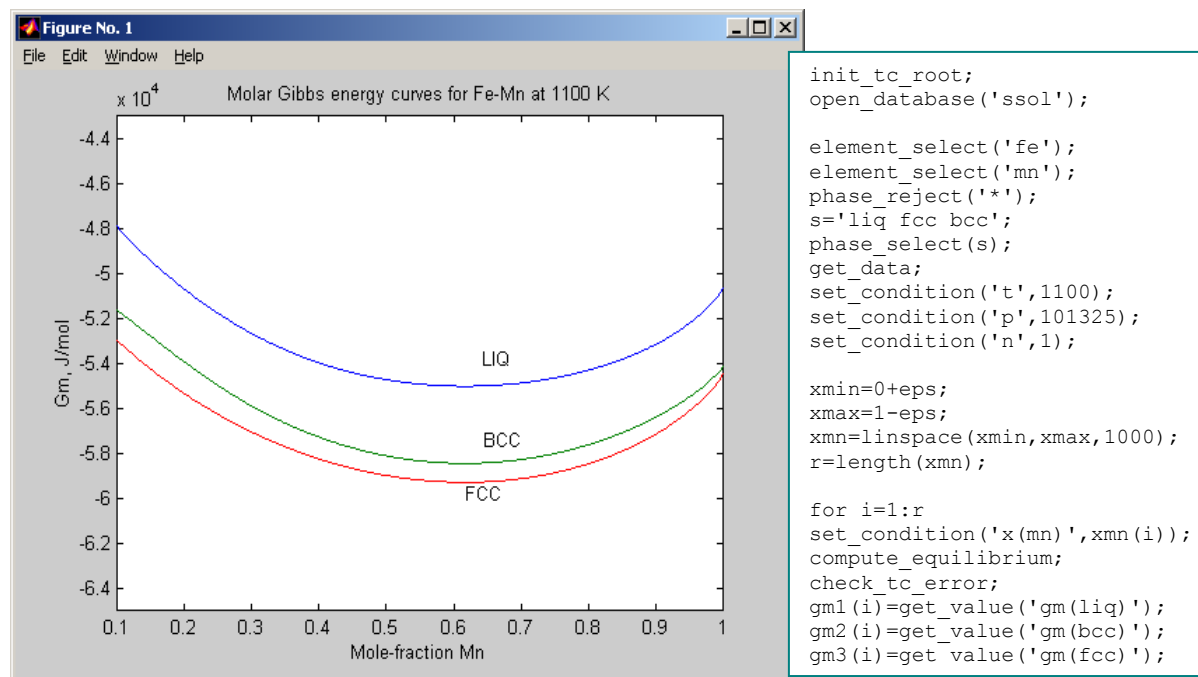
The microstructural model calculates a microstructure after hot rolling. Inputs to the model are time, temperature and strain sequence during hot rolling. This calculated microstructure is then used as input to the flow stress model. The flow stress model calculates a stress-strain curve from which $R_{p0.2}$, R_m and A_g can be evaluated directly. The different sub-models describing the microstructural evolution during hot rolling are particle dissolution and precipitation, grain growth, recrystallisation, the evolution of dislocations and vacancies, the transformation from austenite to ferrite and eutectoid and the description of flow stress. The models must be fast enough to be able to run on process computers, but still give a resonably general description of the microstructure evolution. Both experimental data taken from literature and laboratory experiments are used for model tuning. During the model development, the MATLAB® software has been used.

To predict the driving force and supersaturation in the matrix, as well as the paraequilibrium that occurs during the decomposition of austenite, thermodynamic data is needed. The thermodynamic data is taken directly from the Thermo-Calc software using the TC-MATLAB Toolbox. A specially developed database for HSLA steels is used for the calculations.
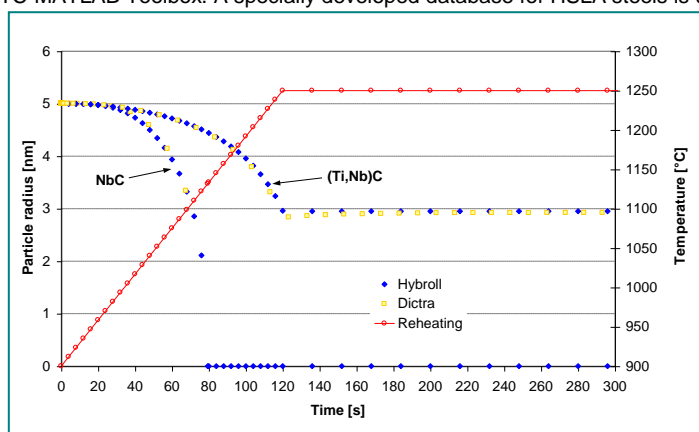
Figure 17a.   A Particle Dissolution During a Heating Sequence, using the TC-MATLAB Toolbox. The HYBROLL model is compared to the DICTRA software for NbC and (Ti,Nb)C particles, and the deviation between these two is negligible.

The second application is a process simulation model, which contains a whole range of sub-models, used for prediction of mechanical properties in hot rolled products. The thermodynamic data needed in the model calculations are retrieved through the TC-MATLAB Toolbox.


```
init_tc_root;
open_database('ssol');

element_select('fe');
element_select('mn');
phase_reject('*');
s='liq fcc bcc';
phase_select(s);
get_data;
set_condition('t',1100);
set_condition('p',101325);
set_condition('n',1);

xmin=0+eps;
xmax=1-eps;
xmn=linspace(xmin,xmax,1000);
r=length(xmn);

for i=1:r
set_condition('x(mn)',xmn(i));
compute_equilibrium;
check_tc_error;
gm1(i)=get_value('gm(liq)');
gm2(i)=get_value('gm(bcc)');
gm3(i)=get_value('gm(fcc)');
```

Figure 17b.   The code and output of a sample program calculating the molar Gibbs energy curves, using the TC-MATLAB Toolbox. For the liquid, BCC and FCC phases, respectively, in the Fe-Mn binary system at 1100 K.

5.4   Applications of Materials Property Calculations and Materials Process Simulations

There are many successful applications of the TQ and TCAPI programming interfaces and TC-MATLAB Toolbox, intercommunicating the Thermo-Calc Engine (plus DICTRA extensions) with user-preferred application programs or third-party software, in materials property calculations, materials process simulations, materials production optimizations and materials utility controls.

Proven examples of such applications are:

a) Computational design of high-performance alloy steels
      e.g., Hierarchically Structured Materials Design System by North Western University, USA, 1997, and PrecipiCalc Software by QuesTek Innovations LLC, USA, 2003.

b) Microstructure evolution simulations in multicomponent alloys
      e.g., Alloy Microstructure Simulation System by ACCESS e.V., Germany, 1998.

c) Property evolution simulations in multicomponent alloys
      e.g., Computer Aided Materials Design System by CISRI (China Iron & Steel Research Inst. Group), China, 1999.

More interesting applications may be available in the near future, in the field of development of a comprehensive Materials Interface using both the Thermo-Calc and DICTRA software as thermodynamic and kinetic engines.

6   Thermo-Calc Functionality and Applications

As mentioned earlier, being a very general and extreme flexible software system, the Thermo-Calc Software/Database/Programming-Interface Package can be widely used for all kinds of calculations/simulations where thermodynamics is possibly involved (Sundman *et al.,* 1985; 1993; Jansson *et al.,* 1993; Sundman and Shi, 1997, Shi *et al.,* 2004). For instance,

- ☞ Calculations of thermodynamic properties (as functions not only of temperature, pressure and composition, but also of magnetic contribution, chemical-/magnetic-ordering, crystallographic structures/defects, surface tension, amorphous glass-formation, mechanic-induced deformation, electro-static state, electronic potential, *etc.*).

- ☞ Calculations of equilibrium and partial/local-equilibrium quantities.

- ☞ Calculations of chemical driving forces (thermodynamic factors).

- ☞ Calculations of various types of stable/meta-stable phase diagrams and property diagrams of multicomponent systems for many types of materials. It can efficiently handle a very complex multicomponent and heterogeneous interaction system defined with up to 40 elements, 1000 species and many different solution or stoichiometric phases.

- ☞ Calculations/simulations of many other types of diagrams that are useful information in various materials systems/processes, such as: CVD/PVD depositions, CVM calculations of ordering/disordering phenomena, Scheil-Gulliver solidification simulations (with or without back-diffusions of fast-diffusing components), liquidus surface projections, solidus surface projections, Pourbaix diagrams, Ellingham diagrams, partition coefficients, partial pressures in gases, and so forth.

- ☞ It is the only software that can calculate arbitrary phase diagram sections with up to five independent variables in a defined system (which, is very useful, for instance, in finding the lowest melting temperature in a multicomponent alloy that has up to five independently-varying compositions), as well as the only software that can calculate chemical driving forces (thermodynamic factors, *i.e.,* the second derivatives of Gibbs free energy with respect to compositions) which are important fundamental information for kinetic simulations (such as in diffusion-controlled phase transformation, nucleation, particle growths/dissolutions, and so on).

6.1   Functionality of Thermo-Calc

Thermo-Calc has a wide range of unique functionality. *Table 6* summarizes the major functionality of the software and interfaces.

Table 6.   Major Functionality of the Thermo-Calc Software and Interfaces

Functionality
thermodynamic properties of pure substances or solution phases
thermodynamic properties of chemical reactions
thermodynamic factors, driving forces
heterogeneous equilibria *(up to 40 components and 1000 species)*
metastable equilibria, para-equilibria
miscibility-gap of all types of solution phases
magnetic contributions (curie temperature, magneton number)
electrostatic contributions (Born functions), aqueous solvation/association
transport properties of aqueous solutions
high-pressure contributions for steels/alloys/minerals, gas and supercritical fluids
special quantities: *e.g.,* T_o, A_3-temperature, adiabatic T, chill factors, $\partial T/\partial X$, *etc.*
multicomponent phase diagrams *(up to 5 axis variables)* (binary, ternary, isothermal, isoplethal, *etc.*)
property diagrams *(up to 40 components and 1000 species)*
CVD diagrams, thin-film formation
partial gaseous pressures, chemical potentials of volatile species
Pourbiax diagrams and many other diagrams for aqueous-involving interaction systems
Scheil-Gulliver solidification simulation
CVM calculations, chemical ordering-disordering
glass transition
oxide-layer formation of steel surface, emergency-conditions for preventing oxide-formations
steel/alloy refining, PRE
evolution of hydrothermal, metamorphic, igneous, sedimentary, weathering processes
speciation in corrosion , recycling, remelting, sintering, incineration, combustion
steady-state reactors
assessment of various thermodynamic parameters based on experiments
establishment and modification of datasets or databases

Please refer to relevant chapters in associated *User's Guides and Examples Books*, on various functions in different modules in the Thermo-Calc software (and its programming interface).

6.2   Applications of Thermo-Calc

The Thermo-Calc software package is connected with many high-quality thermodynamic databases useful for applications in R&D of steels, alloys, ceramics, semi-/super-conductors, automotive industries, food production, energy transfer, earth materials, environmental protection, and so on. With such databases, any thermodynamically sound problem should be possible to define and calculate.

Some existing applications of TCS-provided or customized databases in conjunction with the Thermo-Calc software and databases are listed *Table 7*. With the continuous development of new databases, and further implementation of more comprehensive models and advanced modules, new application fields are constantly becoming suitable.

Table 7.   Some Existing Applications of the Thermo-Calc Software and Databases

Materials-oriented	Industry-oriented
steels (incl. SS, HSLA, HS, CI, *etc.*)	steel-making industries
alloys (Al-/Ti-/Ni-/Mg-/Zr-based & others)	alloy/superalloy productions
hard materials (carbides, nitrides, *etc.*)	cutting equipment, heavy/precision instrument
ceramics, solid oxide fuel cells	automotive and aerospace industries
melts, slags	process-/powder-/hydro-metallurgy industries
salts, glasses	lighting equipment
semi-/super-conductors	electronic components
heat-bearing & corrosion-resistant oxides	coating, welding, joining
gases, sub-supercritical fluids	energy transfer and utility, combustion
aqueous solutions	environmental protection, solution separation
earth materials	mining industries (diamond, gold, petroleum, …)
nuclear materials (alloys and oxides)	nuclear fuel and waste management
solders	building engineering, chemical engineering
other inorganic materials	recycling, sintering, incineration
organic substances	food production, fat formation

Tremendous amount of Thermo-Calc application examples can be found in various international journals and conference proceedings. The following is a list of the journals, *among many others,* with the most frequent publications of Thermo-Calc calculations and assessment results by authors worldwide:

> *Calphad*
> *Journal of Phase Equilibria & Diffusion (formerly "Journal of Phase Equilibria")*
> *Metallurgy and Materials Transactions (A and B)*
> *Acta Metallurgy*
> *Z Metallkde*
> *Scripta Metallurgy*
> *Journal of Materials*
> *Journal of Materials Research*
> *Journal of Materials Science*
> *Journal of Advanced Materials*
> *Journal of Physics and Chemistry of Solids*
> *Journal of Alloys and Compounds*
> *Materials Science and Engineering*
> *Materials Science Forum*
> *Journal of the American Ceramic Society*
> *Journal of the European Ceramic Society*
> *Journal of the Electrochemical Society*
> *Physical Review (A and B)*

In the document ***Thermo-Calc Reference List***, some selected references on various applications are listed, which you may find in your local libraries.

Some representative examples are illustrated in the collection pages on the TCS web site (www.thermocalc.com), and many examples are given inside the ***Thermo-Calc Console Mode Example.***

Moreover, the two flexible application programming interfaces (namely TQ and TCAPI) and the thermodynamic calculation toolbox (TC-MATLAB Toolbox), all internally connected with the standardized Thermo-Calc Engine (with DICTRA extensions), have been applied in materials property calculations, materials process simulations, materials production optimizations and materials utility controls.