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Jun 2000  6th revised and extended edition (Edited by Pingfang Shi)
Nov 2002  7th revised edition (Edited by Pingfang Shi)
Jun 2004  8th revised edition (Edited by Pingfang Shi)
Apr 2006  9th revised edition (Edited by Pingfang Shi)
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/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 (TCC and TCW)

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/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 are two different user-interface types of the Thermo-Calc software, namely TCC (Thermo-Calc Classic) and TCW (Thermo-Calc Windows). 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), has been made available to our users. There has been an update almost every year and the most recent ones, TCCR and TCW4, are released in May 2006.

Any modern PC (Microsoft Windows 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/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 online help facilities. The general GUI-driven (Graphic User Interface) version TCW has been made available for Windows XP/2000/NT4 environments, while such a general GUI version for UNIX and Linux environments is still under development.

Thermo-Calc has gained a worldwide reputation as the best software for calculations of multicomponent phase diagrams. There are more than 1000 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 TCC and 20 elements in TCW, 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 TCC Examples Book and TCW Examples Book, and can also be found on 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 thermodynamic models of 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 databases for substances and solutions in inorganic and metallurgical systems, TCFE for steels and Fe-alloys, TCNi/TTNi for Ni-based superalloys, TTAI/TTMg/TTTi for Al-/Mg-/Ti-based alloys, SLAG for slag, ION for carbides/nitrides/oxides/silicates/sulfides (solids/liquids/gases), TCMP for materials processing and applications to environmental problems associated with metallurgical, chemical and waste-treatment processes, particularly in recycling, remelting, sintering, incineration and combustion), SMEC for semiconductors, NSLD/USLD for lead-free solders, SNOB for noble metals, NUMT/NUOX for nuclear substances and nuclear oxides, GCE for minerals, and TCAQ/AQS for aqueous solutions, etc. For more details on various available databases, please see the Thermo-Calc Database Guide.

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. Thermo-Calc Software AB is now actively devoted to developments of more application-oriented databases of various industrial interests. 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 TCC 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 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, MISCRESS™ software (coupling via TQ) and PrecipCalc™ software (coupling via TCAPI).

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 TRAnsmformation) 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 35 years and 150 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 (TCC/TCW) 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 on our web site (www.thermocalc.se/Download/Updates.html) 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 TCC/TCW/DICTRA software, should usually be synchronized and transplanted into the new version of the programming interfaces, too. The most recent major-versions that are formally released in May 2006 are: TCCR, TCW4 and DICTRA24; TQ6, TCAPI4 and Toolbox4. For a rather complete list of the TCC software revision history (since TCCN), please refer to the Section 1.4 of the TCCR Users’ Guide.

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 databases (such as TCFE3, SSOL4, TCMP2, SLAG2, ION2, TTNi7, TTTi3, TTAi5, TTMg3, TCAQ2, AQS2, GCE2, NOX2, NSLD2) are promptly announced on our web site (www.thermocalc.se/Products/Databases.html) or in our company newsletters (which are also available at www.thermocalc.se/News/Newsletter_download.html) 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 TCC/TCW/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, SLAG2.2 and TCMP2.2 are the second sub-versions of the second major-versions of the SLAG and TCMP databases, respectively. 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., SLAG2), while any database sub-version (e.g., SLAG2.2) 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 TCC/TCW/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 cooperations 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:
- TCCR Manual Set (TCCR Users’ Guide and TCCR Examples Book);
- TCW4 Manual Set (TCW4 Users’ Guide and TCW4 Examples Book); and

It used to be one chapter (i.e., Chapter 3 - Thermo-Calc Software System) in the TCC User’s Guide; but started from this version (TCCR), it has been extracted and separately prepared as this individual document.

It gives the details of the entire Thermo-Calc software/database/interface package and of various terms/concepts within the thermodynamic framework and data strategies applied within the Thermo-Calc software (TCC and TCW), as well as within the DICTRA software.

Extensive descriptions and many application examples of the Thermo-Calc software/database/interface package are given inside the TCCR Manual Set and TCW4 Manual Set, which can be found within the TCCR/TCW4 installation and on our web site (www.thermocalc.se/Download/Manuals_and_examples.html).
2 Some Thermodynamic Terms

This section gives a basic introduction and an overview of some thermodynamic terms used in the Thermo-Calc Software/Database/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), 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:


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., Fe₂C, Fe₃Si, Fe₅Si₃O₆, SiO₂, H₂O, CH₃COOH] or charged [e.g., Fe²⁺, Fe³⁺, HO₂⁻, OH⁻, Fe₄(OH)₆⁶⁻]. 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 8.12.

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⁺, Cr, Fe and ZE]. One can even define a system component as an appropriate combination of defined elements (e.g., Cr₂C and Fe₃C 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.
Some Thermodynamic Terms

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:

\[
X(\text{component}) = \frac{N(\text{component})}{N} \\
W(\text{component}) = \frac{B(\text{component})}{B}
\]

where $N$ and $B$ stand for the total mole number of components or total mass (in gram) the defined system, respectively; and $N(\text{component})$ and $B(\text{component})$ 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., $N(\text{constituent}\#\text{sublattice})$, in the defined phase:

\[
y(\text{phase, constituent}\#\text{sublattice}) = \frac{N(\text{constituent}\#\text{sublattice})}{v(\text{sublattice})}
\]

or using the mole numbers or masses (in gram) of each of the elements/components, i.e., $N(\text{phase, component})$ or $B(\text{phase, component})$, in the defined phase:

\[
X(\text{phase, component}) = \frac{N(\text{phase, component})}{N_P(\text{phase})} \\
W(\text{phase, component}) = \frac{B(\text{phase, component})}{B_P(\text{phase})}
\]

where $v(\text{sublattice})$ stands for the stoichiometric coefficient of specific sublattice site in the defined phase; and $N_P(\text{phase})$ and $B_P(\text{phase})$ 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.
2.5 Equilibrium State and State Variables

The Thermo-Calc software (TCC and TCW) 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 H2O 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 TCCR User’s Guide.
Table 1. State Variables that can be used in the Thermo-Calc Package

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

#### Extensive variables – Constitutional Composition (amount of a constituent/species on a sublattice site in a phase)

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$y$</td>
<td>$y(\text{ph, cons#sub})$</td>
<td>dimensionless</td>
<td>Site fraction</td>
<td>of a constituent on a sublattice site (denoted by # and a digit) in a phase</td>
</tr>
</tbody>
</table>

#### Special quantities

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$</td>
<td>$QF(\text{ph})$</td>
<td>dimensionless</td>
<td>Phase stability function</td>
<td>of a phase (being negative when the phase composition is inside a spinodal or positive elsewhere)</td>
</tr>
<tr>
<td>$T_c$</td>
<td>$TC(\text{ph})$</td>
<td>K</td>
<td>Curie temperature</td>
<td>of a phase</td>
</tr>
<tr>
<td>$M_b$</td>
<td>$BMAGN(\text{ph})$</td>
<td>dimensionless</td>
<td>Bohr magneton number</td>
<td>of a phase</td>
</tr>
</tbody>
</table>

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

1) **Normalizing suffixes $M$, $W$, and $V$ for energetic extensive variables of a system:**

Normalizing suffixes like $M$ (per mole), $W$ (per mass in gram) or $V$ (per volume in m$^3$) of the whole system (including all the components) can be supplied on all following energetic extensive variables for the system:

$$ Z = G, A, U, H, S, V \quad \rightarrow \quad Z_M, Z_W, Z_V $$

Such suffixed quantities are calculated via the first derivatives of the energetic extensive variable $Z$ with respect to $N$ or $B$ or $V$ in the whole system. For instance,

- $G_M = \frac{\partial G}{\partial N}$
- $G_W = \frac{\partial G}{\partial W}$
- $G_V = \frac{\partial G}{\partial V}$

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

2) **Normalizing suffixes $M$, $W$, $V$ and $F$ for energetic extensive variables of a phase:**

Normalizing suffixes like $M$ (per mole), $W$ (per mass in gram), $V$ (per volume in m$^3$) or $F$ (per mole formula unit) of a phase can be supplied on all following energetic extensive variables for the phase:

$$ Z = G(\text{ph}), A(\text{ph}), U(\text{ph}), H(\text{ph}), S(\text{ph}), V(\text{ph}) \quad \rightarrow \quad Z_M, Z_W, Z_V, Z_F $$

Such suffixed quantities are calculated via the first derivatives of the energetic extensive variable $Z$ with respect to $NP(\text{ph})$ or $BP(\text{ph})$ or $VP(\text{ph})$ for the phase. For instance,

- $G_M(\text{ph}) = \frac{\partial G(\text{ph})}{\partial NP(\text{ph})}$
- $G_W(\text{ph}) = \frac{\partial G(\text{ph})}{\partial BP(\text{ph})}$
- $G_V(\text{ph}) = \frac{\partial G(\text{ph})}{\partial VP(\text{ph})}$
- $G_F(\text{ph}) = \frac{\partial G(\text{ph})}{\partial NP(\text{ph})} * NA$

One shall note that: if a phase is unstable in the system, and thus its $NP(\text{ph})$, $BP(\text{ph})$ and $VP(\text{ph})$ values equal to zero, $G(\text{ph})$, $A(\text{ph})$, $U(\text{ph})$, $H(\text{ph})$, $S(\text{ph})$ and $V(\text{ph})$ are all assigned with zero value. However, $G_M(\text{ph})$, $AM(\text{ph})$, $UM(\text{ph})$, $HM(\text{ph})$, $SM(\text{ph})$ and $VM(\text{ph})$, 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 $VV(\text{ph})$ is always as unity so it is unnecessary to evaluate such a quantity in the program.

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

Normalizing suffixes like $M$ (per mole), $W$ (per mass in gram), $V$ (per volume in m$^3$) or $F$ (per mole formula unit) of a phase must always be supplied on the energetic extensive variable $DG$ for the phase:

$$ Z = DG(\text{ph}) \quad \rightarrow \quad 2M, 2W, 2V, 2F \quad (\text{Note this can not be used as conditions}) $$

Theoretically, such suffixed quantities can be calculated via the first derivatives of the energetic extensive variable $DG(\text{ph})$ with respect to $NP(\text{ph})$ or $BP(\text{ph})$ or $VP(\text{ph})$ for the phase. For instance,

- $DG_M(\text{ph}) = \frac{\partial DG(\text{ph})}{\partial NP(\text{ph})}$
- $DG_W(\text{ph}) = \frac{\partial DG(\text{ph})}{\partial BP(\text{ph})}$
- $DG_V(\text{ph}) = \frac{\partial DG(\text{ph})}{\partial VP(\text{ph})}$
- $DG_F(\text{ph}) = \frac{\partial DG(\text{ph})}{\partial NP(\text{ph})} * NA$

$$ \text{driving force of the phase per mole of the phase (J/mol)} $$

$$ \text{driving force of the phase per mass of the phase (J/mol)} $$

$$ \text{driving force of the phase per volume of the phase (J/mol)} $$

$$ \text{driving force of the phase per formula unit of the phase (J/mol)} $$
However, please note that the $\Delta G(\text{ph})$ 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) **Normalizing suffixes $\mathbf{M}$, $\mathbf{W}$ and $\mathbf{V}$ for compositional extensive variables of a system:**

Normalizing suffixes like $\mathbf{N}$ (per mole), $\mathbf{V}$ (per mass in gram) or $\mathbf{V}$ (per volume in m$^3$) of the whole system (including all system components) can be supplied on all following compositional extensive variables for the system:

$$Z = N, B \rightarrow 2M, ZW, ZV$$

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable $Z$ with respect to $N$ 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/m$^3$)
- $BM = \partial B / \partial N$ 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/m$^3$)

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) **Normalizing suffixes $\mathbf{M}$, $\mathbf{W}$ and $\mathbf{V}$ for compositional extensive variables a component in the system:**

Normalizing suffixes like $\mathbf{N}$ (per mole), $\mathbf{V}$ (per mass in gram) or $\mathbf{V}$ (per volume in m$^3$) of the whole system (including all system components) can be supplied on all following compositional extensive variables for a component in the system:

$$Z = N(\text{comp}), B(\text{comp}) \rightarrow 2M, ZW, ZV$$

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable $Z$ with respect to $N$ or $B$ or $V$ in the whole system. For instance,

- $NM(\text{comp}) = \partial N(\text{comp}) / \partial N$ Mole number of a component per mole of the system (mole fraction)
- $NV(\text{comp}) = \partial N(\text{comp}) / \partial V$ Mole number of a component per mass of the system (mol/g)
- $BV(\text{comp}) = \partial B(\text{comp}) / \partial V$ Mass (gram) of a component per volume of the system (g/mol)
- $BV(\text{comp}) = \partial B(\text{comp}) / \partial V$ Mass (gram) of a component per mass of the system (mass fraction)

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

- $NM(\text{comp}) = X(\text{comp})$ for mole fraction of a component in the system;
- $BW(\text{comp}) = W(\text{comp})$ for mass fraction of a component in the system.

6) **Normalizing suffixes $\mathbf{M}$, $\mathbf{W}$ and $\mathbf{V}$ for compositional extensive variables of a phase in the system:**

Normalizing suffixes like $\mathbf{N}$ (per mole), $\mathbf{V}$ (per mass in gram) or $\mathbf{V}$ (per volume in m$^3$) of the whole system (including all system components) can be supplied on compositional extensive variables $NP(\text{ph})$ and $BP(\text{ph})$ [as well as the $VP(\text{ph})$ quantity] for a phase:

$$Z = NP(\text{ph}), BP(\text{ph}), VP(\text{ph}) \rightarrow 2M, ZW, ZV$$

Such suffixed quantities are calculated via the first derivatives of such extensive variable $Z$ with respect to $N$ or $B$ or $V$ in the whole system. For instance,

- $NPM(\text{ph}) = \partial NP(\text{ph}) / \partial N$ Mole number of a phase per mole of the system (mole fraction)
- $NPW(\text{ph}) = \partial NP(\text{ph}) / \partial B$ Mole number of a phase per mass of the system (mol/g)
- $NPV(\text{ph}) = \partial NP(\text{ph}) / \partial V$ Mole number of a phase per volume of the system (mol/m$^3$)
- $BPW(\text{ph}) = \partial BP(\text{ph}) / \partial B$ Mass (gram) of a phase per mass of the system (g/mol)
- $BPV(\text{ph}) = \partial BP(\text{ph}) / \partial V$ Mass (gram) of a phase per volume of the system (mass fraction)
- $VPV(\text{ph}) = \partial VP(\text{ph}) / \partial V$ Volume (m$^3$) of a phase per volume of the system (volume fraction)

$$\left[\begin{array}{c}
\begin{array}{c}
\text{Mole number of a phase per mole of the system (mole fraction)}
\text{Mole number of a phase per mass of the system (mol/g)}
\text{Mole number of a phase per volume of the system (mol/m^3)}
\text{Mass (gram) of a phase per mass of the system (g/mol)}
\text{Mass (gram) of a phase per volume of the system (mass fraction)}
\text{Volume (m^3) of a phase per volume of the system (volume fraction)}
\end{array}
\end{array}\right]$$
Some Thermodynamic Terms

Note that the \( V_{\text{P}}(\text{ph}) \) variable is exactly the \( V(\text{ph}) \) property, but their \( M/W/V/F \)-suffixed quantities are different; \( V_{\text{P}}(\text{ph}) \) can be \( V \)-suffixed (but not \( F \)-suffixed) while \( V(\text{ph}) \) can be \( F \)-suffixed (but not \( V \)-suffixed).

Also note that: if a phase is unstable in the equilibrium system, the \( N_{\text{P}}(\text{ph}), B_{\text{P}}(\text{ph}) \) and \( V_{\text{P}}(\text{ph}) \) values equals to zero, and do so their \( M/W/V \)-suffixed quantities.

One should also keep in mind that: the phase amount variables, \( N_{\text{P}}(\text{ph}), B_{\text{P}}(\text{ph}) \) and \( V_{\text{P}}(\text{ph}) \), as well as all their \( M/W/V \)-suffixed quantities, should not be used as conditions. Instead, one can use the \textit{CHANGE\_STATUS} command to set a relevant condition, e.g., \textit{CHANGE\_STATUS phase <phase>=fix <amount>} where the fixed \(<amount>\) is roughly the same as the \( F \)-suffixed quantity \( N_{\text{P}}(\text{ph}) \) \{i.e., mole number of a phase per mole formula unit of the phase\} which can not be directly evaluated or listed/shown.

7) Normalizing suffixes \( M, W \) and \( V \) for compositional extensive variables of a component in a phase:

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:

\[
Z = N(\text{ph}, \text{comp}), B(\text{ph}, \text{comp}) \quad \Rightarrow ZM, ZW, ZV
\]

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable \( Z \) with respect to \( N \) or \( B \) or \( V \) in the whole system. For instance,

\[
\begin{align*}
NM(\text{ph}, \text{comp}) &= \frac{\partial N(\text{ph}, \text{comp})}{\partial N_{\text{P}}(\text{ph})} \quad \text{Mole number of a component per mole of a phase (mole fraction)} \\
NW(\text{ph}, \text{comp}) &= \frac{\partial N(\text{ph}, \text{comp})}{\partial B_{\text{P}}(\text{ph})} \quad \text{Mole number of a component per mass of a phase (mol/g)} \\
NV(\text{ph}, \text{comp}) &= \frac{\partial N(\text{ph}, \text{comp})}{\partial V_{\text{P}}(\text{ph})} \quad \text{Mole number of a component per volume of a phase (mol/m\(^3\))} \\
BM(\text{ph}, \text{comp}) &= \frac{\partial B(\text{ph}, \text{comp})}{\partial N_{\text{P}}(\text{ph})} \quad \text{Mass (gram) of a component per mole of a phase (g/mol)} \\
BW(\text{ph}, \text{comp}) &= \frac{\partial B(\text{ph}, \text{comp})}{\partial B_{\text{P}}(\text{ph})} \quad \text{Mass (gram) of a component per mass of a phase (mass fraction)} \\
BV(\text{ph}, \text{comp}) &= \frac{\partial B(\text{ph}, \text{comp})}{\partial V_{\text{P}}(\text{ph})} \quad \text{Mass (gram) of a component per volume of a phase (g/m\(^3\))}
\end{align*}
\]

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

- \( NM(\text{ph}, \text{comp}) = X(\text{ph}, \text{comp}) \) for mole fraction of a component in a phase;
- \( BW(\text{ph}, \text{comp}) = W(\text{ph}, \text{comp}) \) for mass fraction of a component in a phase;

8) Special compositional (extensive) variables of a component or a species:

The derived compositional variables, \( X(\%)(\text{comp}) \) and \( W(\%)(\text{comp}) \) 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 \( X(\%)(\text{comp}) \) and \( W(\%)(\text{comp}) \) can be used as axis variables in the POST module but they must be instead specified as the followings, respectively:

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

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:

- \( \text{Mole-Fraction} <\text{comp}> \) for mole-fraction of a component in the system, \( X(\text{comp}) \);
- \( \text{Weight-Fraction} <\text{comp}> \) for mass-fraction of a component in the system, \( W(\text{comp}) \).

rather than directly using their relevant state variables, \( X(\text{comp}) \) or \( W(\text{comp}) \).

9) Special quantity \( QF \) of a phase:

The Thermo-Calc software system also calculates a special quantity, the \textit{phase stability function} \( QF(\text{ph}) \), 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, or positive elsewhere. 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 \( BMAGN \) of a phase with magnetic contribution:

The Thermo-Calc software system also calculates other two special quantities, the \textit{Curie temperature} \( TC(\text{ph}) \) and \textit{Bohr magneton number} \( BMAGN(\text{ph}) \), 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
section 2.13 (Reference State and Standard State)
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):

\[
HM.T = \frac{\partial HM}{\partial T} \quad \text{heat capacity for the system at either constant } P \text{ (if pressure is a condition)}
\]

or constant \( V \) (if volume is a condition)

\[
HM\,(ph).T = \frac{\partial HM\,(ph)}{\partial T} \quad \text{heat capacity for a phase at either constant } P \text{ (if pressure is a condition)}
\]

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 various modules of the TCC software):

- 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 `H/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, PARROT, ED_EXP), 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 POLY3/POST/TAB modules. However, there are more properties (regarding model-related parameters in describing certain phases) can be used. Some examples are given below:

\[
G\,(ph,sp;0) \quad \text{for standard Gibbs energy of a species in a phase}
\]

\[
TC\,(ph,sp;0) \quad \text{for curie temperature of a species in a phase}
\]

\[
BMAGN\,(ph,sp;0) \quad \text{for Bohr magneton number of a species in a phase}
\]

\[
V0\,(ph,sp;0) \quad \text{for molar volume at 1 bar and reference } T_0 \text{ of a species in a phase}
\]

\[
VA\,(ph,sp;0) \quad \text{for integrated thermal expansivity of a species in a phase}
\]

\[
VC\,(ph,sp;0) \quad \text{for isothermal compressibility of a species in a phase}
\]

\[
VK\,(ph,sp;0) \quad \text{for high-pressure fitting parameter of a species in a phase}
\]

\[
WR\,(AQ,sp;0) \quad \text{for Born function for electro-static contribution } \omega_{j,Pr,Tr} \text{ of an aqueous species in aqueous solution phase}
\]

\[
G\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order interaction energy between interacting species in a phase}
\]

\[
L\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order interaction energy between interacting species in a phase}
\]

\[
TC\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order composition dependence of curie temperature in a phase}
\]

\[
BMAGN\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order composition dependence of Bohr magneton number in a phase}
\]

\[
V0\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order composition dependence of molar volume in a phase}
\]

\[
VA\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order composition dependence of thermal expansivity in a phase}
\]

\[
VC\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order composition dependence of isothermal compressibility in a phase}
\]

\[
VK\,(ph,sp1,sp2,...;i) \quad \text{for } i^{th} \text{ binary, ternary, or higher-order composition dependence of high-pressure fitting parameter in a phase}
\]

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) Units for various state variables and derived variables:

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)
- \( \text{TempC} = T - 273.15 \) Celsius (C)
- \( \text{TempF} = 1.8 \times T - 459.67 \) Fahrenheit (F)
- \( = 1.8 \times \text{TempC} + 32 \)

Pressure
- \( \text{PB} = P / 1E5 \) bars (bar)
- \( \text{PKb} = P / 1E8 \) kilobars (kbar)
- \( \text{PAtm} = P / 101325 \) atmosphere (atm)
- \( \text{PSI} = P / 6894.76 \) pounds/sq. inch (psi)
- \( \text{PIHg} = P / 3342.11 \) inches of Hg
- \( \text{PTor} = P / 133.322 \) Tors (millimeters of Hg)

Gibbs Energy
- \( \text{GCal} = G / 4.1858 \) cal
- \( \text{GmCal} = G_m / 4.1858 \) cal/mol
- \( \text{GphCal} = G_{ph} / 4.1858 \) cal
- \( \text{GmphCal} = G_{mph} / 4.1858 \) cal/mol

Heat Capacity
- \( \text{Cp} = H M / 4.1858 \) cal/mol/K
- \( \text{Cpph} = H M_{ph} / 4.1858 \) cal/mol/K

Chemical Potential
- \( \text{MU} = M U (\text{comp}) / 4.1858 \) cal/mol
- \( \text{MUR} = M U R (\text{comp}) / 4.1858 \) 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 TCCR User’s Guide.
2.6 Derived Variables (Partial Derivatives)

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.

Actually, some variables listed in Table 1 are derived variables, e.g., $\text{HM} \cdot T$ and $\text{HM} (\text{ph}) \cdot T$, where a dot “.” notation is used. As an important feature of the Thermo-Calc software, any partial derivatives of one state variable with respect to another can be evaluated, by using the dot “.” notation between the two state variables. However, the state variable after the dot must be set as a condition. For example,

$$\text{HM} \cdot T = \left( \frac{\partial \text{HM}(\text{ph})}{\partial T} \right)_{\text{condition}}$$

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)

$$\text{HM} (\text{ph}) \cdot T = \left( \frac{\partial \text{HM}(\text{ph})}{\partial T} \right)_{\text{condition}}$$

heat capacity for a phase at either constant $P$, $C_p(\text{ph})$ (if pressure is a condition)

or constant $V$, $C_v(\text{ph})$ (if volume is a condition)

$$H \cdot T = \left( \frac{\partial H}{\partial T} \right)$$

heat capacity for the system multiplied by total mole number of components

i.e., $\partial H / \partial T = C_p \cdot N$ (if pressure is a condition in a close system)

$\partial H / \partial T = C_v \cdot N$ (if volume is a condition in a close system)

$H (\text{ph}) \cdot T = \left( \frac{\partial H (\text{ph})}{\partial T} \right)$

heat capacity for a phase multiplied by NP (ph) plus $\text{HM} (\text{ph})$ multiplied by total mole number of components

i.e., $C_p(\text{ph}) \cdot NP(\text{ph}) + \text{HM}(\text{ph}) \cdot N$ (if pressure is a condition)

$C_v(\text{ph}) \cdot NP(\text{ph}) + \text{HM}(\text{ph}) \cdot N$ (if volume is a condition)

$$V \cdot T = \left( \frac{\partial V}{\partial T} \right)$$

thermal expansivity of the system (already multiplied by the total molar volume)

i.e., $\partial V / \partial T = \alpha \cdot VM$

$$V (\text{ph}) \cdot T = \left( \frac{\partial V (\text{ph})}{\partial T} \right)$$

thermal expansivity of a phase (already multiplied by its molar volume)

i.e., $\partial V (\text{ph}) / \partial T = \alpha(\text{ph}) \cdot V(\text{ph})$

$$V (\cdot) \cdot T = \left( \frac{\partial V (\cdot)}{\partial T} \right)$$

thermal expansivity of the system (already multiplied by the total volume)

i.e., $\partial V / \partial T = \alpha \cdot V$

$$V (\text{ph}) \cdot P = \left( \frac{\partial V (\text{ph})}{\partial P} \right)$$

isothermal compressibility of the system (already multiplied by the total molar volume)

i.e., $\partial V / \partial P = -\kappa \cdot VM$

$$V (\cdot) \cdot P = \left( \frac{\partial V (\cdot)}{\partial P} \right)$$

isothermal compressibility of the system (already multiplied by its molar volume)

i.e., $\partial V (\cdot) / \partial P = -\kappa(\cdot) \cdot VM(\cdot)$

$$V (\text{ph}) \cdot P = \left( \frac{\partial V (\text{ph})}{\partial P} \right)$$

isothermal compressibility of the phase (already multiplied by the phase volume)

i.e., $\partial V (\text{ph}) / \partial P = -\kappa(\text{ph}) \cdot V(\text{ph})$

$$T \cdot X (\text{comp}) = \left( \frac{\partial T}{\partial X (\text{comp})} \right)$$

slope of a phase boundary on a $T-X (\text{comp})$ phase diagram with respect to mole fraction of the component in the system

$$T \cdot W (\text{comp}) = \left( \frac{\partial T}{\partial W (\text{comp})} \right)$$

slope of a phase boundary on a $T-W (\text{comp})$ phase diagram with respect to mass of the component in the system

$$T \cdot X (\text{ph}, \text{comp}) = \left( \frac{\partial T}{\partial X (\text{ph}, \text{comp})} \right)$$

slope of a phase boundary on a $T-X (\text{ph}, \text{comp})$ phase diagram with respect to mole fraction of the component in the phase

$$T \cdot W (\text{ph}, \text{comp}) = \left( \frac{\partial T}{\partial W (\text{ph}, \text{comp})} \right)$$

slope of a phase boundary on a $T-W (\text{ph}, \text{comp})$ phase diagram with respect to mole fraction of the component in the phase

$$P \cdot T = \left( \frac{\partial P}{\partial T} \right)$$

slope of a phase boundary on a $P-T$ phase diagram (Note that the equilibrium with phase assemblage must be calculated first)

Restrictedly speaking, those energetic extensive variables with normalizing suffixes like $M$ (per mole of component), $W$ (per mass in gram), $V$ (per volume in m$^3$) or $F$ (per mole formula unit) of the entire system, or a specific phase, as 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. Therefore, the derived variable $G$, $B$ is exactly the same as the $W$-suffixed state variable $\mathcal{G} \cdot W$ when $B$ (total mass of all components in the system) has been defined as an equilibrium condition in the system. In case a phase is not stable in the system, such derived quantities for the phase will be still precisely calculated by the program and saved in the workspace. See the comments below the table.
Moreover, those compositional extensive variables with normalizing suffixes like $M$ (per mole), $V$ (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 $N(\text{comp})$, $N$ is exactly the same as the $M$-suffixed state variable $NM(\text{comp})$ or $X(\text{comp})$ when $N$ (total moles of all components in the system) has been defined as an equilibrium condition in the system. For instance,

\[
\begin{align*}
N(\text{comp}).N &= NM(\text{comp}) = X(\text{comp}) \\
N(\text{ph},\text{comp}).NF(\text{ph}) &= NM(\text{ph},\text{comp}) = X(\text{ph},\text{comp}) \\
N(\text{ph},\text{comp}).V &= VP(\text{ph})/\text{NA} \\
B(\text{ph},\text{comp}).B &= BW(\text{ph},\text{comp}) = W(\text{ph},\text{comp}) \\
B(\text{ph},\text{comp}).BP &= BW(\text{ph},\text{comp}) = W(\text{ph},\text{comp}) \\
V(\text{ph}).N &= VP(\text{ph})/\text{NA} \\
V(\text{ph}).V &= VP(\text{ph})/\text{NA} \\
W(\%)(\text{comp}) &= \text{W(\%)(\text{comp})} \times 100
\end{align*}
\]

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 Software System, 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 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:

\[
\begin{align*}
\text{Rc}<\text{name}> &= \text{ACR(component)/X(component)} \\
\text{Pc}<\text{name}> &= X(\text{phase1,component})/X(\text{phase2,component})
\end{align*}
\]

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
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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 be calculated by:

\[ \text{RC<name>} = \frac{\text{ACR(species,phase)}}{\text{Y(phase,species)}} \]

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 \( \{ (\text{Fe})_3 (\text{C}, \text{N}, \text{VA}) \} \) 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 Raoult's Law). The reference state for a solute species is set on 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 activity coefficients for both solvent and solute species can be calculated as follows:

\[ \text{RCH2O} = \frac{\text{ACR(H2O,aqueous)}}{\text{Y(aqueous,H2O)}} \quad \text{(for solvent)} \]

\[ \text{RC<spec>} = \frac{\text{AI(species,aqueous)}}{\text{ML(aqueous,H2O)}} \quad \text{(for solute)} \]

\[ \text{AI(species,aqueous)} = \frac{\text{ACR(species,aqueous)}}{\text{Y(aqueous,species)}} \cdot \frac{\text{Y(aqueous,H2O)}}{\text{Y(aqueous,species)}} \]

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 H2O must be identical to those for the pure gaseous species H2O, 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/hydrate/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 H2O, and any other element (such as Fe and C) or substance [such as a pure SO2 gas, stoichiometric phase Cu2S and solution phase \( \{ (\text{Fe}, \text{Ni}), (\text{O}, \text{VA}) \} \) may have a solubility limit under a specific condition of temperature-pressure and other aqueous compositions;
- An O2-dominant gaseous mixture phase may dissolve certain amounts of FeO\textsuperscript{2+}/FeO\textsuperscript{3+} species from magnetite (Fe3O4) 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

<table>
<thead>
<tr>
<th>Name</th>
<th>Mnemonic</th>
<th>Possibly Units</th>
<th>Meaning</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>For Aqueous Solution Phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>PH</td>
<td>dimensionless</td>
<td>Acidity</td>
<td>of the aqueous solution phase, ( pH = -\log_{10}(AC_2(H^+))<em>{AQ} = -\log</em>{10}(ACR(H^+,AQ)) )</td>
</tr>
<tr>
<td>Eh</td>
<td>EH</td>
<td>V, mV</td>
<td>Hypothetical electric potential</td>
<td>of the aqueous solution phase, ( Eh = u(ZE)/96485.309 )</td>
</tr>
<tr>
<td>pe</td>
<td>PE</td>
<td>dimensionless</td>
<td>Logarithm of the hypothetical electron activity</td>
<td>of the aqueous solution phase, ( pe = u(ZE)/(2.3025851*RT) )</td>
</tr>
<tr>
<td>( \Delta h )</td>
<td>AH</td>
<td>kJ, kcal</td>
<td>Thermodynamic affinity per electron</td>
<td>of a redox couple wrt the standard hydrogen electrode in the aqueous solution phase, ( AH = u(ZE) )</td>
</tr>
<tr>
<td>( \gamma_w )</td>
<td>YH2O</td>
<td>dimensionless</td>
<td>Mole fraction</td>
<td>of the solvent ( H_2O ) in the aqueous solution phase, ( YH2O = Y(AQ,H2O) )</td>
</tr>
<tr>
<td>( N_w )</td>
<td>AH2O</td>
<td>mole</td>
<td>Mole number</td>
<td>of 1.0 kg of solvent ( H_2O ), ( AH2O = 55.508435 )</td>
</tr>
<tr>
<td>( NSH2O )</td>
<td>NSH2O</td>
<td>mole</td>
<td>Mole number</td>
<td>of the solvent ( H_2O ) in the aqueous solution phase, ( NSH2O = Y(AQ,H2O) )</td>
</tr>
<tr>
<td>m</td>
<td>ML#</td>
<td>mol/kg_( H_2O )</td>
<td>Molality</td>
<td>of a solute species in the aqueous phase, ( ML#_1 = Y(AQ,sp)_1*AH2O/YH2O )</td>
</tr>
<tr>
<td>( m^* )</td>
<td>TIM</td>
<td>equivalent molality</td>
<td>Total molality</td>
<td>of all solute species in the aqueous solution phase, ( TIM = \sum[ML#_1] * V(sp1-in-spJ) )</td>
</tr>
<tr>
<td>( I )</td>
<td>ISTR</td>
<td>dimensionless</td>
<td>Ionic strength</td>
<td>of the aqueous solution phase, ( ISTR = 1/2*\sum[ML#_1]*Z^2(AQ,sp) )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>RCH2O</td>
<td>dimensionless</td>
<td>Activity coefficient, ( RCH2O = ACH(H_2O)_{AQ} )</td>
<td>of the solvent ( H_2O ), ( RCH2O = ACH(H_2O)_{AQ} = ACR(H_2O,AQ) )</td>
</tr>
<tr>
<td>( \alpha_w )</td>
<td>A1H2O</td>
<td>dimensionless</td>
<td>Activity</td>
<td>of the solvent ( H_2O ), ( A1H2O = ACR(H_2O,AQ) )</td>
</tr>
<tr>
<td>( \alpha_w )</td>
<td>AIH2O</td>
<td>Activity, ( AIH2O = ACR(H_2O,AQ) )</td>
<td>of a solute species in the aqueous solution phase, ( AIH2O = ACR(sp,AQ)*AH2O/YH2O )</td>
<td></td>
</tr>
<tr>
<td>( \log AI# )</td>
<td>LogAI#</td>
<td>Log10 Activity, ( LogAI# = log_{10}(AIH2O,AQ) )</td>
<td>of the solvent ( H_2O ) or a solute species in the aqueous solution phase, ( LogAI# = log_{10}(AIH2O,AQ) )</td>
<td></td>
</tr>
<tr>
<td>( \phi_w )</td>
<td>OS</td>
<td>dimensionless</td>
<td>Osmotic coefficient</td>
<td>of aqueous solution phase, ( OS = -55.508435*ln(AN)/TIM )</td>
</tr>
<tr>
<td>( A1 )</td>
<td>AT1</td>
<td>equil_mol/kg_( H_2O )</td>
<td>Titration alkalinity ( (\text{definition 1}) )</td>
<td>of the aqueous solution phase, generally defined as the equivalent molality of carbonate and bicarbonate at the methyl orange endpoint (( pH=4.5 ))</td>
</tr>
<tr>
<td>( A1 )</td>
<td>AT2</td>
<td>equil_mol/kg_( H_2O )</td>
<td>Titration alkalinity ( (\text{definition 2}) )</td>
<td>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 ))</td>
</tr>
<tr>
<td>For Gaseous Mixture Phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>RA#</td>
<td>dimensionless</td>
<td>Activity coefficient, ( RA(sp,GAS) )</td>
<td>of a gaseous species in the gaseous mixture, ( RA(sp,GAS) = \text{function}(T,P) )</td>
</tr>
<tr>
<td>( \gamma^* )</td>
<td>RF#</td>
<td>dimensionless</td>
<td>Fugacity coefficient, ( RF(sp,GAS) )</td>
<td>of a pure gaseous species under ( P ), ( RF(sp,GAS) = \text{function}(T,P,V) )</td>
</tr>
<tr>
<td>( f )</td>
<td>FUG#</td>
<td>pa, bar, psi</td>
<td>Fugacity, ( FUG(sp,GAS) )</td>
<td>of a gaseous species in the gaseous mixture, ( FUG(sp,GAS) = RA(sp,GAS)*RF(sp,GAS)*Y_{GAS} )</td>
</tr>
<tr>
<td>( f )</td>
<td>TFUG</td>
<td>pa, bar, psi</td>
<td>Total gas fugacity</td>
<td>of the gaseous mixture phase, ( TFUG = \sum[FUG(sp,GAS)] )</td>
</tr>
</tbody>
</table>

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:

\[
\begin{align*}
\mathcal{G} & = -SdT + VdP + \sum_i \mu_i dN_i - Dd\xi \\
\mathcal{A} & = -SdT - PdV + \sum_i \mu_i dN_i - Dd\xi \\
\mathcal{U} & = TdS - PdV + \sum_i \mu_i dN_i - Dd\xi \\
\mathcal{H} & = TdS + VdP + \sum_i \mu_i dN_i - Dd\xi
\end{align*}
\]

These characteristic state functions can simplify the description of the equilibrium state, at which the driving force \( D = 0 \) and thus \( Dd\xi = 0 \). 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 (\( \mathcal{G} \)) the most useful function since \( \mathcal{G} \) has its minimum at the equilibrium.
- Controlling the temperature, volume and composition of a system forces the Helmholtz energy (\( \mathcal{A} \)) to be at its minimum when the system is at equilibrium.
- Controlling the entropy, volume and composition of a system ensures the Internal energy (\( \mathcal{U} \)) will be at its minimum when the system is at equilibrium.
- Controlling the entropy, pressure and composition of a system leads the enthalpy (\( \mathcal{H} \), 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/interface package, and currently available models and related databases.

<table>
<thead>
<tr>
<th>Phase Type</th>
<th>Phase Examples</th>
<th>Available Models</th>
<th>Database Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure stoichiometric phase</td>
<td>Pure metals</td>
<td>appropriate EOS</td>
<td>PURE, SSUB</td>
</tr>
<tr>
<td></td>
<td>Pure stoichiometric oxides, sulfides, hydroxides, silicates, <em>etc.</em></td>
<td>appropriate EOS</td>
<td>SSUB, TCMP</td>
</tr>
<tr>
<td></td>
<td>Pure stoichiometric condensed substances under high pressure and high temperature</td>
<td>Murnaghan, Birch-Murnaghan, General PVT EOS</td>
<td>TCFE, TCNI, GCE, PGEO, (SSOL)</td>
</tr>
<tr>
<td></td>
<td>Pure gaseous species in standard states</td>
<td>Ideal Gas</td>
<td>SSUB, TCMP</td>
</tr>
<tr>
<td></td>
<td>Simple organic substances</td>
<td>appropriate EOS</td>
<td></td>
</tr>
<tr>
<td>Pure ferro-, antiferro- or para-magnetic phase</td>
<td>Magnetic elements</td>
<td>CEM with Inden MO</td>
<td>TCFE, SSOL</td>
</tr>
<tr>
<td></td>
<td>Magnetic oxides</td>
<td>CEM with Inden MO</td>
<td>TCFE, SSOL</td>
</tr>
<tr>
<td>Condensed substitutional solution</td>
<td>Alloys with metallic components</td>
<td>CEM</td>
<td>SSOL, TCFE</td>
</tr>
<tr>
<td></td>
<td>Complex oxides, silicates, <em>etc.</em></td>
<td>CEM</td>
<td>ION, NOX, GCE</td>
</tr>
<tr>
<td>Interstitial solution</td>
<td>Alloys with carbon, nitrogen, <em>etc.</em></td>
<td>CEM</td>
<td>SSOL, TCFE</td>
</tr>
<tr>
<td>Solution phase with several sublattices</td>
<td>Alloys with metallic component occupying different lattice sites</td>
<td>CEM</td>
<td>SSOL, TCFE, TCMP</td>
</tr>
<tr>
<td></td>
<td>Solid salts with charged ions</td>
<td>TSIM, AM, QCM</td>
<td>SALT, TCMP</td>
</tr>
<tr>
<td>Solution phase with chemical defects</td>
<td>Non-stoichiometric oxides with charged ions</td>
<td>TSIM, AM, QCM</td>
<td>ION, NUOX, NOX, TCFM</td>
</tr>
<tr>
<td></td>
<td>Non-stoichiometric salts with charged ions</td>
<td>TSIM, AM, QCM</td>
<td>SALT, TCMP</td>
</tr>
<tr>
<td>Solution phase with ordering transformations</td>
<td>Chemically and/or magnetically ordered alloys, oxides, silicates, <em>etc.</em></td>
<td>CEM with CVM, with Inden MO</td>
<td>TCFE, TCNI, SSOL, TCMP</td>
</tr>
<tr>
<td>Solution phase with forming species</td>
<td>Gaseous mixtures</td>
<td>SUPERFLUID</td>
<td>SUPERFLUID</td>
</tr>
<tr>
<td></td>
<td>Aqueous solutions</td>
<td>SIT, HKF, Pitz</td>
<td>TCAQ, AQS</td>
</tr>
<tr>
<td></td>
<td>Melts/Liquids</td>
<td>TSIM, AM, QCM</td>
<td>SSOL, TCFE, ION</td>
</tr>
<tr>
<td></td>
<td>Molten salts</td>
<td>TSIM, AM, QCM</td>
<td>SALT</td>
</tr>
<tr>
<td></td>
<td>Glasses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution phase with covalence bonding</td>
<td>Complex organic substances</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metal-organic complexes</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymers</td>
<td>FHM</td>
<td></td>
</tr>
</tbody>
</table>

*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, TCC User’s Guide and Thermo-Calc Database 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/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). 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 TCCR 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 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 **Generate PVT EOS 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 the symmetrical binary Redlich-Kister parameters plus several extensions for composition-dependent ternary parameters (Hillert, 1980; Sundman, 2004), i.e., Redlich-Kister_Muggianu, Redlich-Kister_Kohler and Redlich-Kister_Toop, or with unsymmetrical binary excess models with either simple or legendre polynomials,
- **Sublattice Model** or the so-called **Compound-Energy Model** (Sundman and Ågren, 1981; Andersson et al., 1986).

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

- **Two-Sublattice Ionic Liquid Model** (Hillert et al., 1985), **Associated Model** (Jordan, 1979), **Kapoor-Frohberg-Gaye Cell Model** (Gay and Welfringer, 1984), **Quasi-Chemical Model or Quasi-Chemical_Kongoli Model** (Kongoli et al., 2002) for oxide liquids;
- **Two-State Model** for handling 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-critical 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 PIZT (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 Chapter 11 - Gibbs Energy System (GES) in the TCCR User’s Guide.

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., H2O 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 FCC form.

There are normally more than one way 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 default defined 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.
Some Thermodynamic Terms

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

$$\alpha G_m^\Theta - H_m^{\text{SER}} = \Delta_f \alpha G_m^\Theta + \sum_i v_i \left( \alpha G_i^\alpha - H_i^{\text{SER}} \right)$$

When the substance is a solution phase $\alpha$ 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:

$$G_m^\alpha(x_i) - H_m^{\text{SER}} = E^G_m^\alpha(x_i) + \sum_i x_i \left( \alpha G_i^\alpha - H_i^{\text{SER}} \right)$$

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}] 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 (Units for State Variables and Derived Variables) in the TCCR 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 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 H\(_2\)O 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 Raoult'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:

$$\text{AI}(\text{sp}, \text{aqueous}) = \text{ACR}(\text{sp}, \text{aqueous})$$  (for solvent)

$$\text{AI}(\text{sp}, \text{aqueous}) = \text{ACR}(\text{sp}, \text{aqueous}) \times 55.5084$$  (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 $\frac{\partial^2 G_m}{\partial x_A \partial P} = 0$. 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 $\mu_{Mo}$-T plots], where a solid miscibility gap of the BCC solution phase is stable. The critical point of the miscibility gap is around $T=941^\circ C$ 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 $\mu_{Mo}$ variation (with the default reference of state SER) in two-phase regions BCC#1+BCC#2 and Liquid+BCC (please note that the lower $\mu_{Mo}$ 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 $\mu_{Cr}$-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 ($\sigma$) solution phase is stable and coexists with the BCC phase (as illustrated in the diagram 2A-a). By calculating the metastable
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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 1B. Phase Diagram of the Fe-Cr Binary System: Miscibility Gap.](image)

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°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°C and x_{Cr}=0.507. The graph 1A-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 1A-d only plots the µ_{Cr} variation (with the default reference of state SER) for the BCC miscibility gap in both its stable and metastable regions (up to its critical range).
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 ($\sigma$) 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.

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 SPECIAL_OPTION (with the SET_MISCIBILITY_GAP 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 in the current version TCCR) 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 and Chapter 8 in the TCCR 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 \(\xi\). According to the second law of thermodynamics, it is proportional to the internal entropy production \(d_{\text{p}}S\) and can be expressed as the relation \(D = T \frac{d_{\text{p}}S}{d\xi}\). If a system is not in a state of equilibrium, there may be a spontaneous internal process for which the second law gives \(d_{\text{p}}S > 0\) and thus \(Dd\xi > 0\) that drives the process to approach the equilibrium.

Equilibrium thermodynamics deals with systems where \(d_{\text{p}}S = 0\) 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 \(\xi\). Thus the driving force at the equilibrium state can be expressed as:

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

In the Thermo-Calc software system which is based on Gibbs energy minimization for equilibrium systems, the driving force of a phase \(\alpha\) 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 phase 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 \(DGM(\text{phase})\) [as well as \(DGW(\text{phase}), DGV(\text{phase})\) and \(DGF(\text{phase})\)], but please keep in mind that such a \(DG(\text{phase})\) 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 plane. **Figure 2** can be used as a perfect example 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 (\(\sigma\)) 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 \([\text{i.e.} \ x_{\text{Cr}} \simeq 0.133 - 0.906 \text{ at } 450^\circ\text{C}]\), the driving forces \(\Delta G_m^{\text{ph}}\) (as marked to right of the graph) and phase stability functions \(Q_F(\text{phase})\) 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 \(\Delta G_m^{\text{ph}}\) (not shown on the graph) and phase stability functions \(Q_F(\text{phase})\) of all the other metastable phases (e.g., FCC, SIGMA and Liquid) will alter accordingly.
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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., \( \Delta G_{m}^{ph} \). 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).

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 new versions of Thermo-Calc (TCCR and TCW4) software is that the newly-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 \texttt{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 subsequent POLY optimization in order to reach a truly global minimum (the most stable equilibrium state in the defined alloy).

In the current versions TCCR and TCW4, fully-supported equilibrium conditions in the Global Minimization Technique are: \( N \), \( N(\text{component}) \), \( B \), \( B(\text{component}) \), \( W(\text{component}) \) and \( X(\text{component}) \). 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 and partially in a stepping or mapping calculation, but can of course be turned off by the user.

![Figure 3. Global Minimum vs Local Minimum](image)

The diagram illustrates the Gibbs energy surfaces for BCC (\( \alpha \)), FCC (\( \beta \)) and SIGMA (\( \sigma \)) 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 (\( \sigma \)) 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 TCCR 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 8.10.1 in the TCCR 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 (TCC/TCW) software/database 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\textsubscript{y} 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 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 (TCC/TCW) software. Since TCCP 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 TCCR User’s Guide, and two cases using the module are included in the in
the TCCR Examples Book (i.e., Examples 15 and 30).

A T₀-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 T₀-temperature is located within the two-phase
field between the phases and it is the theoretical limit for a diffusionless transformation. Calculations of T₀-
temperatures are thus of interest e.g. when studying diffusionless transformations. The T₀ 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 TCCR User’s Guide) for the two phases in
partial equilibrium of a diffusionless transformation becomes a plane or surface, and T₀ 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
components (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_j/(x_{Fe} + x_{M})] have
the same values. Under the paraequilibrium state, dT = dP = dµ_C = du_Fe = du_M = 0, the driving force should
be zero, and T, P, µ_C and u_Fe,µ_Fe + u_M,µ_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 TCCR
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 PARAEQUILIBRIUM) have been
made available in the POLY commands SPECIAL_OPTIONS and STEP_WITH_OPTIONS, respectively,
which automatically calculate the so-called T₀ 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 SPECIAL_OPTIONS command) and 8.9.4 (the STEP_WITH_OPTIONS command) in the
TCCR User’s Guide, as well as Examples 42 and 43 in the TCCR 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 a steel. 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 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.

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 and many internally-consistent databases and datasets have been formulated, through many international and national collaborations over the last two decades, such as CALPHAD community, SGTE community, NIST institution, Ringberg Forum, CAMPADA consortium, STT foundation, and so on.

This section introduces data structure, data formats, data assessment, data quality and data sources in the Thermo-Calc package. The document Thermo-Calc Database Guide and Chapter 5 of the TCCR 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 section of Database Manager’s Guide in the document Thermo-Calc Database Guide, more details will be given. The following paragraphs will provide some brief descriptions on the general Thermo-Calc Data Structure (or the so-called 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 “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 TDB DEFINE_SYSTEM value (ELEMENT or SPECIES) and the GES-reference type index
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- 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 dependence is basically a power series of \( T \), 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. Mineral phases modelled by the Birch-Murnaghan Model will have data on thermal expansion, compressibility and their derivatives with respect to temperature and pressure, which can describe the \( P-V-T \) relations for 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 H2O 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, 1992) and AQSCONV program (Shi and Sundman, 1999) can convert the GCE and AQS databases to the Thermo-Calc 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 workspace. 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; Sanders and Miodownik, 1998; Sundman et al., 2000; Sundman et al., 2006), 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 high quality general and specified databases for many applications (see Chapter 4, Thermo-Calc Database Description). 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 either 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 (for steels and alloys) and the SGTE databases (for pure elements, inorganic and metallurgical 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 and TTTi databases) 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 databases for substances and solutions in inorganic and metallurgical systems, TCFE/FEDAT/TCNI 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 next three chapters (Chapters 3, 4 and 5) of this guide, 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, MIT, UES Software, 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 Chapter 4, *Thermo-Calc Database Description*.

The Thermo-Calc Group at KTH have initiated and participated in many international projects in order to create general and validated databases. Thermo-Calc Software AB is now actively devoted to developments of more application-oriented databases of various industrial interests.

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

Since TCCP (as well as TCW2.1 and DICTRA22), 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.

Such database encryption has caused some problems in TCCP/TCW2/DICTRA22 in the simultaneous use of databases of different types. Since TCCQ/TCW/DICTRA23, significant efforts have been done to remove those inconveniences and it is now possible to combine encrypted databases with each other or with public databases.

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 TCC/TCW/DICTRA software, as well as in the TQ/TCAPI programming 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 TCC/TCW/DICTRA 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).

Previously, the database files are occasionally CPU-dependent, implying the files for UNIX/Linux system and for PC Windows OS are incompatible, due to different data structures. Since TCCP, TCW2.1 and DICTRA22, 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 GES workspace, from such encrypted databases remain the same as for unencrypted ones. But thermodynamic parameters and related functions retrieved from an encrypted commercial database (except for two SGTE-owned databases, namely SSUB3 and SSOL2/SSOL4), 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. However, upon special requests, a simple-textual version (i.e., without data encryption) of a commercial Thermo-Calc or DICTRA database could be received and installed, on the necessary condition that a “TCS Database License Agreement” would have been bilaterally signed between the client and TCS; if you are interested in such a service, please contact info@thermocalc.se for the related details.
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 software/database/interface package. Thanks not only to the fast development of hardware and software environments, but also the constructive suggestions from many Thermo-Calc/DICTRA users, TCS (Thermo-Calc Software) 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/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

<table>
<thead>
<tr>
<th>Levels</th>
<th>Purposes</th>
<th>Versions</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Command-Line User Interface</td>
<td>Provide the users with a textual command line interface.</td>
<td>Classical</td>
<td>TCC</td>
</tr>
<tr>
<td>2) Modular Interface</td>
<td>Provide the users with simple inputs (only answers to few questions) to perform certain calculations like solidification simulations.</td>
<td>Classical</td>
<td>TCC</td>
</tr>
<tr>
<td>3) Graphical User Interface</td>
<td>Provide a graphical user interface in the Windows environments.</td>
<td>Windows</td>
<td>TCW</td>
</tr>
<tr>
<td>4) User Programming Interface</td>
<td>Provide programmers with the possibility to include the Thermo-Calc Engine into their own application programs.</td>
<td>Classical or Windows</td>
<td>TQ TCAPI</td>
</tr>
<tr>
<td>5) Software Toolbox Interface</td>
<td>Provide the Thermo-Calc Engine as a merged toolbox in some third-party software packages (such as MATLAB®, Fluent®, and Phoenix®).</td>
<td>TC toolbox</td>
<td>TC MATLAB Toolbox</td>
</tr>
</tbody>
</table>

The first two levels of the user interface are borne within the TCC (Thermo-Calc Classic) and DICTRA software. This part primarily describes the current situation of the command-line user interface and modular structure within the TCC software. Detailed information for some special modules will be given in the Chapter 10 of the TCCR User’s Guide.

The third level is found in the TCW 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 last level (within the merged 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 Section 4.3 and Part 4.

4.1 TCC User Interface

The TCC (Thermo-Calc Classic) software 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.

### 4.1.1 Common structure

Commands may always be chosen from a menu and may be entered at the prompt. Typing a question mark “?” or giving the command HELP in a certain module obtains the available commands as a menu. A command usually is several words connected by the underscore character, e.g., LIST_EQUILIBRIUM. It is therefore easy to understand what the commands perform just by reading the menu. More extensive explanations are obtained by typing HELP followed by the name of any command, e.g., HELP LIST_EQUILIBRIUM.

If the menu is long, it is possible to list just those with a common part, e.g., all commands starting with LIST by typing HELP LIST.

### 4.1.2 Abbreviations

To save time, it is important that the amount of required typing be minimized. This is especially important for people prone to spelling mistakes or who are not used to computers. However, an input of one letter or digit makes it difficult to remember the exact command.

Thus, all Thermo-Calc commands can be abbreviated by word beginnings as long as the abbreviation is not ambiguous. Each word separated by an underscore can be abbreviated separately.

The underscore character “_” used to separate the command words can be replaced by a hyphen “-” but never a space (when typing the command) because the space is used as a separator between the command and its parameters.

Almost all kinds of characters in command-line inputs can be typed in lower case letters.

Users can thus choose their own abbreviations to easily remember. This command-line rule of abbreviation applies to almost all kinds of input including phase names and other arguments.

Some examples are given below:

<table>
<thead>
<tr>
<th>Normal Commands</th>
<th>Abbreviated Commands</th>
</tr>
</thead>
<tbody>
<tr>
<td>CALCULATE_EQUILIBRIUM</td>
<td>c-e</td>
</tr>
</tbody>
</table>
CALCULATE_ALL_EQUILIBRIA       c-a
LIST_EQUILIBRIUM               l-e
LIST_INITIAL_EQUILBRIUM        li-i-e
LOAD_INITIAL_EQUILBRIUM        lo-i-e
LIST_PHASE_DATA CBCC           l-p-d cb
LIST_PHASE_DATA CEMENTITE      l-p-d ce
SET_ALL_START_VALUES           s-a-s, or s-al
SET_AXIS_VARIABLE 1 X(FCC,FE) 0 0.89 0.025 s-a-v 1 x(f,fe) 0 .89 .025
SET_START_CONSTITUENT         s-s-c
SET_START_VALUE                s-s-v
SET_AXIS_PLOT_STATUS           s-a-p
SET_AXIS_TEXT_STATUS           s-a-t-s, or s-a-te
SET_AXIS_TYPE                  s-a-ty
SET_OPTIMIZING_CONDITION       s-o-c
SET_OPTIMIZING_VARIABLE        s-o-v
SET_OUTPUT_LEVEL               s-o-1, or s-ou

4.1.3 History mechanism

The system remembers the last 20 commands given which can be listed by typing the two exclamation marks “!!” as a command. It is possible to execute the same command again just by typing an “!” and the number of the previous command typed. By typing “!?”, a full explanation of the history facilities will be given.

In the Windows NT/2000/XP environments, using the upward or downward arrow keys, “↑” or “↓”, can also recall and switch between the previously performed commands. These can be further modified on the line by using the “←” or “→” arrow keys, to make the changes (with the “Insert” key on). Unfortunately, this easy feature may not be available for the Windows 95/98/ME environments.

4.1.4 Working directory and target directory

The “current working directory” or “current working area” is referred to the directory where the TCC/TCW/DICTRA software systems can, under various modules, directly open (read) or save a binary file (e.g., GES5, POLY3 or PAR files), a simple textual file (e.g., TCM, LOG, TDB, SETUP, POP or EXP files), or a graphically-formatted file (e.g., PostScript-PS5/6, HPGL-P7/8, etc.). The “target directory” stands for the directory where a specific version of the executable program of a software system is located.

Upon the successful installation of a TCC/TCW/DICTRA software/database package, its target directory should remain the same for all executions related to that particular installation (for the reasons that an installation is usually associated with some modifications in the computer system administrations). However, every user may have his own working directories on a local computer or connected server that is accessible to the installation. An UNIX/Linux installation allows all designated users at the designated site to access the package (in the target directory) from their own working directories. A user may call the program at a certain directory that is called his current working directory in the present session of running the program. In order to open or save various files in different directories, he should start the program from such directories independently each time.

A Windows NT/2000/XP installation provides much more flexibility but maybe also more directory-related administration work, as explained below:

As described in Section 2.3 in the TCCR User’s Guide, the user can make use of appropriately defined shortcuts to work with the TCC/TCW/DICTRA software/database package (of a particular version) that is installed on a designated computer or server. By modifying or manipulating such a shortcut (through its properties), the current working directory can be set up in the Start-in box as one that is already created on a local computer or connected server. Therefore, the program can consequently read and generate all kinds of binary, textual and graphical files in this working directory.

Users should be aware of that, whenever the program pops up an Open file or Save file window on screen, the Look in box allows to change directories (even drivers or computers), in order to appropriately find an existing file or locate an generated file. This will result in the current working directory changed to another one for all the subsequent performance in the present session. By closing the program, the present session is ended, and it
is thus possible to restart the program with the predefined Start-in path as the “current working directory” again.

Under Windows NT/2000/XP environments, it is possible to use all types of standard DOS commands on-line inside the TCC/DICTRA programs, but must start with a “@” sign for each DOS command. For instance, @DIR, @TYPE, etc. (Unfortunately, this easy feature may not be available for the Windows 95/98/ME environments). Therefore, it may return to the predefined “current working directory” after performing a series of commands @CD <directory>, without quitting the program.

4.1.5 Parameters to a command

Typed commands should always be followed by pressing the <RETURN> key. Most commands need supplementary information of parameters, in order to be performed. The program asks for these parameters after pressed the <RETURN> key.

An expert user who knows a command requires parameters can type them on the same line as the command. The parameter values must be separated by spaces in this case.

4.1.6 Default values

The program usually provides an appropriate default value as an answer on an assigning parameter or a question. This value will be given within slashes after the question, e.g.,

```
OUTPUT FILE /TERMINAL/:  
```

Press the <RETURN> key to accept the default value as an answer to the question. In this case, the terminal will receive the output file if the <RETURN> key is pressed.

Some commands have many parameters. This is a design problem when trying both to keep the menu short and to provide commands for all features of the system. Usually the most important parameters are given first and those that normally take their default values are grouped last. Default values for the remaining parameters can be accepted by typing commas “,” separated by spaces for each remaining parameter, after the last adjusted parameter. There should be at least one comma for each parameter. Several continuous commas can be typed together, i.e., “,,,” is identical to “,,,,”.

In other cases, the program may take the previously defined values for some parameters as default values when the same command is recalled. The above rules apply here as well. For instance, if the first stepping/mapping axis variable is,

```
SET_AXIS_VARIABLE 1 X(FCC,FE) 0 0.89 0.025  
```

some parameters can be changed while rest remain as default values as the previously defined, e.g.,

```
SET_AXIS_VARIABLE 1 , 0.1 ,,  
SET_AXIS_VARIABLE 1 , 0.1 ,,  
```

which is equivalent to

```
SET_AXIS_VARIABLE 1 X(FCC,FE) 0.1 0.89 0.025.  
```

4.1.7 Wide card and other special signs

When showing calculated properties in the POLY module or choosing axis variables for plotting diagrams in the POST module, the wild card “*” can be used to denote all components, or all phases, or sometime all species. One may also use the dollar “$” sign to denote all stable phases but only when showing calculated properties in the POLY module. For instance,

```
SHOW_VALUE B(*) … lists mass (gram) of all components in the system  
SET_AXIS_VAR Y B(*) … sets mass (gram) of all components in the system as Y-axis variable  
SHOW_VALUE MUR(*) … lists chemical potentials of all components in the system  
SET_AXIS_VAR Y ACR(*) … sets activities of all components in the system as Y-axis variable  
SHOW_VALUE HM(*) .T … lists heat capacities of all phases  
SET_AXIS_VAR Y GM(*) … sets molar Gibbs free energies of all phases as Y-axis variable  
SHOW_VALUE TC($) … lists curie temperature of all stable phases  
SHOW_VALUE W(*,* … lists mass fractions of all components in all phases  
```
SHOW_VALUE \( W(\$,*). \) ... lists mass fractions of all components in all stable phases
SHOW_VALUE \( W(\text{FCC,*}). \) ... lists mass fractions of all components in the FCC phase
SHOW_VALUE \( W(*,\text{FE}). \) ... lists mass fractions of the Fe component in all phases
SHOW_VALUE \( W(\$,\text{FE}). \) ... lists mass fractions of the Fe component in all stable phases
SHOW_VALUE \( y(*,*) \) ... lists site fractions of all species in all sublattices of all phases
SHOW_VALUE \( y(\$,*) \) ... lists site fractions of all species in all sublattices of all stable phases
SHOW_VALUE \( y(*,*) \) ... lists site fractions of all species in all sublattices of all phases

However, the wild card “*” or the dollar “$” sign normally does not work properly for the activity and/or chemical potential properties. For example, one should NOT use e.g. \( \text{ACR}(*,*) \) for all the species in all phase, or \( \text{ACR}(*,\text{phase}) \) for a specified phase or \( \text{ACR}(\text{species,*}) \) for a specific species in all phases. But one can use specific names for species and phase in such cases. For example,

SHOW_VALUE \( \text{MUR(C2,GAS)} \) ... lists chemical potential of the C2 species in GAS mixture phases
SET_AXIS_VAR Y AC(C2,GAS) ... sets activity of the C2 species in GAS mixture phases as Y-axis

4.1.8 Incomprehensive questions

Typing a question mark “?” at any time throughout the command sequence will obtain a brief explanation of an expected answer. In some cases, more extensive help is available by typing two consecutive question marks “??”. After the intermediary help session, the question returns waiting for a proper answer.

4.1.9 Help and information

There are two basic commands for help in the menu: HELP and INFORMATION. The most important help facility is the possibility to type a “?” whenever understanding is lacking or more information is needed to answer the question.

The command HELP has three levels: listing the whole menu, listing the commands with a common part and listing a description of a specific command.

The INFORMATION command allows more general information about the system to be obtained. It can give information on various subjects related to the system in order to make it easier to understand various features.

4.1.10 Error messages

The program may issue some error messages, when retrieving unsolicited databases, reading previously created binary files, saving program status, performing calculations, generating diagrams, or when a command or its parameters are typed incorrectly or not unique or inappropriate. Some messages are just for Users’ information, but other errors may be fatal for the performance of the program. For more details on how to handle various types of error messages occurred in different modules, please refer to the corresponding chapters in the TCCR User’s Guide.

4.1.11 Control characters

In some parts of the system it is useful to control the output. Pausing or stopping a long list on a display terminal before it is finished allows reading of relevant information before its disappearance. Typing a control character shown below will affect the output on screen:

\( \text{ctrl-S} \) temporarily pauses the output and program and waits for a \( \text{ctrl-Q} \) to resume
\( \text{ctrl-Q} \) resumes the output and program
\( \text{ctrl-C} \) terminates the current region of mapping
\( \text{ctrl-C} \\text{ctrl-C (twice quickly)} \) terminates the program

4.1.12 Private files

It is possible to save the status of the program on a binary file, by using the command \( \text{SAVE_WORKSPACE} \) in either the GES or POLY or PARROT modules. This command may be useful when saving the setting of a
system and results from calculations for later uses or when terminating a session for any reason. This file will be of GES, POLY3 or PAR type accordingly, and will contain much information that can only be opened by the corresponding module (GES, POLY, or PARROT) and are not readable by using any textual editor outside the program. Both the original and modified thermodynamic data, the last set of conditions and options set by the user, and the results of the calculations or optimizations will be stored. For details of such privatized working files, refer to the corresponding sections in the later chapters in this manual.

### 4.1.13 MACRO facility

A MACRO file (normally with the extension TCM in the TCC software or DCM in the DICTRA software) containing all kinds of commands can be executed with the TCC/DICTRA user interface as if the commands are given interactively. Such a MACRO file can be created initially as a log file (through the SET_LOG_FILE command in the SYS Module), and is editable using any textual editor (such as NotePad, Emacs, PFE). Several levels of MACRO files can be used in a single run of the TCC/DICTRA software, which makes it very easy and convenient to conduct many calculations (with similar or totally-different settings) at once. A MACRO file can also be built in a way that the TCC/DICTRA software will interact with the user by asking questions and using the answers in various other parts/steps. For more information see the MACRO_FILE_OPEN command in Chapter 14 - System Utility Module (SYS) in the TCCR User’s Guide.

### 4.1.14 Modularity

The Thermo-Calc software system consists of several basic application programs and modules that utilize the thermochemical database, make the calculations and optimizations, and present the results in various forms. There are also a couple of so-called special, or easy-to-use, modules designed for specific types of calculations and simulations (such as binary diagrams, ternary diagrams, potential diagrams, solidification simulations, Pourbaix diagrams and other property diagrams). These special modules require only answering some simple questions on system definitions and calculation settings. In the next section, and in Chapters 5 through 15 in the TCCR User’s Guide, comprehensive descriptions will be given on such basic and special modules.

Each basic module has a specific purpose that simplifies the addition of new modules and the improvement of existing ones. Each module has its own prompt (e.g., SYS, TDB, GES, TAB, POLY_3, POST, PARROT, ED_EXP), displayed whenever the system is expecting the user to give a new command. The menus of each module are different, while some of them might be common or similar.

There are two specific commands related to the modular structure, which are in all the modules. One command is GOTO_MODULE, which uses the name of a module as its parameter, and transfers the program to the specified module. Two exceptions: the POST and ED-EXP modules may only be entered as commands in the POLY and PARROT modules, respectively. It is therefore unnecessary to use the GOTO_MODULE command to access, because it is impossible to directly access to the POST and ED-EXP modules from any module other than POLY and PARROT.

The other specific command is BACK, which always switches back to the most recent module. This command also works in the POST and ED-EXP modules, but the connection is only one-way for the reason explained above.

### 4.2 Modules in TCC

The basic and special modules in the menu-driven TCC (Thermo-Calc Classic) software are summarized in the Table 5.

The TCW (Thermo-Calc Windows) software has a GUI-driven user interface, while some of the TCC basic and special modules (e.g., TDB, GES, POLY, BIN, TERN, SCHEIL, POST) have also been implemented into the TCW software, in an implicit way that certain TCC basic/special modules are connected with specific TCW sub-windows (modules) for various definitions in calculations/simulations. For the details of TCW sub-window/module structure, please refer to the TCW 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
Thermo-Calc User Interface and Modules

Thermo-Calc 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.

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

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

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 TCC software. One should instead use the PARROT module to perform critical thermodynamic assessments.
Within the Thermo-Calc (TCC/TCW) software, all modules share a global data area with thermodynamic data, and internally connect with each other.

### 4.2.1 Basic modules

All the TCC basic modules are command-line based and require that comprehensive understanding of the chemical systems under investigation is essential to appropriately perform executions of such modules. The following paragraph briefly describes the basic modules' functions:

The TDB module allows selecting an appropriate database and defining a chemical system, and reads from the database into the global data area. The GES module allows interactively access to models, and enter, list or amend data. The POLY module permits setting the temperature-pressure-composition conditions and calculates equilibria and phase diagrams. The POST module can plot various phase diagrams and property diagrams resulting from equilibrium calculations. The TAB module allows tabulations of thermochemical properties for substances (being either stoichiometric or solution phases) or chemical reactions under certain conditions. The PARROT module can fit thermodynamic (and kinetic, in the DICTRA package) model parameters to available experimental data. The ED-EXP module can help editing experimental data points in order to make a reliable optimization. The SYS module is used for interactions with various operating systems, and for creations and executions of MACRO files.

### 4.2.2 Special modules

All the TCC special modules (except for REACTOR) are question-line based and easy-to-use modules. The user needs just to specify the chemical system and problem by answering some simple questions. The modules automatically select data, set all the system definitions and conditions, make the equilibrium calculations and simulations, define the plotting variables, plot and export the desired phase diagrams and property diagrams.

The BIN and TERN modules are for calculation of binary and ternary phase diagrams. These two modules require special designed databases (such as PBIN, SBIN and PTER) with information about the respective diagrams. The POT module allows quick calculation and plotting of a ternary system at a given temperature with the potential of two gas species as axes. The SCHEIL module simulates solidification processes with no diffusion in the solid phases or with back diffusions of interstitial components (such as C, N, O, S, etc.), and is often more realistic than equilibrium solidification. The POUBAIX module calculates pH-Eh diagrams (the so-called Pourbaix diagrams) and property diagrams for heterogeneous interaction systems involving aqueous solutions. Other easy-to-use modules for specific purposes will most likely be implemented into the Thermo-Calc package in the near future.

Another special (but command-line based) module REACTOR is unfortunately less user-friendly module, which allows simulations of chemical reaction processes in several steady-state stages where the input in one stage is dependent on the output of another or in several dynamic stages where time becomes a dependent parameter.

Users may also write their own application modules or programs using the facilities of the available basic modules. This requires rich experience of using the Thermo-Calc package and skill in application-oriented programming. For programming guides and examples, please refer to the manual sets of the programming interfaces TQ, TCAPI and TC MATLAB Toolbox.

### 4.2.3 Interactions between the user and the modules

Unlike within the TCW (Thermo-Calc Windows) software that is completely GUI-driven and usually presents the preferred choice for beginners and for occasional-users, both the TCC (Thermo-Calc Classic) and DICTRA software are designed in a menu-driven and command-line structure, and thus require users to directly interact (typing commands) with various basic and special modules for various purposes (calculations, simulations, or assessments).

As mentioned in Section 4.1 (TCC User Interface), many great efforts (such as clear modular structure, common structure for user interactions, command abbreviations, command history, MACRO facility, directory
sorting, default values for parameter inputs, on-line help and information, error message handling, control characters, private files) have been enforced, which on one hand make user interaction much easier and convenient, and on the other permit calculations/simulations very flexible and efficient. Especially the MACRO feature, either on a single-layer or at multiple levels, is extremely user-friendly, powerful, effective and convenient, which tremendously simplifies calculation/simulation routines and post-processing procedures, within the TCC and DICTRA software.

Application programming interfaces can dramatically extend the thermochemical tools and facilities in various R&D activities.

*Figure 5* illustrates the interactions between a user and various modules of the Thermo-Calc package.
4.3 Graphical User Interface of Thermo-Calc

The TCC (Thermo-Calc Classic) software 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, TCC 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 interface (i.e., 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 Windows, the complete GUI-driven Thermo-Calc

Since the TCC version N, a fully implemented GUI version of the Thermo-Calc software/database system, i.e., Thermo-Calc Windows, TCW, has been in parallel developed for Windows environments (XP/2000/NT4). TCW is really easy to learn and permits all types of Thermo-Calc calculations.

Beginners find the TCW program very straightforward to use (Figure 6). Complex equilibrium and phase diagram calculations can be performed, by just clicking on buttons and menus with the mouse without needing to remember the TCC commands!

Figure 6. TCW -- The Easiest Way to Interact with Thermo-Calc (an example)

The first version of TCW (as TCW1 released in June 2000) had a somewhat reduced functionality, but since the second version (as TCW2 released in November 2002) it has been extensively expanded features and improved functionality. The current version TCW4 (released in May 2006, which is compatible with TCCR) has many further improved features (please refer to TCS Newsletter No. 32). Some of the functions not yet implemented
in this specific version are: optimization (i.e., PARROT and ED-EXP modules) and some special modules (e.g., POURBAIX, REACTOR, etc.). However, these functions and special modules will be implemented into forthcoming releases of TCW. The flexibility will be improved without reducing the user friendliness, to finalize a complete TCW version including all the TCC functionality. This general GUI-driven version for UNIX and Linux environments are also under development. For the details and examples of running the TCW4 software, please refer to the TCW4 User’s Guide and TCW4 Examples Book.

4.3.2 Thermo-Calc Graphs in 3D

Since TCC version P, 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) and alternative viewers listed at the VRLM Repository at www.web3d.org (Wed3D Consortium). In some browsers, it is needed to set correct background color 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 7 shows an example on how a Thermo-Calc diagram is viewed in 3D by a VRML web browser. For more information, please refer to Section 9.7 in the TCCR User’s Guide.

![Thermo-Calc Graphs in 3D Viewed by a VRML Web Browser.](image)
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 8). 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-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 9).

The TC-toolbox implemented recently 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 8. Programming and Graphical Interfaces of the Thermo-Calc Engine
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., $G$, $H$, $S$, $U$, $C_p$; $\Delta G$, $\Delta H$, $\Delta S$, $\Delta U$, $C_p$; and so forth), derivatives of state functions (e.g., $\frac{\partial G_m^0}{\partial x_j}$, $\frac{\partial^2 G_m^0}{\partial x_j \partial x_k}$), 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., PC Windows XP/2000/NT4, PC Linux and UNIX platforms (Solaris, SGI, etc.). Its most current version TQ6 is compatible with the TCCR/TCW4 software.
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 PC Windows XP/2000/NT4 and Linux environments. Its most current version TCAPI4 is compatible with the TCCR/TCW4 software.

To be able to run a user-written TQ6/TCAPI4 interfaced application program, it is necessary to have the TCCR or TCW4 software/database package installed on the same computer or server, because the programming interface must interact the Thermo-Calc Engine for all kinds of thermodynamic and equilibrium calculations.

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 T0-temperature using the TQ interface, is demonstrated below:

```c
C ... A number of lines initialising the program
C ... Do the calculation from minimum carbon content (Xmin) to maximum carbon 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) 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 10.

**Figure 10. 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 recrystallisation can be studied. It has been linked to Thermo-Calc using the latest version of the TQ4. Using this version of the TQ interface, basically any thermodynamic or kinetic information as available in Thermo-Calc and/or DICTRA can be incorporated into your application software. The TQ interface provides MICRESS with a reliable basis for treating complex thermodynamic and kinetic behaviors in multicomponent alloys. For more information, please visit [www.access.rwth-aachen.de](http://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. TCW and TC-Toolbox is 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 are 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 11 gives a simple example of using the TCAPI interface.

![Figure 11. A Simple Example of Using the TCAPI Interface](image-url)
Another but very much advanced application example using the TCCPI 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 12.

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 uncertainty 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 12. An Advanced Example of Using the TCAPI Interface: PrecipiCalc**

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.
5.3 Development of Thermo-Calc Toolboxes in Other Software

Since the Thermo-Calc version M, there has been a TC MATLAB Toolbox in the well-known and widely used MATLAB® software package for specific applications (Figure 13). Its most current version (v4) is compatible with the TCCR/TCW4 software.

Using the Thermo-Calc engine (with DICTRA extension) and linking it to the TCAPI programming interface, the TC MATLAB Toolbox can be utilized for materials property calculations, materials process simulations and even materials engineering controls.

![Figure 13. The TC MATLAB Toolbox in the MATLAB® Software Package](image)

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.

In the current version of the TC MATLAB Toolbox more than 50 commands 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 15-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.

Similar to the situation for the TQ and TCAPI programming interface, it is necessary to have the TCC or TCW software/database package installed on the same computer or server in order to run the TC MATLAB Toolbox in such a third-party software package. The toolbox calls the Thermo-Calc Engine for all kinds of thermodynamic and equilibrium calculations.

Further implementation of such toolboxes into other third-party software packages will probably occur in the near future.
Figure 14 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 14. Liquidus Surface of the A-B-C System Calculated and Plotted Using the TC MATLAB Toolbox in the MATLAB® Software
Figure 15 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 $R_{0.2}$, $R_{m}$ and $A_{p}$ 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 reasonably 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.

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.

![Figure 15a. 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.](image)

![Figure 15b. 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.](image)
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

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 (Central Iron & Steel Research Inst.), 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/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, 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

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

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>
<thead>
<tr>
<th>Materials-oriented</th>
<th>Industry-oriented</th>
</tr>
</thead>
<tbody>
<tr>
<td>steels (incl. SS, HSLA, HS, CI, etc.)</td>
<td>steel-making industries</td>
</tr>
<tr>
<td>alloys (Al-/Ti-/Ni-/Mg-based &amp; others)</td>
<td>alloy/superalloy productions</td>
</tr>
<tr>
<td>hard materials (carbides, nitrides, etc.)</td>
<td>cutting equipment, heavy/precision instrument</td>
</tr>
<tr>
<td>ceramics</td>
<td>automotive and aerospace industries</td>
</tr>
<tr>
<td>melts, slags</td>
<td>powder-/hydro-metallurgy industries</td>
</tr>
<tr>
<td>salts, glasses</td>
<td>lighting equipment</td>
</tr>
<tr>
<td>semi-/super-conductors</td>
<td>electronic components</td>
</tr>
<tr>
<td>gases, sub-supercritical fluids</td>
<td>energy transfer and utility, combustion</td>
</tr>
<tr>
<td>aqueous solutions</td>
<td>environmental protection, solution separation</td>
</tr>
<tr>
<td>earth materials</td>
<td>mining industries (diamond, gold, petroleum, …)</td>
</tr>
<tr>
<td>nuclear materials</td>
<td>nuclear fuel and waste management</td>
</tr>
<tr>
<td>solders</td>
<td>building engineering, chemical engineering</td>
</tr>
<tr>
<td><strong>other inorganic materials</strong></td>
<td><strong>recycling, sintering, incineration</strong></td>
</tr>
<tr>
<td>organic substances</td>
<td>food production, fat formation</td>
</tr>
</tbody>
</table>

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

- Calphad
- Journal of Phase Equilibria & Diffusion (previously “Journal of Phase Equilibria”)
- Metallurgy and Materials Transactions (A and B)
- Acta Metallurgy
- Z Metallkd.
- 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 *TCCR Examples Book* and *TCW4 Examples Book*.

Moreover, the two flexible application programming interfaces (namely TQI and TCAPI) and the thermodynamic calculation toolbox (TC-Toolbox in the MATLAB® software package), 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.