Thermodynamic Modeling of High-Temperature Systems

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ABSTRACT

An outline of thermodynamic modeling of high-temperature systems is presented, including a historical introduction. There is no intention to provide a complete history of thermodynamic modeling, so neither vapor-liquid equilibria nor the thermodynamics of non-ideal solutions is discussed. This article reflects the author's personal vision of the state of the art.

Keywords: thermodynamics, modeling, equilibria

Introduction

Methods of computational thermodynamics have been successfully used for the investigation of various processes, and for the development of new technologies for many years. There is no need to prove the practical value of the calculation of equilibrium composition and properties of thermodynamic systems. A number of examples illustrating how thermodynamic calculations may be used as a basic tool in the development and optimization of materials and processes are presented in the excellent book by Hack.[1]

Some fields of science and technology where thermodynamics works best are:

- development of the new high-temperature technological processes,
- the optimization of chemical processes, including synthesis of refractory materials and materials for microelectronics,
- examination of the stability of materials at high temperatures and in various media,
- investigation of the chemical processes occurring in power-generating facilities, including nuclear plants,
- the optimization of the use of raw materials,
- waste management,
- the study of the emissions of burning products and industrial exhaust gases into the atmosphere,
- development of processes to reduce environmental pollution, and
- investigation of the processes of mineral genesis, formation of the atmospheres of planets and of stars, as well as other geo- and astro-chemical processes.

Thermodynamic Modeling

The basic concept of thermodynamics is thermodynamic equilibrium. Thermodynamic equilibrium is some final state of a thermodynamic system isolated from the external medium (i.e., thermal, mechanical and chemical equilibrium exists at each point of the system and there are no flows). In practice, the requirement of isolation means that the processes leading to equilibrium occur faster than any changes on the system's boundaries (local equilibrium hypothesis). Such external changes include changes of pressure, temperature and chemical composition, etc. For example, when the thermodynamics of a combustion process is studied it is common to assume adiabatic conditions (i.e., heat losses are not taken into consideration). When the processes in a chemical reactor are modeled the common assumption is that the rates of chemical reactions are much higher than the velocity of flow, and consequently, that chemical equilibrium is reached while the part of flow is in the reactor. There is much evidence that the equilib-

rium model is valid for high temperature processes (T > 1500 K) or when there is sufficient time to reach equilibrium. Two extreme examples of equilibrium systems are combustion processes in a rocket engine chamber, where equilibrium is reached in approximately 0.00001 s, and some parts of the earth's crust where millions of years are required to reach equilibrium. On occasion, another, less restrictive, hypothesis is used, which assumes partial equilibrium in the system. According to this hypothesis, full chemical equilibrium cannot be reached because of the slow rates of several reactions, nonetheless it can be reached partially because other chemical reactions are sufficiently fast.

The most popular models for the investigation of high-temperature systems and processes are based on the hypothesis of an ideal system. These models assume that the behavior of the gas phase may be described by the ideal gas equation of state and that all mixtures in the system may be treated as ideal. However there are many thermodynamic systems that cannot be adequately described by ideal models. Examples include combustion processes in a closed volume, detonation processes, many metallurgical processes, and so on. To investigate such processes the researcher should use more realistic thermodynamic models that take into account intermolecular forces and other physico-chemical effects in gaseous and condensed phases. Unlike the universal ideal model, most non-ideal models may be applied only for the investigation of specific systems in a narrow range of pressures and temperatures. The main problems are the parameters of the model and the range of application. In some cases it is possible to find relatively universal non-ideal models. An example would be the calculation of equilibrium composition and properties of combustion products at moderately high pressure (up to 600 MPa) using real gas equations of state.[2] A literature review shows that progress in thermodynamic modeling now depends mostly on the development of new, more realistic models that are well-founded theoretically, and ways of obtaining the parameters needed for these models.

The components of a thermodynamic model are:

- two thermodynamic parameters and their values that specify thermodynamic equilibrium;
- a list of chemical elements and their amount in the system;
- a list of the substances that make up the system;
- the thermodynamic properties of those substances;
- equations of state of the phases, and, primarily, the equation of state of the gas phase;
- distribution of substances among possible phases, and the possible existence of condensed phase solutions;
- assumptions concerning the behavior of the condensed solutions if there are any (models of solutions with their parameters); and
- additional constraints that restrict the assumption of equilibrium.

The results of modeling depend on many parameters. Software for thermodynamic modeling is now usually supplied with a database of thermodynamic properties of substances. The list of substances included in the system is determined mostly by the content of the corresponding database. The question of the quality of thermodynamic data is often not taken into account. However, variation of the heat of formation of a substance in the system may have a significant effect on the results of calculations. There is very often some conflict between the number of substances that can be included in the system and the quality of the data available for their thermodynamic properties. One can say that it is equally unreasonable to use either too small a list of substances with reliable thermodynamic properties, or an extensive list of substances with unreliable properties.

Often the question arises—can we believe the results of modeling? There is no definite answer to this question.

The best way to address the question is to compare the results of the calculations with experimental data where possible. The researcher should have answers to the following questions:

- Is there thermodynamic equilibrium in the system under examination?
- Are the components used in the model valid?

Sometimes the specific behavior of the system caused by the *chemical kinetics* of the processes can be taken into account by the exclusion of some substances from the system if one knows from experiment or theory that these substances cannot be formed. Another possibility is the assignment of concentrations for one or several substances, if that can be justified.

One may conclude that thermodynamic modeling is simultaneously a science and an art. The researcher should have a "feel" for the system that he or she is investigating.

Historical

The famous study by Gibbs[3,4] in the 1870s provided the theoretical background for thermodynamic examination of complex chemically reacting systems. Lewis and Randall's remarkable book,[5] published in 1923, provided the bridge from theory to practice, but until the development of digital computers there were no really appropriate instruments for thermodynamic modeling. Brinkley and Kandiner[6,7] developed one of the first algorithms for the calculation of equilibrium composition. The algorithm described by these authors used equilibrium constants. White et al.[8] introduced another algorithm, based on the minimization of the Gibbs free energy, in 1958.

Zeleznik et al.[9] at NASA developed the first "industrial" computer program, supplied with a database of thermodynamic properties of substances. A similar program was also developed in Russia.[10]

The intensive development of thermodynamic modeling was driven by the need to produce better rocket engines. It would have been impossible to create modern rocket engines without preliminary theoretical investigations of the combustion processes and of the expansion of the combustion products, where hundreds of simultaneous chemical reactions occur.

The next stage in the development of thermodynamic modeling is linked with metallurgy. Traditional metallurgical chemistry was based on investigation of the leading (or dominant) reactions. This approach is very unreliable, as variation of parameters such as the temperature, pressure, or composition of the reacting system often changes the dominant reactions. As a result, computational thermodynamics appeared helpful for the examination of metallurgical processes.[11–13]

The book by Siniarev et al.[13] contains FORTRAN source codes of a powerful computer program for the calculation of complex chemical equilibrium, developed by Trusov (Bauman Moscow State Technical University). Today, there are hundreds of algorithms and computer programs intended for the calculation of equilibrium composition of thermodynamic systems. Detailed reviews have been presented in various books.[14–16]

Smith and Missen's book[16] also contains FORTRAN and BASIC source codes for the calculation of complex chemical equilibria.

There are several reasons for the existence of so many algorithms. The most significant is the great variety of thermodynamic systems, ranging from combustion processes to the processes in the earth's crust. Parameters of most thermodynamic models are known only for a small group of substances. The situation is complicated by the fact that the relationship between the equilibrium composition and the parameters of the model is non-linear. The phase composition of the equilibrium system is usually unknown *a priori* and must be found during the calculation. Hence the target function is not continuous but can have disruptions at the phase transition points, which causes some difficulty in solving the problem. One should also take into account the limitations of the computer, which can accomplish calculations only with a limited number of significant digits. Therefore, even if mathematics guarantees the solution for some algorithm, the computer version of that algorithm will fail in some cases. Besides, as noted by McKinnon and Mongeau,[17] the phase and chemical equilibrium problem is atypical of many optimization problems. The aim is not so much to obtain a solution with an objective value that is close enough to the optimal objective value, as is usually the case when the objective function has an economic interpretation. Rather,

the aim is to find a solution sufficiently close to the optimal solution that the phase and chemical composition correspond to the equilibria found in nature.

Calculation of the equilibrium composition of the system may be accomplished through the solution of a set of the non-linear equations. The questions of existence and uniqueness of the solution are reviewed in many literature sources.[16] It is shown that if the gas phase behavior is described by the ideal gas equation of state and the condensed mixtures are ideal, the target function is convex and a unique solution usually exists. However, this is not so in the general case when non-ideal models are used in calculations.

Thermodynamic and Thermochemical Properties of Individual Substances

The basis of any serious computer system intended to accomplish thermodynamic modeling is a database of thermodynamic properties of individual substances. The main sources of this information are reference books.[18–20]

Belov et al.[21,22] discuss the problems concerning the quality of thermodynamic data. These references also contain information about other sources of data.

IVTANTHERMO for Windows

Over many years researchers at the Thermocenter of the Russian Academy of Science performed a theoretical study of thermodynamic properties of individual substances and compiled this information in the form of a reference book and a database called IVTANTHERMO. This information is intended for practitioners of various branches of science and engineering, and it must be delivered to them in a practical and easy-to-handle form.

The most important characteristic feature of IVTANTHERMO is that the stored information is not borrowed from any other databases or reference books but was obtained by critical analysis and treatment of original data available in the primary literature. Information analysis and all necessary calculations have been performed with the use of original methods, algorithms and software developed for the *Thermodynamic Properties of Individual Substances* handbook[18] and brought up to date by its authors for the IVTANTHERMO database. Presently the database contains information on approximately 2500 substances, formed by 96 chemical elements.

The software package IVTANTHERMO has been developed to enable researchers and engineers to investigate a wide range of thermodynamic systems. Recently a new version of the software appeared, which consists of six programs and the database of thermodynamic properties of individual substances. The software has an intelligent interface, which does not require the user to have special computer knowledge. All six programs with the database represent one software suite—IVTANTHERMO for Windows. These programs are:

THERBASE provides access to all information about substances stored in the database: substance formula and name, heat of dissociation or sublimation for each substance, standard enthalpy of formation, heat capacity, entropy and enthalpy in standard state, nuclear spin, and coefficients of the approximating polynomials for the thermodynamic properties. It allows the user to review the contents of the database, extract information about substances, modify this information, add new information, examine thermodynamic properties of chemical reactions, and to carry out a quick search for a given substance or group of substances. THERBASE can display information as TPIS and JANAF tables, save it into a text file and display it as charts.

EQUICALC allows the calculation of the equilibrium composition and related thermodynamic properties of complex chemically reacting systems. EQUICALC can handle simultaneously up to 700 substances, up to 60 single-component phases and one or two condensed mixtures along with the gas phase. A new algorithm of the calculation of equilibrium parameters has been developed specially for the Windows version. EQUICALC can also display the results of calculations as charts or extract some of them into the table. Not only does the program accomplish the traditional calculations for assigned pressure or volume and temperature val-

ues, but it can also handle assigned values of (p, H), (p, S), (U, V), (S, V), etc. It permits the determination of the composition of combustion products at constant pressure or volume even if the gas phase is absent.

DATANAL is a tool for statistical analysis of the data stored in the database. It may help to elicit correlations among thermodynamic properties of substances stored in the database. It is known that some interdependence exists among chemical and physical properties of substances. However, the laws of this interdependence are not yet well investigated. DATANAL can help to estimate some unknown properties, or verify existing ones, by examination of the information stored in the database.

HB allows the computation of heat, material and temperature balances between given sets of the source components and reaction products, provided that the temperature and quantity of each input and output component is known.

APPROX is intended for the calculation of the coefficients of an approximating polynomial for a given set of heat capacity and temperature values, provided the values of thermodynamic parameters in the reference state and the heats of the phase transitions are known. Results of calculations may be saved into a text (ASCII) file or written into the IVTANTHERMO database. It is possible also to 'construct' a polynomial different from that adopted in IVTANTHERMO and calculate its coefficients. One can say that this program is a complement for THERBASE.

REPORTER is a service tool that allows the user to view the text files and print them.

More detailed information about IVTANTHERMO for Windows may be found in references 23 and 24.

Thermodynamic Data and Thermodynamic Property Calculation Sites on the Web

The growth of the Internet and the World Wide Web marks a new stage in the development of thermodynamic modeling. One can now use remote computers for the calculations. However, stand-alone computers still have their place, and it is more convenient to have one's own software on the table.

Listed below are references to some interesting internet sites where thermodynamic and thermochemical information can be found. Inevitably, the list is incomplete and contains only those references that the author has managed to find. The brief descriptions are borrowed from the original sites.

Chemical WorkBench[25] is a simulation software tool intended for modeling, optimization and design of a wide range of industrially, environmentally or educationally important chemistry loaded processes, reactors and technologies. The software package is a chemistry-centered, desktop simulation environment for detailed, user-friendly, complete-cycle physicochemical modeling of the chemically related processes, reactors and technologies. Chemical WorkBench is a well-furnished suite of software tools that enables researchers and engineers to model the "virtual prototypes" of chemically active systems and to simulate their operation behavior before detailed engineering and physical prototyping. Its most attractive feature is the possibility to simulate a complicated process by means of chains of reactors, each of which models some defined part of the process. There are not only ideal and non-ideal equilibrium thermodynamic reactors available, but also non-equilibrium reactors that take into account chemical kinetics, such as plug-flow reactor, calorimetric bomb, well-stirred reactor, etc. The researcher can combine these reactors on the virtual workbench, define links among them, set input species and parameters, accomplish calculations and visualize the results of modeling.

NIST WebBook provides access to thermochemical data for over 6000 organic and small inorganic compounds,[26] enthalpy of formation, enthalpy of combustion, heat capacity, entropy,

phase transition enthalpies and temperatures, and vapor pressure; reaction thermochemistry data for over 9000 reactions: enthalpy of reaction and free energy of reaction. You can search for data on specific compounds in the Chemistry NIST WebBook based on name, chemical formula, CAS registry number, molecular weight or chemical structure.

CEA[27] is the famous NASA program that calculates chemical equilibrium product concentrations from any set of reactants and determines thermodynamic and transport properties for the product mixture. Built-in applications include calculation of theoretical rocket performance, Chapman-Jouguet detonation parameters, shock tube parameters, and combustion properties. Associated with the program are independent databases with transport and thermodynamic properties of individual species. Over 1900 species are contained in the thermodynamic database.

MTDATA[28] is a software / data package for the calculation of phase equilibrium in multicomponent multiphase systems using, as a basis, critically assessed thermodynamic data. It has numerous applications in the fields of metallurgy, chemistry, materials science, and geochemistry depending on the data available. Problems of mixed character can be handled, for example equilibrium involving the interaction between liquid and solid alloys and matte, slag and gas phases. The thermodynamic models necessary to describe the properties of a wide range of phase types are incorporated in the software and database structures.

MALT2[29] is a comprehensive *ma*terials-oriented *l*ittle *t*hermodynamic database for personal computers. The task group of the thermodynamic database was organized in the Japan Society of Calorimetry and Thermal Analysis. MALT2 stores thermodynamic data such as the standard enthalpy change for formation, ΔH_f (298.15 K), the standard Gibbs energy change for formation, ΔG_f (298.15 K), the standard entropy, S(298.15 K), the heat capacity, C_p, and the transition temperature and the enthalpy change for transition, if any, for approximately 5000 species. This covers those compounds important to ceramic materials, semiconductors, inorganic / organic gases for plasma processes in semiconductors, transition metal oxides, nuclear fuels, nuclear reactor materials, etc. From such stored data, the thermodynamic tables and the equilibrium constants at any temperature can be calculated. In addition, molecular mass, coefficient of heat capacity equation, and references for data can be also available.

HSC Chemistry[30] was produced by Outokumpu Research Oy. However, many of the important calculation options are based on code and ideas from other sources. The aim of this software is to simulate chemical reaction equilibrium and processes in the personal computer, to develop new processes, and to improve old ones. HSC Database is a compiled database on thermodynamic properties of individual substances. The number of species in the database is more than 15,000.

These data are not critically evaluated, but the database gives fast access to data and provides references to the literature. The database also has fields for structural formula, chemical name, common name, CAS number, melting point, boiling point, color and solubility in water. The data in these fields are not yet complete but even now they can help, for example, to identify organic substances.

EQS4WIN[31] is a powerful and easy-to-use software package that solves a wide range of problems related to the calculation of the reaction and phase equilibrium composition of complex chemical systems. EQS4WIN incorporates up-to-date technology in numerical analysis, programming, and thermodynamics. It was written under the supervision of Smith, senior author of a classic text in the field (see reference 16). EQS4WIN solves equilibrium problems by minimizing the overall Gibbs free energy of systems involving up to 4 multi-species ideal-solution phases (a gas phase and up to 3 condensed liquid or solid solutions) and any number of pure (condensed) phases. Calculations can be performed for several different types of thermodynamic conditions, either at a single state point, or for up to two simultaneously varying parameters. All versions of EQS4WIN incorporate a thermochemical database based on the species listed in the JANAF Tables.

Thermo-Calc[32] is a software package for equilibrium and phase diagram calculations. It can be applied to any thermodynamic system in the fields of chemistry, metallurgy, material science, alloy development, geochemistry, semiconductors, etc. depending on the kind of database it is connected to. It can also be used as a subroutine package in application programs, for example in phase transformation or process simulations. Thermo-Calc consists of modules for the various tasks the user may wish to perform. There are modules for the selection of database and data, for listing thermodynamic data or interactive manipulation and entering of such data. The most important module for equilibrium calculation together with its post processor makes it possible to calculate and plot diagrams of many different types on all kinds of devices. A useful facility in Thermo-Calc is the module for assessment of experimental data in terms of thermodynamic models. There is also a module for tabulation of data for substances or chemical reactions. The user may also develop and add their own modules by using a documented software interface. With Thermo-Calc one may simulate processes where the time-dependence can be ignored, for example by stepwise calculation of a sequence of equilibria with transfer of heat and matter between the equilibria.

F*A*C*T, which stands for *F*acility for the *A*nalysis of *C*hemical *T*hermodynamics, is a fully integrated thermochemical database that couples software for thermodynamic modeling with critically assessed thermodynamic data. Originally developed as a research tool for chemical metallurgists, F*A*C*T is now employed in many diverse fields of chemical thermodynamics by chemical engineers, corrosion engineers, organic chemists, geochemists, ceramists, electrochemists, etc. Information about F*A*C*T databases as well as many references to similar web sites in inorganic chemical thermodynamics may be found at reference 33.

FactSage is an amalgam of two older programs—ChemSage (GTT Technologies) and FACT-Win (Thermfact). Decades of calculations by hundreds of corporate and academic users have led to a reliable tool that quickly converges to the correct equilibrium state. FactSage includes many non-ideal solution models. These models can be used to describe non-ideal gases, brines, alloys, salts, slags, mattes, alloys, and non-stoichiometric solids. FactSage solution models cover temperatures up to 6,000 K and pressures up to 1 Mbar. FactSage includes pure substance / solution databases from either F*A*C*T or SGTE (Scientific Group Thermodata Europe).[34] Each includes data for over 3,300 pure compounds. The F*A*C*T Solution Database is strong on inorganic oxides, sulfides and salts. The strength of the SGTE Solution Database is metals and alloys. Hundreds of custom databases prepared originally for ChemSage are also available. Custom files to meet specific needs can be supplied. The contents can be searched in detail on the GTT Technologies web site.[35]

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