

Computational thermodynamics: A mature scientific tool for industry and academia*

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Abstract: The paper gives an overview of the general theoretical background of computational thermochemistry as well as recent developments in the field, showing special application cases for real world problems. The established way of applying computational thermodynamics is the use of so-called integrated thermodynamic databank systems (ITDS). A short overview of the capabilities of such an ITDS is given using FactSage as an example. However, there are many more applications that go beyond the closed approach of an ITDS. With advanced algorithms it is possible to include explicit reaction kinetics as an additional constraint into the method of complex equilibrium calculations. Furthermore, a method of interlinking a small number of local equilibria with a system of materials and energy streams has been developed which permits a thermodynamically based approach to process modeling which has proven superior to detailed high-resolution computational fluid dynamic models in several cases. Examples for such highly developed applications of computational thermodynamics will be given. The production of metallurgical grade silicon from silica and carbon will be used to demonstrate the application of several calculation methods up to a full process model.

Keywords: complex equilibria; Gibbs energy; phase diagrams; process modeling; reaction equilibria; thermodynamics.

INTRODUCTION

The concept of using Gibbsian thermodynamics as an approach to tackle problems of industrial or academic background is not new at all. Its early applications go back to the beginning of the 20th century, however, mostly on the basis of investigating stoichiometric reactions. Only the later development of Gibbs energy models for non-ideal condensed solutions, the collection of comprehensive databases, and the development of computer code for the calculation of complex equilibria, which have all taken place in the second half of the 20th century, have led to what we now call “computational thermodynamics”. Current thermodynamic databanks cover fields for many classes of substances ranging from organic and biochemical systems to various inorganic and metallurgical materials. Accurate theoretical studies of the phase stability and equilibria of systems with a great number of chemical components can be made. Recently, new algorithms have emerged, which also facilitate modeling of time-dependent dynamic changes in multiphase systems.

In order to fully understand what computational thermochemistry is all about one needs to go back to the work on thermodynamics done in the 19th century. One hundred and thirty-five years ago,

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the essence of thermodynamics was summarized by Josiah Willard Gibbs in his famous publication *On the Equilibria of Heterogenous Substances* [1]. In this work, he gives what we rightly now call fundamental equations, which link a set of thermodynamic potentials with their conjugate extensive properties.

Equation 1 gives the relationship for temperature, pressure, and composition as the independent variables.

$$dG = S dT + V dp + \sum \mu_i dn_i + \sum z_j F \phi_j dn_j + \sum \sigma_k dA_k + \dots = 0 \quad (1)$$

Gibbs already noted that for another set of independent variables, e.g., S , V , and n_i , one would obtain another fundamental equation, this time for the internal energy U as the overall function. The method to change from $G(T, P, n_i)$ to $U(S, V, n_i)$ is mathematically a Legendre transformation. In other words, what are now called the Maxwell relations between the different fundamental functions were already described by Gibbs.

The major contribution of Gibbs in this equation is the introduction of the new potential, which, multiplied with the amount variable (number of moles), gives an energy just as the pairs entropy and temperature as well as volume and pressure do. He called it *chemical potential*. However, it should also be noted that he already discussed the contributions from electrical work and surface work, thus opening the door to electrochemistry and introducing surface tension in a special chapter of his work on capillary forces. Gibbs also discussed the relationships of phase equilibria in terms of diagrams of the form which we would now call phase diagrams. In summary, the relations between the different basic properties and the mathematical methods discussed in Gibbs paper(s) can be depicted in the schematic diagram in Fig. 1.

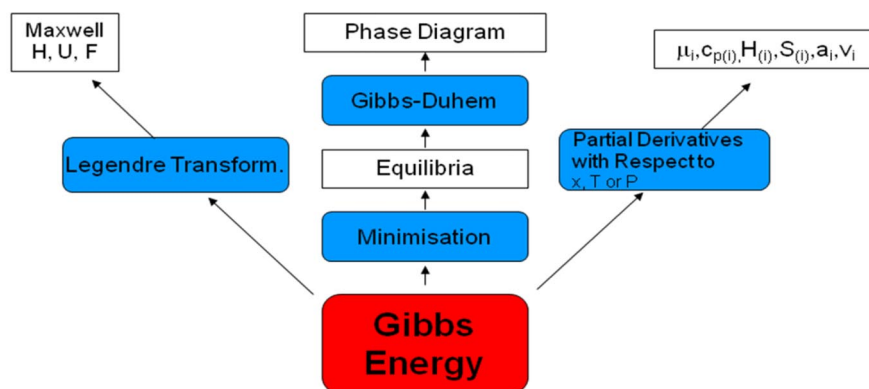


Fig. 1 Gibbs energy tree.

One could say that with Gibbs work everything was there that is needed to get started with computational thermodynamics, except computers. Fortunately, it did not take until the invention of computers that Gibbs' new concept was used by the chemists.

Leaving the fact of the missing computers aside, it was nevertheless possible to apply the new principles if one decided to simplify the method of handling the composition dependence of the Gibbs energy of a system. This led to what one could call *reaction thermodynamics*. If one assumes the predominance of a single reaction equation in a chemical system, for example, $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$, then the composition dependence, i.e., the change of Gibbs energy dG by the change of amounts of the chemical species dn_{H_2} , dn_{O_2} , and $dn_{\text{H}_2\text{O}}$ can easily be expressed by the change of a new single variable ξ , the extent of reaction. With the constant stoichiometric coefficients of the species as given in the reaction equation, one obtains: $dn_{\text{H}_2} = -1 d\xi$, $dn_{\text{O}_2} = -1/2 d\xi$, and $dn_{\text{H}_2\text{O}} = 1 d\xi$ for a small change in extent of

reaction $d\xi$ (taking into account that reactants are counted negative and products positive). Thus, the change in Gibbs energy for the present case is $dG = (\mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2} - \frac{1}{2}\mu_{\text{O}_2})d\xi$. From this follows directly $dG/d\xi = 0$ because a minimum of the Gibbs energy has to be found for equilibrium to be obtained. Note that the variable ξ can be dropped immediately after this step, because it follows then that the stoichiometric sum of the chemical potentials, the Gibbs energy change, is ZERO: $\Delta G = \mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2} - \frac{1}{2}\mu_{\text{O}_2} = 0$. From this one obtains with $\mu = \mu^\circ + RT \ln a$ (μ° being the reference chemical potential and a the chemical activity of a species) the well-known Law of Mass Action: $\Delta G^\circ = RT \ln K$ with $K = \exp(-\Delta G^\circ/RT) = a_{\text{H}_2\text{O}}/(a_{\text{H}_2} \cdot a_{\text{O}_2}^{1/2})$.

It should be noted that Guldberg and Waage [2] discovered this relationship between what they called the “active masses” experimentally and reported it in 1864, just before the theoretical work of Gibbs. It took in fact until 1923 when de Donder [3] properly introduced reaction affinity and the concept of extent of reaction. However, in the years before Raoult had found (1878) [4] that under certain conditions activity could be replaced by mole fraction, van't Hoff had realized (1886) [5] the similarity between gases and dilute solutions, Margules (1895) [6] had suggested an equation for the contribution of activity coefficients, van Laar (1908) [7] had already calculated complete binary phase diagrams taking into account miscibility gaps, and Nernst (1912) [8] had introduced the Third Law of Thermodynamics. In 1927 to 1929 Hildebrand [9,10] worked on regular solution theory while Guggenheim suggested in 1937 [11] a general polynomial for the excess Gibbs energy that is still being used under the name of Redlich and Kister [12] who published the same equation independently again in 1947.

However, something was missing in all of these activities: The active and purposeful collection of thermochemical data for large numbers of substances, i.e., work on databases. Around 1950, Meijering [13], following up on the work of van Laar, started systematic work on the lattice stabilities (i.e., the Gibbs energies of the various structural appearances, of the elements), and the first volume of *Metallurgical Thermochemistry* by Kubaschewski [14], which contained large data tables for stoichiometric pure substances, appeared in 1951. While these activities continued, the first steps toward calculating phase equilibria and phase diagrams were taken, for example, by Ellingham (1944) [15] and later Kellogg (1950) [16] with respect to predominance area diagrams (two partial pressure, i.e., chemical potential, axes with T constant) as well as Hillert [17] and Kaufman [18] with respect to binary temperature vs. composition diagrams. The latter found their first level of maturation in the programming success of Sundman, Jansson, and Andersson for systems including ideal and non-ideal condensed solutions (Thermocalc) [19]. Also, the approach of calculating complex equilibria for multicomponent systems containing gases and many stoichiometric condensed substances by Eriksson (SOLGAS [20], later SOLGASMIX [21]) emerged at this time.

First activities to establish stable alliances for large cooperation began very soon after, for example, with the foundation of Scientific Group Thermodata Europe (SGTE, 1979) in the form of a non-profit organization with members from France, Germany, Belgium, England, and Sweden, registered in Grenoble, France, as well as the international community for the Computer Coupling of Thermodynamics and Phase Diagrams (CALPHAD, 1973). At the same time in North America the data activities of the National Institute of Standards and Technologies (NIST, Gaithersburg), Alcock et al. (Notre Dame), Pelton, Bale, and Thompson (Ecole Polytechnique and McGill University, Montreal), were pursued with great effort. For further reading, the reader is referred to the *CALPHAD* journal for more recent developments in computational thermodynamics, for example, new codes such as Pandat [22] and the most recent new code CaTCalc [23], but also to the *International Journal of Materials Research* or *Metallurgical Transactions* for data assessments and practical applications of computational thermochemistry, especially Volume 98 (10) of 2008 which was dedicated to the 60th anniversary of Gunnar Eriksson.

THE STANDARD TOOL: AN INTEGRATED THERMODYNAMIC DATABANK SYSTEM

The tool that results when data administration and the standard calculations that can be derived from the Gibbs energy tree shown above is called an integrated thermodynamic databank system (ITDS). The three major tasks when using such a software package are: (1) administration of thermodynamic databases, (2) execution of thermodynamic application calculations (with tabular and graphical results), and (3) generation of thermodynamic data from experimental information.

Administration of data comprises (i) searching the contents of (public and private) databases and (ii) entering, modifying, and deleting private data

Execution of thermodynamic application calculations means, for example, (i) generation of thermodynamic properties of pure substances and of solution phases and their constituents in tabular and graphical form; (ii) generation of thermodynamic properties of stoichiometric reactions both as isothermal equilibrium properties including equilibrium constants and as non-isothermal balances of the extensive properties of a reaction in tabular and graphical form; (iii) complex equilibrium calculations for multiphase multicomponent systems using global conditions of elementary amounts, temperature, and total pressure, but also under constraints such as fixed extensive balances, predefined phase occurrences, or conditions of an open system; and (iv) phase diagrams of the classical three types with the choice of two potential axes (T , P , chemical potential or partial pressure), one potential axis, and one axis with extensive property ratios (e.g., mole fractions, weight fractions), or two axes with extensive property ratios. (Note: According to Perrot [24], the term *extensive property ratio* can be replaced by *reduced extensity*. He also stated that potentials (which he calls tensions) are special intensive properties.)

Generation of thermodynamic data from experimental information enables the user to invert complex equilibrium calculations such that the results of the calculation are used to optimize the Gibbs energy data of the various phases of a chemical system be they stoichiometric pure substances or ideal or non-ideal solutions.

From the above it should be clear such a tool is called an ITDS. It integrates the capabilities of the administration of thermodynamic databases with the use of the data in standard thermodynamic calculations and also permits the generation of new thermodynamic data using experimental information, and provides this all in an interactive software system.

In the present case, the ITDS FactSage [25] has been used. Tools for the above-mentioned data administration tasks are found in the Databases Group of FactSage modules where the administration of data is handled by the View Data, the Compound, and the Solution modules.

The thermodynamic calculations listed above are performed in the Calculate Group of FactSage modules that comprises the Reaction, Predom, EpH, Equilib, Phase Diagram, and OptiSage modules.

The FactSage software also offers a Manipulate Group of modules that enable the user to perform more elaborate inputs for complex equilibrium calculations (Mixture) or in post-processing the output from such calculations (Results and Fact-XML). There is also a module for the viewing and editing of graphical output (Figure) which was generated by one of the calculational modules.

In the following sections, results from the major modules of FactSage, i.e., Reaction, Equilib, and Phase Diagram, are used to discuss the thermochemical aspects of silicon production.

THERMODYNAMIC ANALYSIS OF THE PRODUCTION OF SILICON USING AN ITDS

Metallurgical grade silicon is produced in an electric arc furnace. The process is shown schematically in Fig. 2. Quartz sand and carbon are fed in appropriate proportions through the top, and liquid silicon is extracted at the bottom. The temperature in the production zone is approximately 2200 K. This is achieved through an electric arc burning between a graphite electrode and the metal bath. Hot gases that are produced in the bottom zone of the reactor during the formation of silicon under input of energy from the electric arc. These gases flow upwards as a convective flux. On their way up, heat exchange

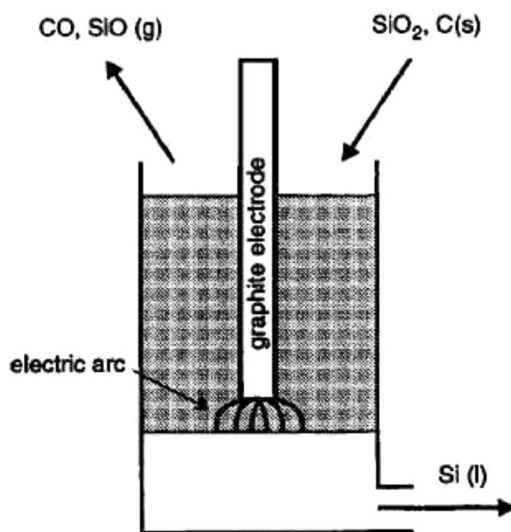


Fig. 2 Schematic drawing of the silicon arc furnace.

with condensed matter falling downwards takes place. To what extent can this process be understood on the grounds of equilibrium thermodynamics available through an ITDS such as FactSage?

The stoichiometric reaction approach

It is often claimed that the production of silicon is governed by the simple stoichiometric reaction



At equilibrium, the Gibbs energy change of the reaction must be zero. As all four phases can be considered as stoichiometric pure substances, the equilibrium constant is equal to unity. Note that the process takes place at atmospheric pressure, and CO is assumed to be the only gas species involved. Thus, the standard Gibbs energy change of the reaction must be zero too

$$K = 1 \rightarrow \Delta G^\circ = 0 \quad \text{where } K \text{ is the equilibrium constant} \quad (3)$$

Figure 3 shows ΔG° as a function of temperature. Indeed, there is a value of T for which the curve changes sign, $T \sim 1940$ K. However, this value is far below the one known from the process (~ 2240 K). Such a difference cannot be explained by deviations from unit activities or errors in the thermodynamic data. There must be other reasons.

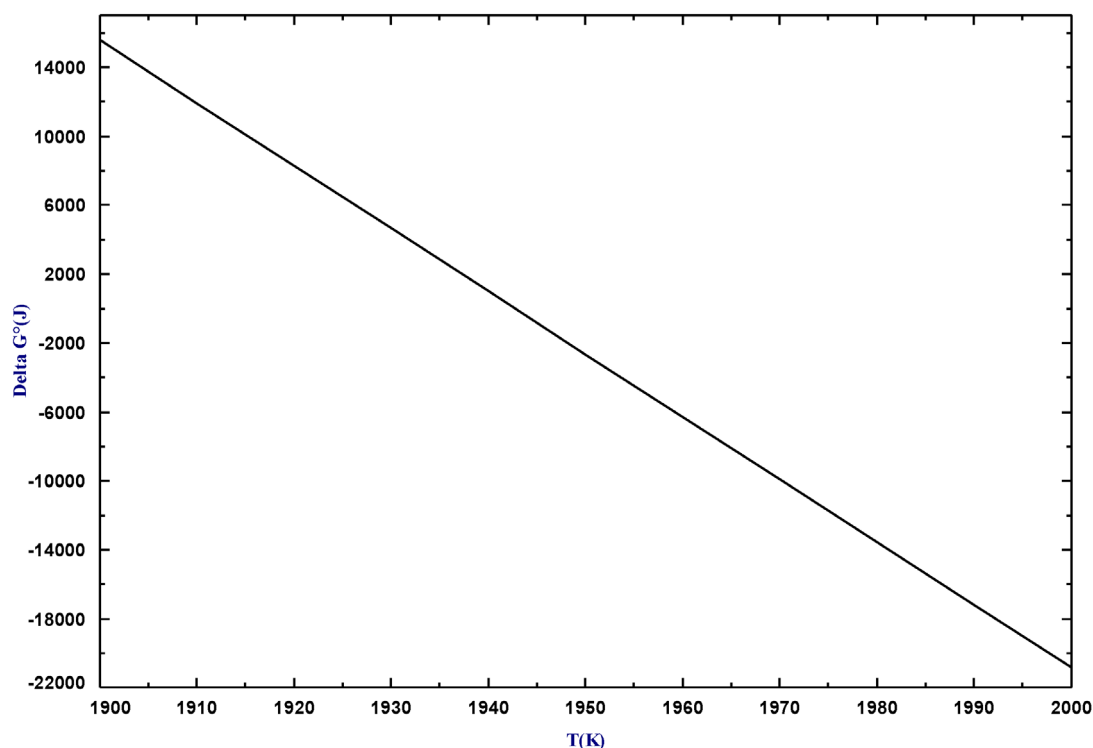


Fig. 3 ΔG° for the reaction $\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}$ as a function of T .

Phase diagrams and the one-dimensional phase mapping approach

If quartz is permitted to react freely with carbon in a system with a given total pressure and temperature, a different type of calculation must be carried out. All phases possible must be considered for set values of temperature, total pressure, and system composition. Especially, all possible gas species have to be introduced into the calculation. A databank search reveals the following list of phases and phase constituents for the system Si–O–C

Gas: Si, Si₂, Si₃, SiO, SiO₂, C, O, O₂, O₃, CO, CO₂

Stoichiometric condensed: C(graphite), SiC, SiO₂(quartz), SiO₂(tridymite), SiO₂(cristobalite), SiO₂(liquid)

For this system as a whole, standard thermochemical calculations can be carried out in the form of phase diagrams and complex equilibria, especially in the form of one-dimensional phase maps.

Phase diagram calculations

Si–C–O is a normal ternary system and thus it is quite possible to generate classical Gibbs triangular phase diagrams. This may seem a bit unusual because one of the components of the system is a gas, but the gas phase can of course be treated like any other (solution) phase in such a diagram.

The Figure series 4a to 4c shows the isothermal sections for $T = 1700$, 2100 , and 2700 K. The composition $1 \text{ SiO}_2 + 2\text{C}$ is marked in the diagram as a point with the resulting molefractions.

It is obvious from the diagrams that at 1700 K (Fig. 4a) the point of operational composition just shifts from the three-phase field C + SiC + SiO₂ (s4 = cristobalite) to C + SiO₂ + Gas. The composition of the gas is CO as can be seen from the appropriate apex of the three-phase triangle. At 2100 K (Fig. 4b), the operational point lies in a two-phase field. SiC and Gas are the stable phases. The phase

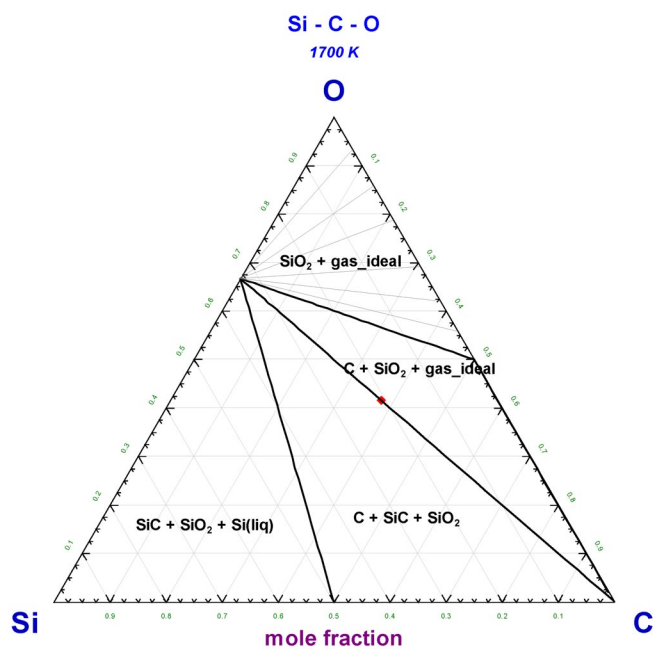


Fig. 4a Isothermal section of the Si-C-O system for $T = 1700$ K.

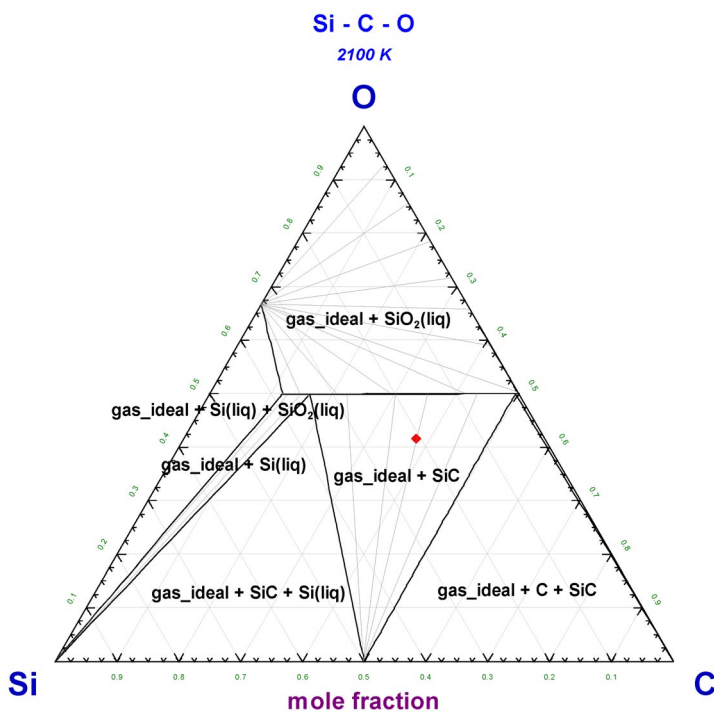


Fig. 4b Isothermal section of the Si-C-O system for $T = 2100$ K.

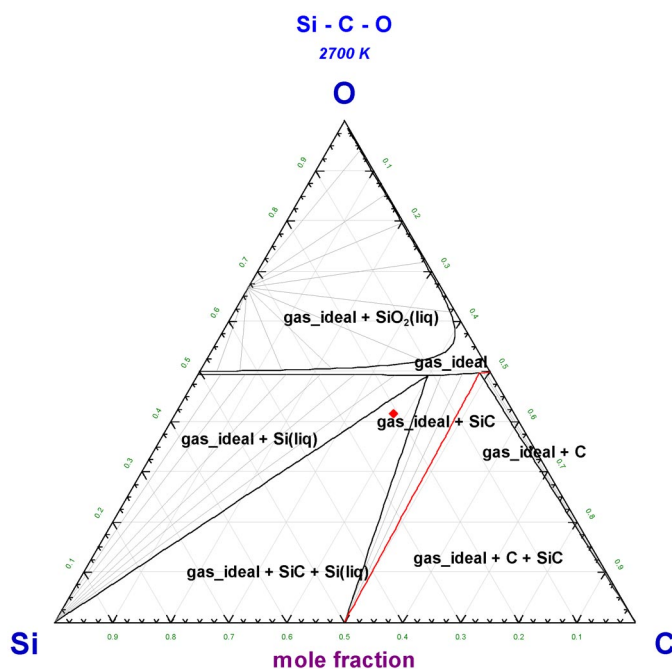


Fig. 4c Isothermal section of the Si–C–O system for $T = 2700$ K.

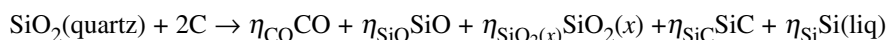
field for the gas is reduced to a line that interlinks SiO and CO (and at higher oxygen molefractions CO and O₂). The end of the tie-line through the operational point shows that the composition of approximately 70 CO:30 SiO. Only at very high temperatures, e.g., $T = 2700$ K (Fig. 4c), the point of the operational composition of the process lies in a three-phase field in which liquid silicon is one of the stable phases. Since the position is near the corner in which the gas phase is stable, the amount of liquid silicon that can be produced is not high.

With respect to the understanding of the process, it can be said that under the assumption of a fixed overall composition (1 SiO₂ + 2C) in the reactor, it will take rather high temperatures to produce silicon and the amount will be rather small.

One-dimensional phase mapping

A more detailed analysis of the behavior of the phases at the operational composition can be obtained if this composition is kept constant and temperature is varied continuously through an interval with total pressure also constant (1 bar). Thus, one would fix the composition in the isothermal phase diagrams discussed above and follow this composition with temperature at constant pressure. If in this calculational sequence all temperatures at which phase boundaries are crossed are picked up especially such a calculation is called a one-dimensional phase mapping, in contrast to a two-dimensional phase mapping which results in a classical phase diagram. The graphical result, i.e., a two-dimensional plot, of a one-dimensional phase mapping generates a set of curves of the phase or phase constituent amounts as function of the one independent variable of the calculation, here the temperature.

The interpretation of the calculation in terms of a reaction with variable amounts of the products can be written as



If the temperature is varied through an interval from below, the value of equilibrium for the simple stoichiometric reaction (~ 1940 K, see above) to a value high enough to obtain liquid silicon, the resulting yield factors (product amounts) can be plotted as in Fig. 5. From this figure it is obvious that the gas phase in this system contains SiO as an essential species. Thus, the simple stoichiometric reaction initially given cannot be right. On the other hand, the assumption that the process can be described as a single although complex equilibrium state is also disproved. The temperature at which silicon would be produced is near 2900 K, and the yield is not more than 50 %. Just as the simple reaction approach is not in agreement, the result of the one-dimensional phase mapping is also not in agreement with values known from the real process.

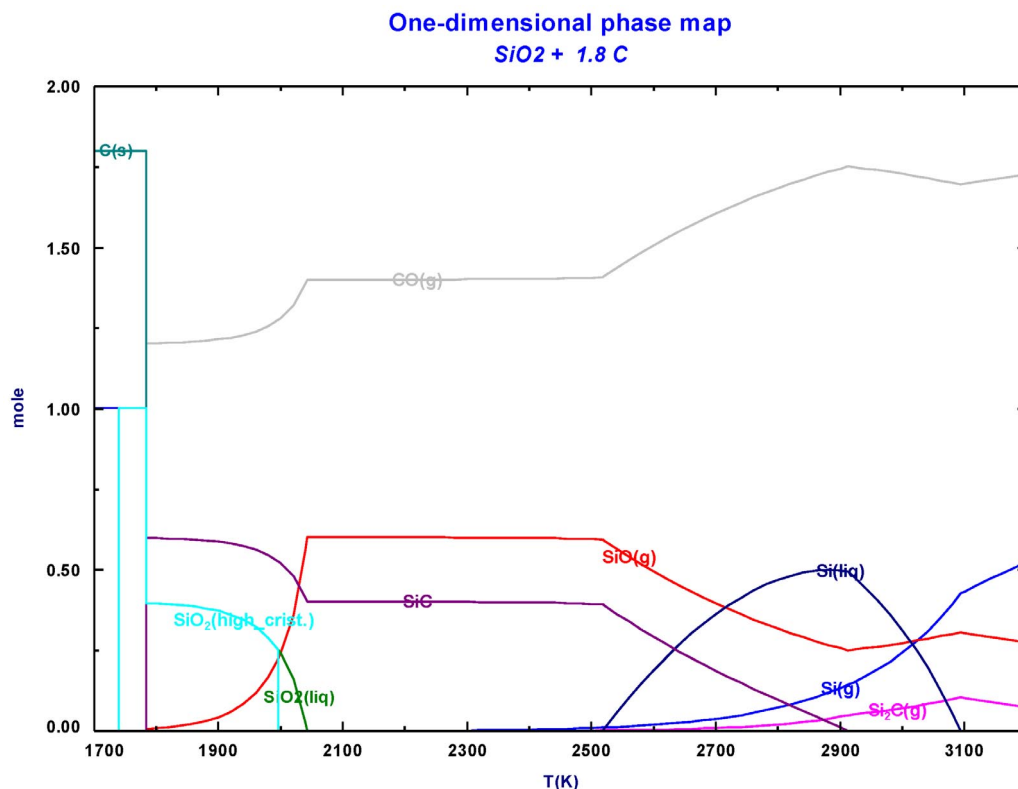


Fig. 5 One-dimensional phase map for 1 mol SiO₂ + 1.8 mol C as a function of T .

Beyond the capabilities of an ITDS: Non-isothermal process modeling with materials flow

Obviously, the use of a standard ITDS does not fully help to understand the thermochemical aspects of the silicon production in an arc furnace. The reasons are that the reactor is neither with respect to temperature nor with respect to composition a homogeneous space. It is therefore futile to try and understand the behavior of this reactor by means of isothermal equilibria, be they depicted as Gibbs triangular phase diagrams or as one-dimensional phase maps. What is needed is an approach that allows for both temperature and composition to depend on the position inside the reactor vessel.

Such an approach is available in terms of the software tool SimuSage [26]. This tool offers a suite of unit operations and a graphical user interface which permit one to set up a process model using a simple drag-and-drop approach.

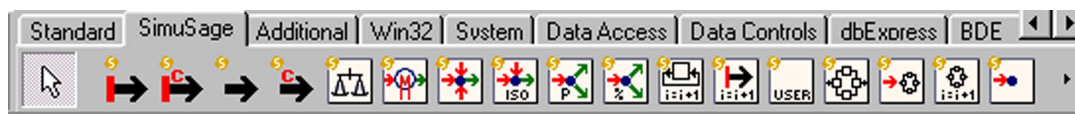


Fig. 6 Major unit operations of the SimuSage software.

The counter-current reactor approach

In order to simulate the arc furnace as a whole, it is necessary to take into account the fact that the substances taking part in the process move in a temperature field while reacting. Cold condensed matter is fed through the top of the furnace, falling downwards, and hot gases flow rapidly upwards. On their way, they meet and exchange heat or even react with each other. Thus, the local mass balances must not be identical to the overall mass-balance of the process. Additionally, the temperature at different levels of the furnace is not controlled from outside, but is mainly determined by the heat exchange and the reactions taking place. Such a complex situation can only be simulated by a thermodynamic equilibrium approach if several separate zones of local equilibrium that are interconnected by materials and heat exchange are assumed.

For the silicon arc furnace, it was found that a reactor with four stages that are controlled by the internal heat balance is well suited for the modeling. The flow scheme, the values for the heat balances in each stage, the input substances, their amounts and initial temperatures, as well as the distribution coefficients for the realization of kinetic inhibitions in the reactions between the gas species and the condensed phases are given in Figs. 7–9. It should be emphasized that all values are the result of a series of parameter optimizations. This set of parameters represents best the process data obtained from the silicon arc furnace of KemaNord at Ljungaverk, Sweden [27].

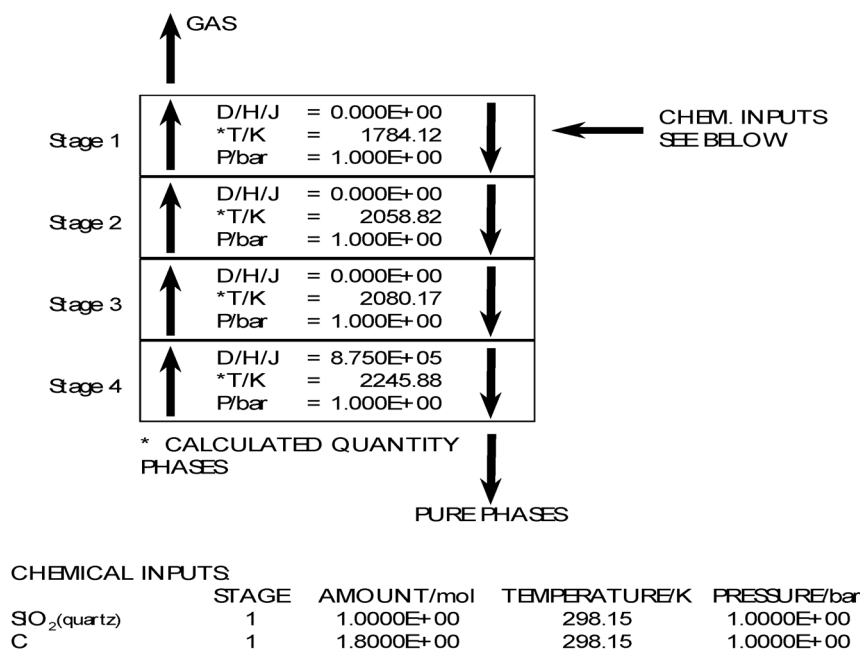


Fig. 7 Flow diagram for the silicon arc furnace model.

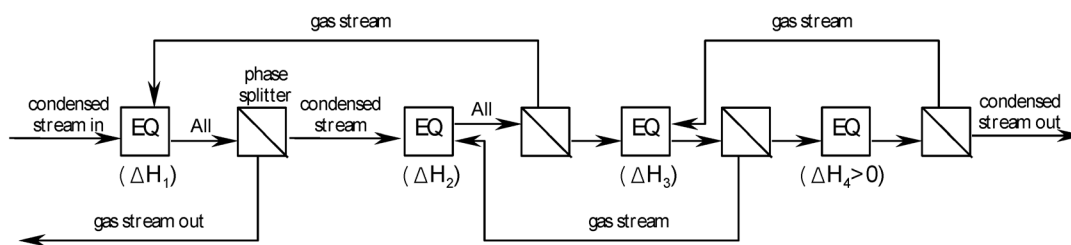


Fig. 8 Flowsheet with counter-current flow and heat balance-controlled stages.

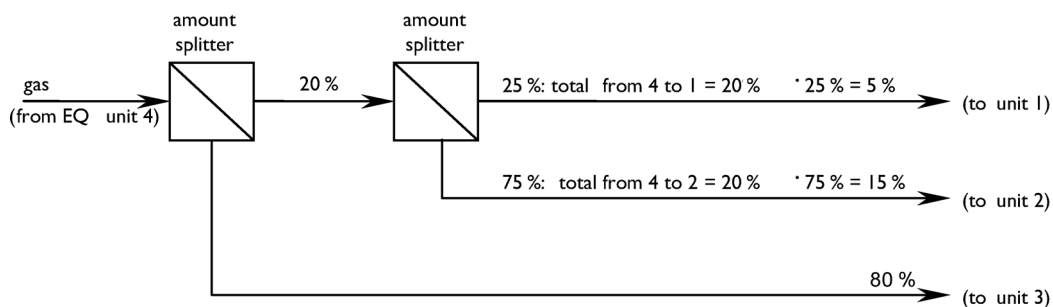


Fig. 9 Realization of a distribution coefficient using amount splitters for gas phase.

The resulting user interface of the process model software is shown in Fig. 10. In order to facilitate parameter studies (see below) it was decided to permit interactive input for the initial amounts of silica and carbon, the heat balance values for the four stages, and the split factors of the stream splitters, i.e., the distribution coefficients (see the input boxes).

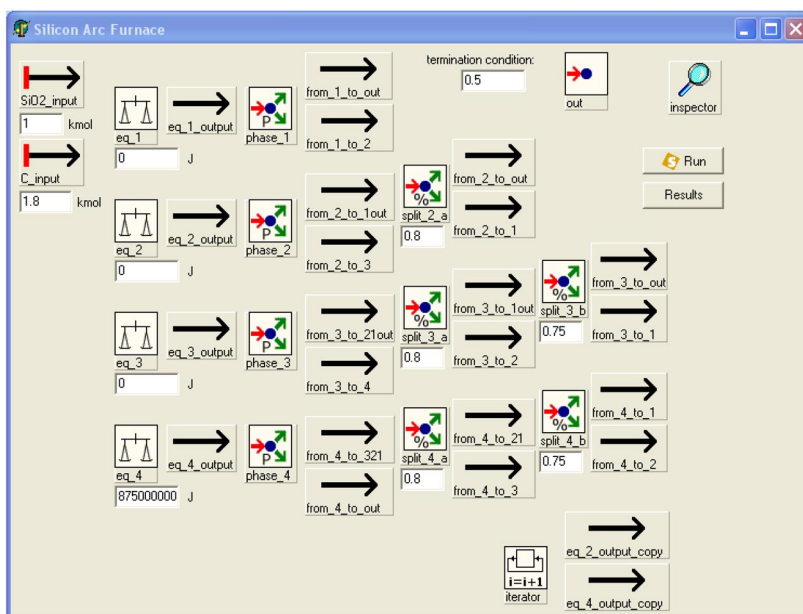


Fig. 10 Flowsheet interface of the process model software.

Using the above flow data, the process model generates a series of output graphs, the most important of which is the one that shows the materials flow through the reactor (Fig. 11). However, also the resulting temperature profile is calculated as the result of the given heat balances for the respective stages. It is depicted in Fig. 12.

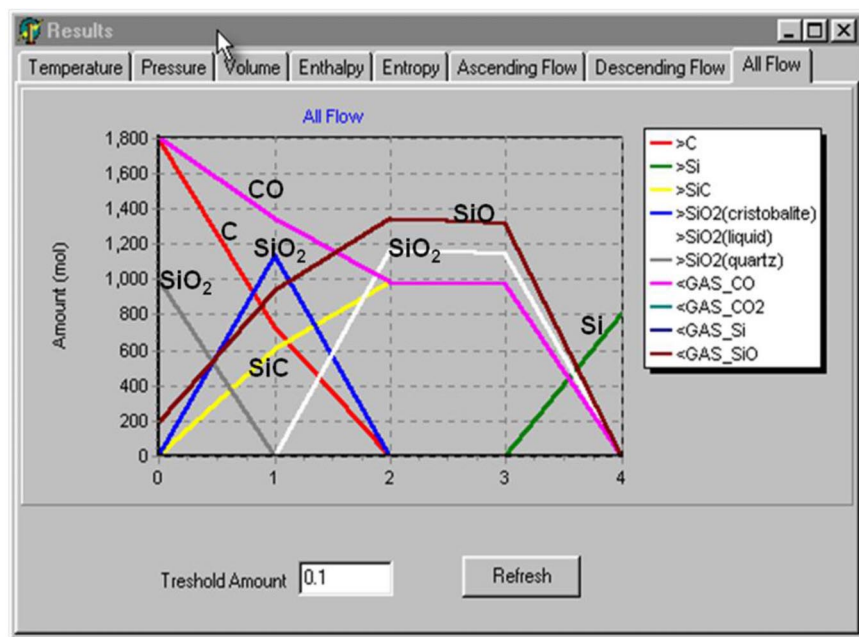


Fig. 11 Materials flow for the calculated steady state (> : descending matter, < : ascending matter).

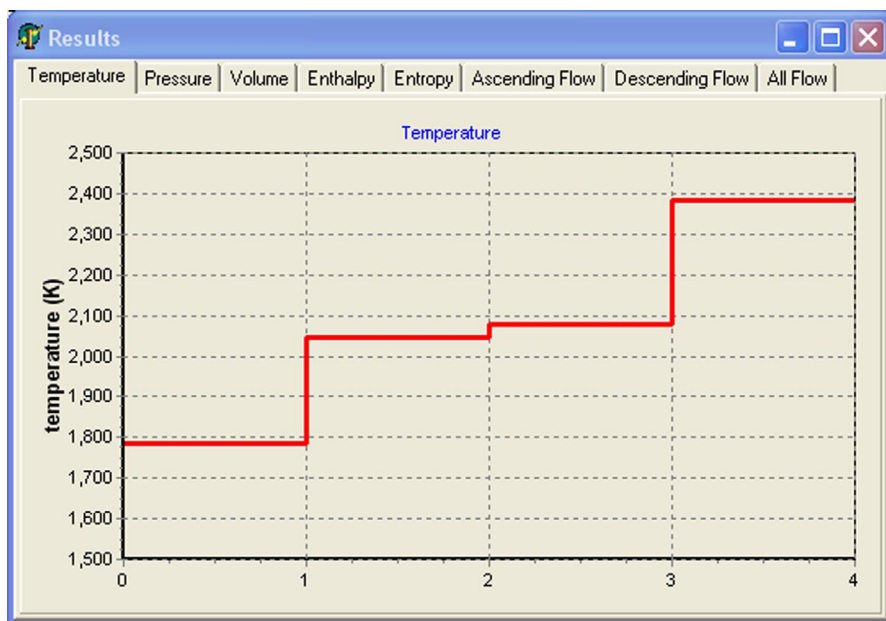
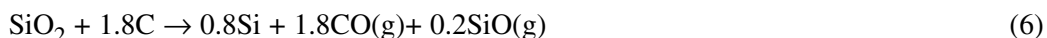


Fig. 12 Temperature profile in the reactor.

Continuous curves are obtained which represent the total materials flow through the reactor relative to 1 mol of silica and 1.8 mol of carbon in the feed. The most important result, the silicon yield, can be read on the lowest abscissa to be 0.8 mol per mole of silica. The total elementary mass balance of the reactor is readily obtained from the values on the outermost abscissae.

The overall mass balance can be written as



Note that this is not an isothermal equilibrium equation as silica and carbon enter the reactor at room temperature, silicon leaves the reactor at 2200 K and the gas phase leaves at 1874 K.

The temperature distribution that results from the energy input in the production zone ($\Delta H = +875 \text{ kJ/mol SiO}_2$) and the assumed adiabatic behavior ($\Delta H = 0$) of the three upper zones is also given in a diagram. The highest temperature is reached in the production zone. Its value (2245 K) is higher than that for which the standard Gibbs energy change of the simple reaction changes sign (1940 K); but it is also considerably lower than the value for which the one-dimensional phase mapping calculation shows a maximum of the silicon yield (approx. 2900 K).

A thermochemical understanding of the different reactions taking place at different levels within the reactor can be obtained from the materials flow between stages 3 and 4 and stages 1, 2, and 3, respectively. The reactor can obviously be split into two distinct zones that are governed by two separate processes. In the bottom zone, silicon is produced according to the mass balance equation



In the top zone, the upflowing silicon monoxide reacts with the carbon according to the mass balance equation



This reaction is, however, usually incomplete because the amount of incoming carbon is too low to allow all $\text{SiO}(\text{g})$ to react. Thus, a loss of silicon (20 %) cannot be avoided.

It is worth noting that SiC is both formed and consumed within the reactor and, therefore, does not occur in the total mass-balance. However, it is an essential phase in the whole process.

A more detailed analysis of the process was given by Eriksson and Johansson [27]. They have also employed modifications of the above set of calculational parameters, e.g., to study the influence of the energy supply and the amount of carbon fed into the process.

Figure 13 shows the silicon yield as a function of energy supply for two different amounts of carbon feed. The lower curve (1.8 mol carbon) shows that the optimum value for the silicon yield (80 %) is reached at an energy supply of approximately 875 kJ/mol SiO_2 .

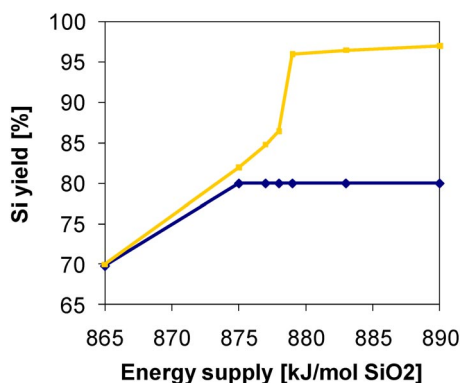


Fig. 13 Si yield as function of energy supply for different carbon input amounts (lower curve: 1.8 mol C, upper curve: 2 mol C).

is obtained for 875 kJ per mole of silica. This value was used in the calculations discussed above. A higher energy supply will not raise the silicon yield. For a higher carbon feed (2 mol per mol of silica), the upper curve indicates a possible silicon yield of more than 95 %. However, the resulting temperature level in the bottom stage (>2700 K) would make such a combination of process parameters technologically unfeasible.

ACKNOWLEDGMENTS

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