

8. INTRODUCTION

HSC Chemistry is designed for many different kinds of **chemical reactions and equilibrium calculations**. The current version contains 15 calculation options for single process unit calculations:

1. Reaction Equations
2. Heat and Material Balances
3. Heat Loss Calculations
4. Equilibrium Compositions
5. Electrochemical Cell Equilibria
6. Formula Weights
7. Phase Stability Diagrams (Tpp- and Lpp-versions)
8. Eh - pH – Diagrams with concentration and temperature variables
9. Enthalpy, entropy, heat capacity, Gibbs-energy and Ellingham diagrams.
10. Mineralogy Iterations
11. Composition conversions
12. Water - Steam Tables and Mollier Diagrams
13. Aqua Module
14. Units Conversions
15. Properties of Elements in tabular and graphical format.

The HSC 7.0 contains also flowsheet simulation module (Sim) for process calculation of the whole process made of several process units. The modules (Geo, Data, Map) support process simulation calculations.

The name of the program is based on the fact that all fifteen calculation options automatically utilize the same extensive **thermochemical database** which contains enthalpy (**H**), entropy (**S**) and heat capacity (**C_p**) data for more than 25000 chemical compounds. This database is equivalent to more than seventeen thick data books.

The HSC Chemistry software enables the user to simulate chemical reactions and processes on the thermochemical basis. This method does not take into account all the necessary factors, such as rates of reactions, heat and mass transfer issues, etc. However, in many cases a pure thermochemical approach may easily give useful and versatile information for **developing new chemical processes and improving the old ones**.

Perfect simulation for all processes means that any chemical process can be designed completely in the computer without any experimental work. This goal is, however, far in the future, because there is no complete general theory or basic data available which would successfully combine **thermodynamics, non-ideality of solutions** as well as **dynamics** (kinetics) for all processes. Nearly perfect simulation may be achieved for a single individual process step by measuring experimentally all the necessary parameters for solution models, kinetic models, as well as for flow and heat transfer models. However, this needs several months or years work to be able to simulate one single process step. Quite often a fast mainframe computer is needed.

With HSC Chemistry it is possible to calculate chemical equilibria between pure

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substances and the ideal and also, to some extent, non-ideal solutions. For these calculations only enthalpy (H), entropy (S) and heat capacity (Cp) data for all prevailing compounds or pure substances is needed. In many cases these calculation results may simulate the real chemical reactions and processes at sufficient accuracy for the practical applications. Important advantage is also that specification of the chemical system, data retrieval and final calculations may be carried out in normal Intel Pentium personal computers within few minutes.

Of course, experimental work is needed to verify the results, because HSC does not take kinetic phenomena into account. However, HSC helps to avoid expensive trial-and-error chemistry, because it quickly and easily gives some kind of clue as to the effects of process parameters on the reaction products and process conditions. Usually, thermochemical calculations at least show what is physically possible and what is impossible, which is highly valuable information when making plans for experimental investigations.

In the thermodynamic equilibrium the rates of reactions and reverse reactions may both be interpreted to have the same rate, ie. this state is only one special case of kinetic phenomena. Of course, some programs are available which also take some kinetic aspects into account. However, these are not general like thermodynamic equilibrium codes are, ie. they are usually valid only for certain geometries and environments.

A number of solution models are available in literature to describe the non-ideality of mixture phases. The practical problem is quite often a lack of valid data for solution parameters. Although solution models have not been installed in the HSC Chemistry, the non-ideality of solutions can be taken into account in the equilibrium calculations to a certain extent by including constant activity coefficients or simple activity coefficient formulae in the Gibbs equilibrium solver.

8.1 Invitation to new Authors

If you have a thermochemical computer program or basic thermodynamic data which may be of more general interest, please send it to the author:

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We may also add your code to future versions of HSC Chemistry. Connection to the HSC-database and fitting the code and user interface to HSC format can be carried out in Outotec Research. Integration is easiest if the original code is written in Visual Basic, QuickBASIC or BASIC.

The new thermodynamic data which is saved in OwnDB7.HSC database can easily be

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transferred to MainDB7.HSC at Outotec Research.

8.2 Physical Background of H, S, C and G

Thermochemical calculations are based on enthalpy **H**, entropy **S**, heat capacity **C_p** or Gibbs energy **G** values for chemical species. They can all be mathematically derived from experimental observations. The following presentation gives a brief and simplified but illustrative idea of the thermochemical quantities and methods.

Enthalpy H: Absolute values of enthalpy **H** of substances cannot be measured, but enthalpy differences between two temperatures can be determined with a calorimeter. Heat capacity **C_p** at constant pressure (specific heat) can be calculated from this data using Eq. (1).

$$C_p = (dH / dT)_{P,n} \quad [1]$$

Equation (1) allows the calculation of enthalpy as

$$H(T) = H_f(298.15) + \int_{298.15}^T C_p dT + \sum H_{tr} \quad [2]$$

where $H_f(298.15)$ is the enthalpy of formation at 298.15 K and H_{tr} is the enthalpy of transformation of the substance. Calorimetric measurements at different temperatures yield the enthalpy curve of zinc shown in Fig. 2.

The enthalpy scale in Eq. 2 is fixed by defining **H = 0 for the elements in their most stable state at 25 °C and 1 bar**, mainly because this is convenient for calculations at elevated temperatures. This is called the reference state. (Another fix point could have been $H = 0$ at 0 K, because the thermal motion of atoms and electrons stops completely at this temperature.)

The ability of a chemical substance to absorb or emit heat depends on the temperature, and therefore the curve in Fig. 2 is not linear. In addition, at phase transformation temperatures the curve is discontinuous, because heat is needed for the phase transformations (ie. for crystal structure changes, as well as for melting and boiling).

The **enthalpy of compounds** also contains their enthalpy of formation DH_f from elements. This is usually measured calorimetrically by letting pure constituent elements react and form the compound at 298.15 K and 1 bar. The enthalpy of the compound is therefore calculated by adding the enthalpy of formation to the experimental enthalpy difference $H(T) - H(298)$, see the solid line in Fig. 3.

The enthalpy values of gaseous zinc can be extrapolated to lower temperatures as shown in Fig. 2 by the dotted line. The reference state for zinc at 25 °C and 1 bar is hexagonal crystal. The enthalpy of gaseous zinc is 130.415 kJ/mol larger compared to solid pure zinc at 298.15 K. This amount of heat is needed to evaporate one mole of zinc at 25 °C and 1 bar, and is called the enthalpy of formation of zinc gas from solid zinc.

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Fig. 2. Enthalpy of pure zinc from 0 K to 1400 K with reference to solid, hexagonal Zn at 298.15 K.

Fig. 3. Enthalpy of zinc sulfide (——). Enthalpy difference $H(T)-H(298)$ (-----) and enthalpy of formation have been measured by calorimeter. Note crystal structure transformation at 1293 K.

Entropy S: Absolute entropy values can be calculated from the experimental heat capacity values using Equation (3) and numerical integration.

$$S = S(298.15) + \int_{298.15}^T (C_p / T) dT + \sum H_{tr} / T_{tr} \quad [3]$$

where $S(298.15)$ is the standard entropy of the substance which can be calculated by integrating C_p/T function from 0 to 298.15 Kelvins, T is temperature and H_{tr} is enthalpy of phase transformation at a temperature T_{tr} , see Fig. 4.

Entropies of crystalline substances approach zero at 0 K. This fundamental experimental observation is compatible with the third law of thermodynamics. If entropy is understood as a measure of disorder, the disorder reaches its minimum at absolute zero and in perfect crystal structures.

Heat Capacity C_p : The absolute heat capacity of substances at constant pressure can be calculated as a first derivative of the enthalpy curve in Fig. 2, using Equation (1). The heat capacity curve is discontinuous at phase transformation temperatures, see Fig. 5. The heat capacity values of crystalline substances in equilibrium approaches zero value at 0 K.

The temperature dependence of heat capacity at elevated temperatures cannot be predicted theoretically by thermodynamics. A fully mathematical correlation is therefore adopted for fitting experimental heat capacities. The Kelley equation is used throughout this program in the following form:

$$C_p = A + B \cdot 10^{-3} \cdot T + C \cdot 10^5 \cdot T^{-2} + D \cdot 10^{-6} \cdot T^2 \quad [4]$$

where A , B , C and D are coefficients estimated from experimental data.

Gibbs Energy G : The mutual stability of substances (elements, compounds, ions, etc.) cannot be compared using enthalpy, entropy or heat capacity functions solely. It must be done using the Gibbs energy defined by Equation (5). The Gibbs energy of pure zinc has been calculated using this equation and data in Figs. 2 and 4. The results can be seen in Fig. 6.

$$G = H - T \cdot S \quad [5]$$

Experimental Methods: Many experimental and theoretical methods are available for evaluating the basic thermochemical enthalpy, entropy and heat capacity data than it is practical to describe in this context. Usually a critical analysis of the values is based on a thorough simultaneous cross-correlation of thermochemical data from different sources, measurement methods (calorimetric, spectroscopic, electromotive force, solubility, etc.) and theoretical calculations. More information of the assessment methods can be found, for example, in the references mentioned in Chapters 32 and 33.

Fig. 4. Entropy of zinc calculated from the experimental heat capacity, by Eq. (3).

Fig. 5. Heat capacity of zinc from 0 K to 1400 K calculated from calorimetric data, by Eq. (1).

Fig. 6. Gibbs energy of zinc at 0 - 1400 K calculated from the enthalpy and entropy values using Equation (5).

Data Format in the HSC Databases: Traditionally, experimental heat capacity values - see Fig. 5 - have been fitted using the empirical Equation (4). The coefficients A, B, C and D provided in HSC are valid in limited temperature ranges only. Usually the temperature ranges are the same as the stability ranges of solid, liquid and gaseous states of the substances.

The heat capacity coefficients can be saved in the HSC database as data sets for each temperature range, together with the enthalpy and entropy values for formation and transformations. The first data set contains the enthalpy of the formation $H_f(298.15)$, standard entropy S° and the coefficients A, B, C and D for the most stable form of the substance at room temperature. The second set contains the enthalpy and entropy of transformation as well as the coefficients for the second temperature range, etc. For further details, see Chapter 28.11.

Table 1 shows the thermochemical data of zinc as printed from the HSC main database. The same enthalpy values can be found in Fig. 2, as well as the entropy values in Fig. 4. The coefficients A, B, C and D have been derived from the experimental heat capacity values, Fig. 5, using curve fitting and Equation (4), see Chapter 28.12.

Note that the data for gaseous substances as Zn(g) has been saved separately. Such a selection allows, for example, equilibrium calculations with the gaseous substances also below their boiling points.

Table 1. Thermochemical data of zinc as printed from the HSC database.

All thermochemical data required in HSC and its modules, including heat capacity, enthalpy, entropy and Gibbs energy of the substances, can be calculated from the basic data in its databases using Equations (1)-(11). HSC Chemistry utilizes the equations automatically whenever needed.

Chemical Reactions: The thermodynamic enthalpy, entropy and Gibbs energy functions for a chemical reaction are calculated as the difference between the products and reactants, using Equations (6) - (9). The commonly needed equilibrium constant K can be calculated using Equation (11). The physical meaning of these functions and values will be described in more detail in Chapters 10.1 - 10.4.

$$\text{Chemical reaction:} \quad aA + bB + \dots = cC + dD + \dots \quad [6]$$

$$\begin{aligned} \text{Enthalpy of reaction:} \quad \Delta H_r &= \sum v_i H_i(\text{Products}) - \sum v_i H_i(\text{Reactants}) \quad [7] \\ &= (c \cdot H_C + d \cdot H_D + \dots) - (a \cdot H_A + b \cdot H_B + \dots) \end{aligned}$$

$$\begin{aligned} \text{Entropy of reaction:} \quad \Delta S_r &= \sum v_i S_i(\text{Products}) - \sum v_i S_i(\text{Reactants}) \quad [8] \\ &= (c \cdot S_C + d \cdot S_D + \dots) - (a \cdot S_A + b \cdot S_B + \dots) \end{aligned}$$

$$\begin{aligned} \text{Gibbs energy of reaction:} \quad \Delta G_r &= \sum v_i G_i(\text{Products}) - \sum v_i G_i(\text{Reactants}) \quad [9] \\ &= (c \cdot G_C + d \cdot G_D + \dots) - (a \cdot G_A + b \cdot G_B + \dots) \end{aligned}$$

$$\text{Equilibrium constant:} \quad K = \frac{[C]^c \cdot [D]^d \cdot \dots}{[A]^a \cdot [B]^b \cdot \dots} \quad [10]$$

$$\ln K = \Delta G_r / (-RT) \quad [11]$$

where the following abbreviations have been used:

- [A] = activity or partial pressure of species A, B, C, etc.
 a = stoichiometric coefficient of species A in reaction

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ν = stoichiometric coefficient of a species in reaction (a, b, c, ...)
R = gas constant = 1.987 cal/(Kmol) = 8.314 J/(Kmol)
T = Temperature in K