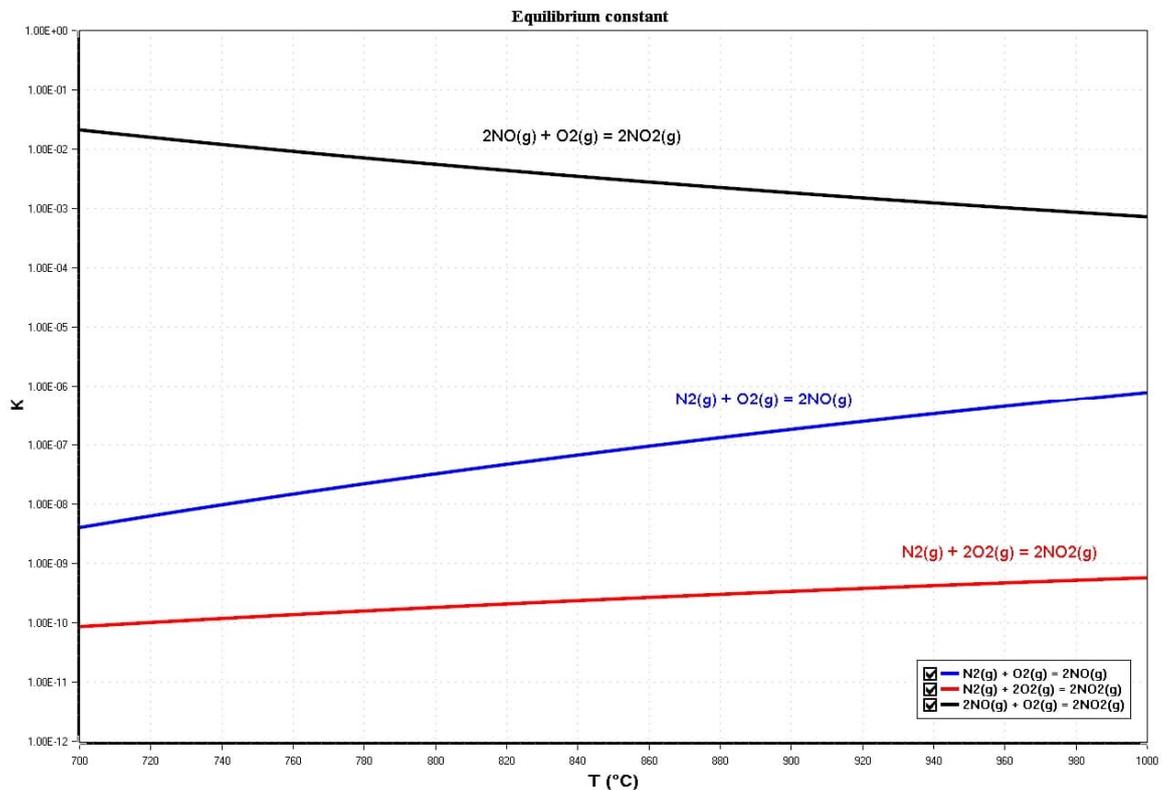


10. Reaction Equations Module



SUMMARY

Clicking the **Reaction Equations** button in the main menu of HSC shows the Reaction Equations Window, see **Fig. 1**. With this module you can calculate the heat capacity, enthalpy, entropy and Gibbs energy values of a single species as well as of specified reactions between pure substances. The module also enables graphing of the results as a function of temperature.

See the reference state definitions, valid notations, and abbreviations for the description of the chemical formulae in Chapter 28 (section 28.2).

10.1. One Chemical Substance

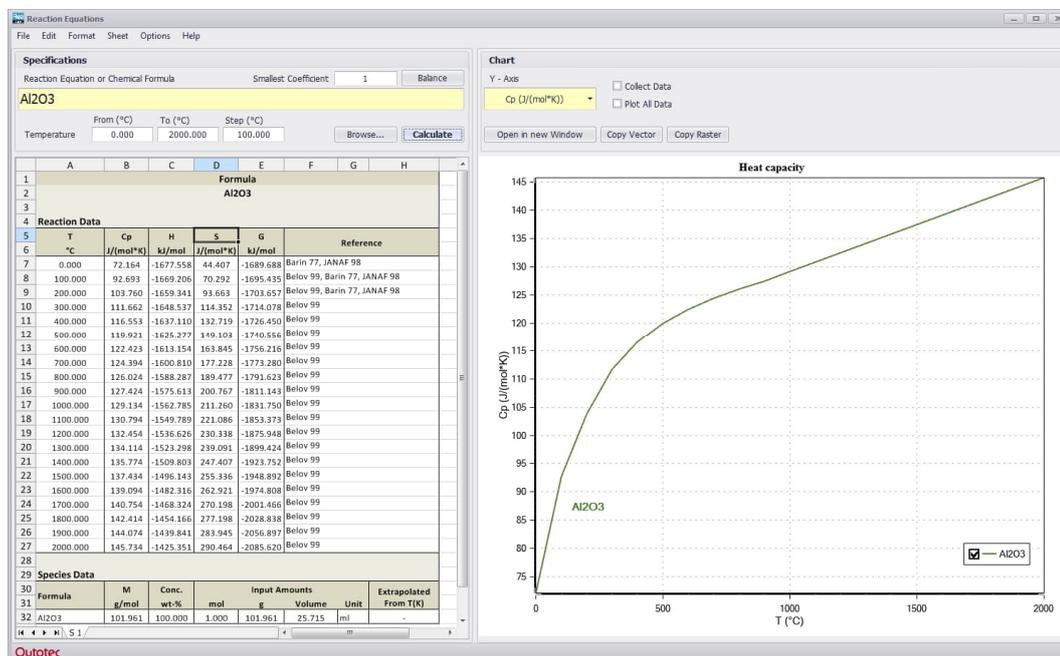


Fig. 1. Reaction Equations window of HSC Chemistry.

By entering a single chemical formula into the **Formula** box you will get similar tables of thermochemical data as presented in many thermochemical data books. HSC will, however, provide the results faster and exactly at the temperatures which you really want. **Calculate** also produces a chart which allows the results to be seen in graphical form as well. Please follow these steps:

- Write a chemical formula in the formula box, (top left in **Fig. 1**)
For example: Fe, Na2SO4, Al2O3, SO4(-a), H(+a) or SO2(g).
See the valid notation and syntax of chemical formulae in Chapter 28 (section 28.2).
- Select the lower limit, upper limit and temperature step.
- Select the Temperature and Energy Units and the format of the results (Normal or Delta) from the "Options" menu.

Normal (Absolute scale):

H(species), S(species) and C(species)

This format is used for example in the famous I. Barin, O. Knacke, and O. Kubaschewski data compilation¹.

Delta (Formation functions):

$$\Delta H = H(\text{species}) - \sum H(\text{elements})$$

$$\Delta S = S(\text{species}) - \sum S(\text{elements})$$

$$\Delta G = G(\text{species}) - \sum G(\text{elements})$$

$$\Delta G = G(\text{ions}) - \sum G(\text{elements}) + z/2 \cdot G(\text{H}_2(\text{g})) - z \cdot G(\text{H}(\text{+a}))$$

z = charge.

This format is used for example in the NBS and Pankratz Tables^{2,3}.

4. The **Collect Data** option will collect several calculation results on different sheets. Data from these sheets can be plotted into a single chart by using the **Plot all data** option in Chart Options. The **Plot all data** feature requires that the calculations of different sheets use the same units (energy and temperature) and also that they are in the same format (Normal or Delta, affects only pure substance calculations). Pure substance calculations and reaction calculations cannot be plotted in the same graph.
5. Select **Show Transitions** from the "Options" menu if you also want to see the data at the phase transformation temperatures, such as crystal structure changes and melting.
6. Select **Criss-Cobble** from the "Options" menu if you want a Criss-Cobble extrapolation for the heat capacity of aqueous species, see Chapter 28 (section 28.4.)
7. Click **Calculate** to get the results on the screen.
8. Click **Print** from the "File" menu to print the results.
9. Click **Copy Sheet** from the "Sheet" menu to get the tabulated results into the Clipboard, then you can easily paste the results to other Windows applications, for example, to MS Excel. It is possible to copy and paste the content of individual cells to other applications using **Copy**.
10. Click **Save As...** from the "File" menu to save the entire workbook as an .rea8 file. These files can be opened for later use with **Open...** from the "File" menu.

Note:

1. It is easy to check the basic data that has been used in the reaction module calculations from the database. In Fig. 1, select the formula in the Reaction Equation box and press **Browse....**
2. The table in Fig. 1 has some formatting and Copy - Paste functions as do other tables in HSC Chemistry. These features help to create a good printed copy of the results for various purposes.
3. HSC searches for the species data first from the **Own database**. If it does not find a species there, it will search from the **Main database**. Therefore HSC always uses data in the Own database if the same species exists in both Own and Main databases.
4. If you have selected **Delta format** for the results, HSC will also search for data for the necessary elements and calculate the formation functions of enthalpy, entropy, and Gibbs energy. Usually the original experimental data is in this format: however, sometimes the comparison of data in this format may be more difficult because the data sources often use different data for elements.
5. HSC will make a **Criss-Cobble extrapolation** for the heat capacity of aqueous species at elevated temperatures ($> 25\text{ °C}$) if the Criss-Cobble option is selected. The extrapolation is not done if A and B of the heat capacity coefficients A, B, C, and D exist in the HSC Chemistry databases. The extrapolation error increases rapidly at higher temperatures. More information on extrapolation is given in Chapter 28 (28.4.)
6. For **aqueous species** it is recommended to set:
Lower temperature = 25 °C
Upper temperature = 300 °C
Step = 25 °C

10.2. One Chemical Substance Results

After pressing the Calculate button in **Fig. 1**, you will get the results in a table in the lower part of the window as well as a graph for a single property. You can save and print these results by using options found in the File and Edit menus:

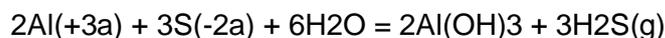
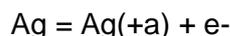
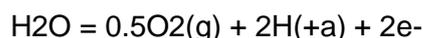
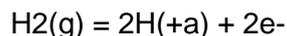
1. Click **Save As...** if you wish to recalculate the results later. The **Save As...** function will also save the settings used in **Fig. 1**. You can read these files back to HSC using **File Open**.
2. Click **Print** if you want a paper copy.
3. Click **Copy** to put the results of selected cells into the Clipboard, then you can easily paste the results, for example, to MS Excel. Click **Copy Sheet** to put all the results of the sheet into the Clipboard.
4. Click **Export To Excel** to save the entire workbook, containing several sheets, in MS Excel format.
5. Click **Copy Chart** from the "Edit" menu to copy the chart to the clipboard, from where the graph can be pasted for example into MS Word.
6. Click **Save Chart** from the "File" menu to save the chart as a vector image.
7. You can also use the tools embedded in the chart to **Save, Copy, Print, Clone, Redraw** and use **Toolbox** to edit the chart (**Fig. 2**).



Fig. 2. Chart tools (Save, Copy, Print, Clone, Redraw, Toolbox).

10.3. Reaction Equations

You can write almost any kind of reaction equation into the HSC Reaction Equation box, see **Fig. 3**. Here are some examples of valid equation syntax:



The screenshot shows a software interface for entering reaction equations. The main input field contains the equation $\text{Ni} + 4\text{CO}(\text{g}) = \text{Ni}(\text{CO})_4(\text{g})$. To the right of this field is a 'Balance' button and a 'Smallest Coefficient' input box with the value '1'. Below the main input field, there are three input boxes for temperature: 'From (°C)' with '70', 'To (°C)' with '160', and 'Step (°C)' with '10'. To the right of these are 'Browse...' and 'Calculate' buttons.

Fig. 3. Input data for Reaction Equation calculations.

Write the reaction equation into the box, see **Fig. 3**. If you have not given the stoichiometric coefficients for the species, you can press Balance to solve unknown coefficients. The balance button solves the coefficients on the basis of element balance equations. Therefore it cannot solve unknown coefficients if their number is larger than the number of elements in the corresponding reaction.

Next to the Balance button, you may give a **multiplier**, which will be used to multiply all the coefficients in the reaction equation. The default value is 1, which means that the smallest stoichiometric coefficient in the reaction equation is 1.

You can continue in the same way as in the One Chemical Formula option, see Chapter 10 (section 10.1).

Note that the **Delta Format** and **Show Transitions** options have no effect on the results, because the enthalpy and Gibbs energy of a reaction are in the Delta format by definition.

HSC calculates the stoichiometry of the reaction given by the user, and points out errors if the element balance is incorrect.

The example in **Fig. 3** refers to the Mond process for refining impure nickel. In this process, raw impure nickel is first treated with CO gas at 60 °C to evaporate the nickel as a carbonyl gas. In the second stage, the temperature of the gas is increased to 200 °C to decompose the nickel carbonyl gas into pure metallic nickel and CO. This process works because the equilibrium of this reaction is on the right side (Equilibrium constant $K > 1$) at lower temperatures and on the left side ($K < 1$) at higher temperatures, **Fig. 4**. The reaction is exothermic (ΔH is negative) at all temperatures.

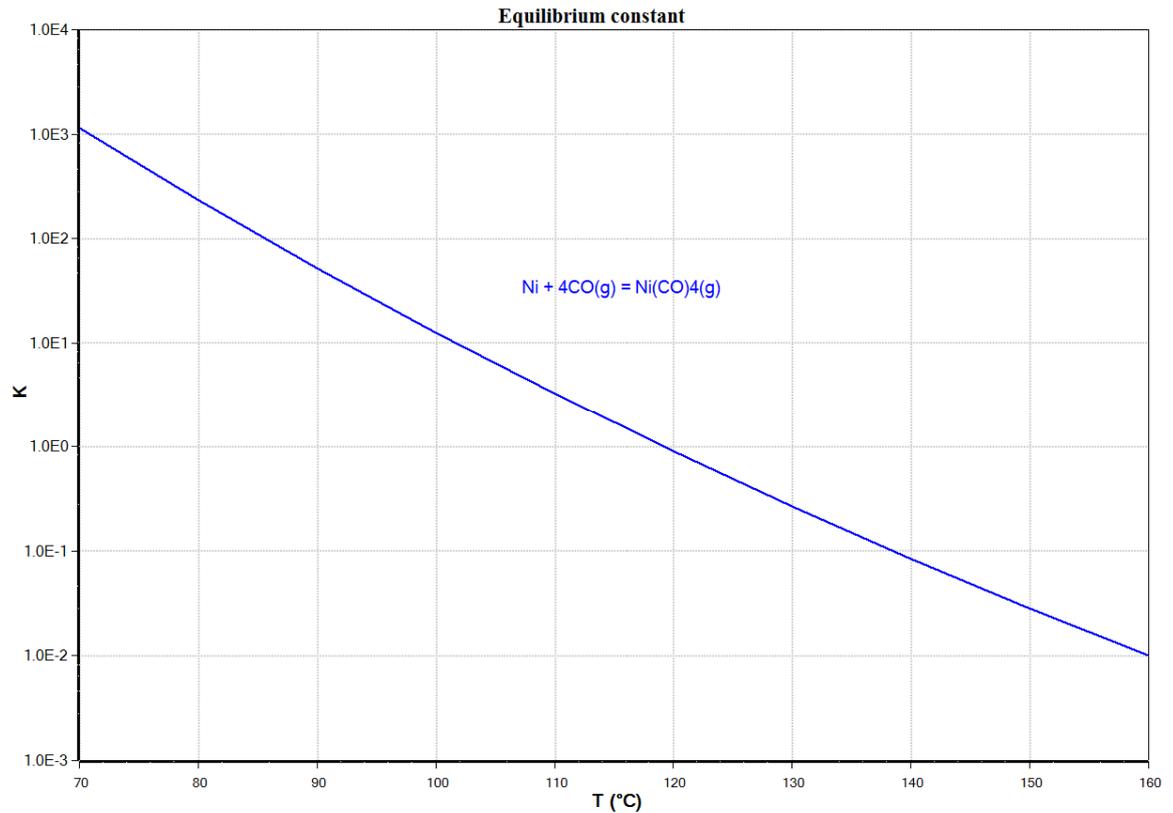


Fig. 4. Graphical results of Reaction Equation calculations.

Vapor pressures p can be calculated by writing the reaction equation for the vaporization reaction concerned. For example, for pure magnesium the equilibrium is **$Mg = Mg(g)$** . The activity a_{Mg} of pure magnesium is 1 and thus the vapor pressure in bar is equal to the equilibrium constant according to Eq. (1) in Chapter 8 Introduction and Eq. (1). See also **Fig. 5** and **Fig. 6**.

$$K = \frac{p_{Mg(g)}}{a_{Mg}} = p_{Mg(g)} \quad (1)$$

If a substance vaporizes into several polymers, all of them must be taken into account. The total vapor pressure is then the sum of all the individual partial pressures, if the gas phase behaves ideally.

Reaction Equation							
Mg = Mg(g)							
Reaction Data							
T °C	ΔH kJ	ΔS J/K	ΔG kJ	K		Log K	
500.000	143.884	110.035	58.811	1.063E-004		-3.974	
550.000	143.398	109.425	53.324	4.130E-004		-3.384	
600.000	142.876	108.810	47.869	1.368E-003		-2.864	
650.000	133.839	99.002	42.445	3.964E-003		-2.402	
700.000	133.163	98.289	37.513	9.689E-003		-2.014	
750.000	132.487	97.612	32.616	2.161E-002		-1.665	
800.000	131.810	96.966	27.751	4.458E-002		-1.351	
850.000	131.134	96.350	22.918	8.591E-002		-1.066	
900.000	130.458	95.761	18.116	1.561E-001		-0.807	
950.000	129.781	95.196	13.342	2.693E-001		-0.570	
1000.000	129.104	94.654	8.596	4.439E-001		-0.353	
1050.000	128.427	94.132	3.876	7.030E-001		-0.153	
1100.000	127.750	93.630	-0.818	1.074E+000		0.031	
1150.000	127.074	93.146	-5.487	1.590E+000		0.201	
1200.000	126.397	92.678	-10.133	2.287E+000		0.359	
1250.000	125.720	92.227	-14.755	3.207E+000		0.506	
1300.000	125.043	91.789	-19.356	4.393E+000		0.643	
1350.000	124.366	91.366	-23.934	5.892E+000		0.770	
1400.000	123.690	90.955	-28.492	7.755E+000		0.890	
1450.000	123.013	90.557	-33.030	1.003E+001		1.001	
1500.000	122.337	90.170	-37.548	1.277E+001		1.106	
Species Data							
Formula	M	Conc. wt-%	Input Amounts				Extrapolated From T(K)
	g/mol		mol	g	Volume	Unit	
Mg	24.305	100.000	1.000	24.305	13.968	ml	-
Mg(g)	24.305	100.000	1.000	24.305	22.414	l	-

Fig. 5. The equilibrium constant K is equal to the vapor pressure in bar according to Equation (1) if the activity of magnesium is 1. The boiling point of magnesium is about 1100 °C beyond which its vapor pressure exceeds 1 bar.

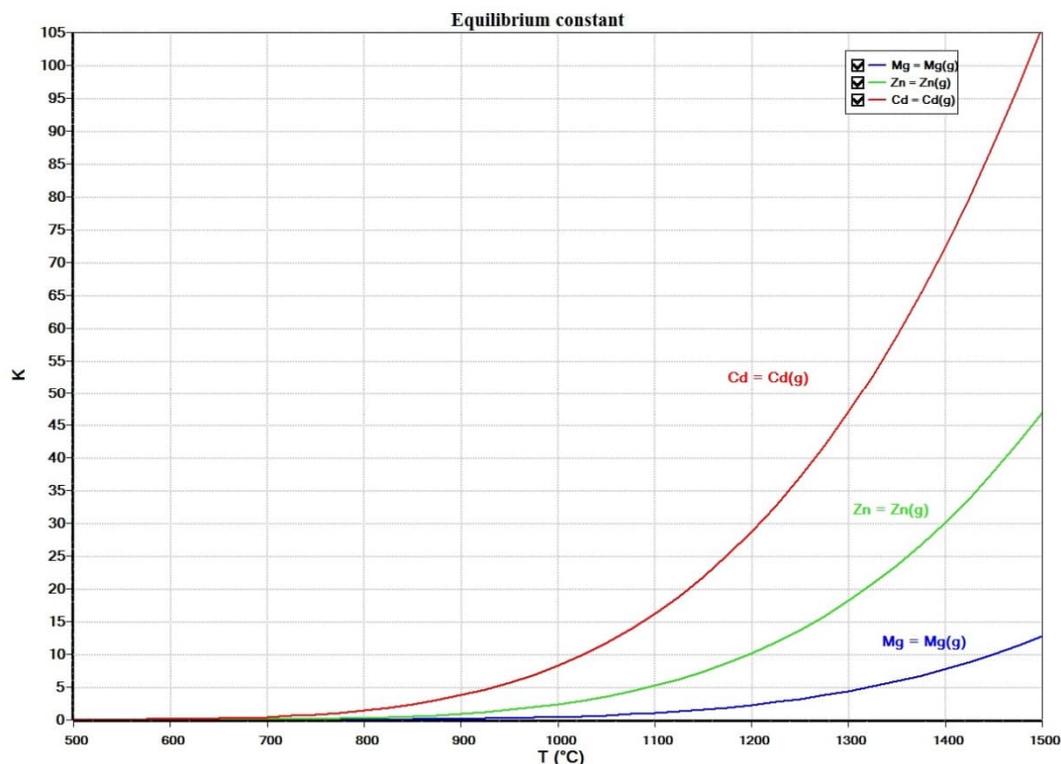


Fig. 6. Results for several reactions can be plotted into a single chart with **Plot all data** to help the comparison.

User can also calculate more complicated reactions. First, write the reaction as shown in **Fig. 7**, then press **Balance** for the coefficients, see **Fig. 8**, and finally press **Calculate** for the results, see **Fig. 9**.

Note that for aqueous ionic reactions, HSC also calculates the electrode potential versus Standard Hydrogen Electrode (E vs. SHE) if an electron (e-) is used in the formula. Sign convention of IUPAC⁴ is used for E vs SHE. In some older books sign convention is different⁵⁻⁶. For example $\text{Zn} + 2\text{a} + 2\text{e}^- = \text{Zn}$, $E^0 = -0.76 \text{ V}$ and $\text{Cu} + 2\text{a} + 2\text{e}^- = \text{Cu}$, $E^0 = 0.34 \text{ V}$.

Specifications

Reaction Equation or Chemical Formula Smallest Coefficient

$\text{FeS2} + \text{H2O} = \text{Fe2O3} + \text{SO4}(-2\text{a}) + \text{H}(+\text{a}) + \text{e}^-$

Temperature From (°C) To (°C) Step (°C)

Fig. 7. Write the reaction equation without stoichiometric coefficients and press **Balance**.

Specifications

Reaction Equation or Chemical Formula Smallest Coefficient

$2\text{FeS2} + 19\text{H2O} = \text{Fe2O3} + 4\text{SO4}(-2\text{a}) + 38\text{H}(+\text{a}) + 30\text{e}^-$

Temperature From (°C) To (°C) Step (°C)

Fig. 8. Press **Calculate** to display the results.

Reaction Equation							
$2\text{FeS}_2 + 19\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 4\text{SO}_4(-2a) + 38\text{H}(+a) + 30e^-$							
Reaction Data							
T °C	ΔH kJ	ΔS J/K	ΔG kJ	K	E vs. SHE V		
0.000	1497.322	1318.489	1137.177	3.300E-218	-0.393		
25.000	1322.639	687.984	1117.516	1.582E-196	-0.386		
50.000	1273.727	530.356	1102.343	6.309E-179	-0.381		
75.000	1227.176	391.590	1090.844	2.097E-164	-0.377		
100.000	1179.891	260.454	1082.702	2.675E-152	-0.374		
125.000	1129.764	130.485	1077.812	3.858E-142	-0.373		
150.000	1074.585	-3.849	1076.214	1.375E-133	-0.372		
175.000	1011.966	-147.532	1078.082	2.149E-126	-0.373		
Species Data							
Formula	M g/mol	Conc. wt-%	Input Amounts				Extrapolated From T(K)
			mol	g	Volume	Unit	
FeS2	119.967	41.210	2.000	239.934	47.796	ml	-
H2O	18.015	58.790	19.000	342.289	373.270	ml	-
Fe2O3	159.692	27.427	1.000	159.692	30.476	ml	-
SO4(-2a)	96.058	65.992	4.000	384.230	0.000	ml	-
H(+a)	1.008	6.578	38.000	38.300	0.000	ml	-
e-	0.001	0.003	30.000	0.016	0.000	ml	-

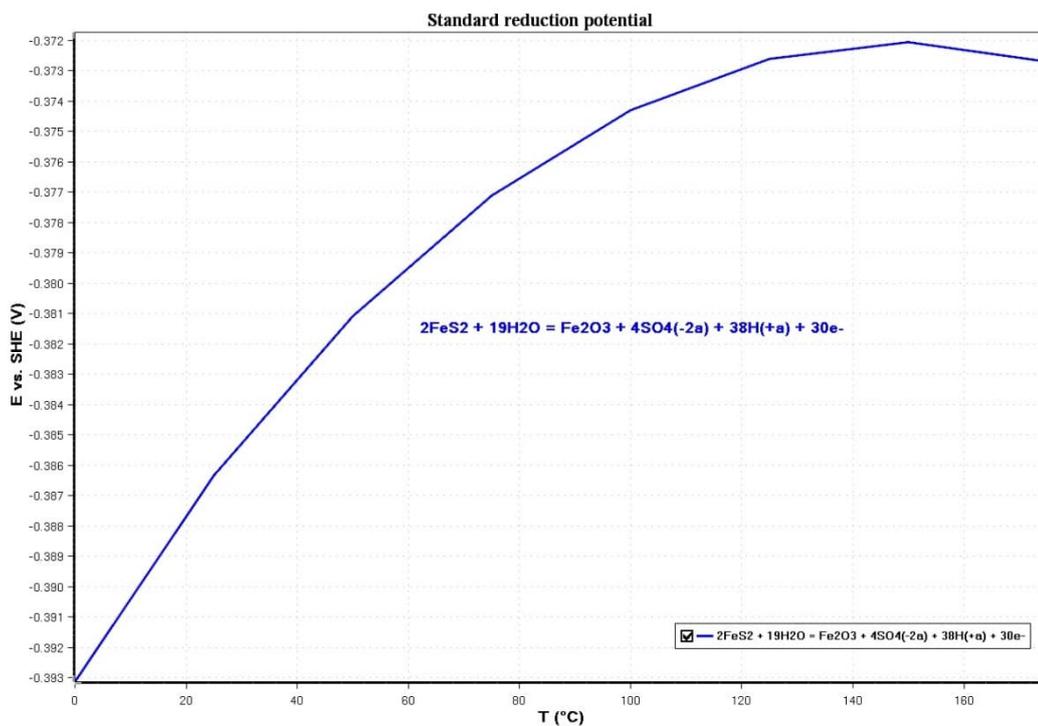


Fig. 9. Results for an aqueous ionic reaction.

The data used to calculate the results can be displayed by selecting a single substance in the **Reaction Equation** box, see **Fig. 3** and then pressing **Browse...** The database content is shown in **Fig. 10**. Species can be imported to the Reaction Equation module

by adding the species first in the **Selected Species** box at the bottom of the database browser and then clicking **Import species**.

Database Browser

File | Joules | Calories | K | °C | Main Database | Own Database | Find by Elements | Diagrams | Help | About

Menu | Unit | Temperature | Database Selection | Tools | Info

Text Filters: Elements, Formula (TiO2), Stoichiometry, Keywords

Possible Species: Start With, Free Ratio, Structural Formula, Che...

Type Filters: Select All, Gases, Gas Ions, Condensed, Electrons, Liquids, Aqueous Ions, Aqueous Neutrals, Fluids

Organic Filter: Include Organics, Range Of Carbon Atoms

Matching Species - 4: TiO2, TiO2(l), TiO2(g), TiO2(A)

Basic Data:

Formula	TiO2	CAS	13463-67-7	H° formation at 298.15 K	-944.747	kJ/mol
Structural Formula	OZTi	Molecular Weight	79.865	S° at 298.15 K	50.291	J/(mol*K)
Chemical Name	Titanium(IV) oxide	Melting Point	2116.000	Cp at 298.15 K	54.949	J/(mol*K)
Common Name	Rutile	Boiling Point	3000.000	ΔG° at 298.15 K	-889.417	kJ/mol

Temperature Ranges $C_p(T) = A + BT \cdot 10^{-3} + CT^{-2} \cdot 10^5 + DT^2 \cdot 10^{-6}$

Range	1	2	3	4	5	6	7	8	9
Tmin (K)	298.15	2143.00							
Tmax (K)	2143.00	3000.00							
Phase	s	l							
H kJ / mol	-944.747	66.944							
S J / (mol * K)	50.292	31.430							
Cp coefficient A J/(mol*K)	70.195	100.416							
Cp coefficient B	7.573	0.000							
Cp coefficient C	-15.439	0.000							
Cp coefficient D	-1.523	0.000							
Density kg/l	4.230	0.000							
Color	7	0							
Solubility in H2O g/l	0.000	0.000							
Reference	Barin 93; Sax	Barin 93							
Reliability Class	1	1							

Selected Species - 1: TiO2

Import species

Outotec Databases in use...

Fig. 10. The database browser window.

10.4. Reaction Equations Results

The operation of the buttons in **Fig. 1** and **Fig. 2** were described in the previous chapter. The meaning of the results can be summarized as follows:

1. If the equilibrium constant K is < 1 (or $\log(K) < 0$), the reaction goes to the left.
2. If the equilibrium constant K is > 1 (or $\log(K) > 0$), the reaction goes to the right.
3. A negative Enthalpy H of the reaction means that the reaction is exothermic, i.e. heat is released, Equation 7 in *8. Introduction*.
4. A positive Enthalpy H of the reaction means that the reaction is endothermic, i.e. heat is absorbed, Equation 7 in *8. Introduction*.
5. Delta Format has no effect on the results of reaction equations.
6. In ionic reactions, potential E yields the electrochemical potential (in Volts) versus the Standard Hydrogen Electrode (SHE). Note, "e-" has to be included in the reaction.
7. Equilibrium constant K is calculated using Equation (12) in *8. Introduction*.

10.5. References

1. Barin I., Knacke O., and Kubaschewski O.: Thermodynamic Properties of Inorganic Substances, Springer-Verlag, Berlin, 1973, Supplement 1977.
2. Pankratz L.B.: Thermodynamic Properties of Halides, U.S. Dept. of the Interior, Bureau of Mines, Bulletin 674, 1984.
3. Bailey S. M., Churney K. L., Nuttall R. L.: The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units, J. of Phys. and Chem. Ref. Data, Vol. 11, Suppl. No. 2, 1982.
4. IUPAC Green Book, <http://www.iupac.org/home/publications/e-resources/nomenclature-and-terminology/quantities-units-and-symbols-in-physical-chemistry-green-book.html>.
5. W. M. Latimer, Oxidation Potentials, 2nd ed., Prentice-Hall, Englewood Cliffs, N.J, 1952.
6. Pourbaix M., Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston, 1974.