

10. REACTION EQUATIONS

Clicking the **Reaction Equations** button in the main menu shows the Reaction Equations Window, see Fig. 1. With this calculation option 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.

See the reference state definitions, valid notations and abbreviations for the description of the chemical formulae in Chapter 28. *Databases*, chapter 2.

10.1 One Chemical Substance

Reaction Equation or Chemical Formula:
Al₂O₃

From: 0.000 To: 1000.000 Step: 100.000 C

Temperature Units:
 Celsius
 Kelvins

Energy Units:
 Calories
 Joules

Format of Results:
 Normal
 Delta

Collect to Sheet
 Show Transitions
 Criss-Cobble

Help File Open HSC 2 File Balance Equation Peep Database
 Exit File Open ... 1 Calculate

Fig. 1. Reaction Equations Window of HSC Chemistry.

	T	Cp	H	S	G	Reference
1	Al2O3	Aluminum oxide				
2	T	Cp	H	S	G	Reference
3	C	cal/(mol*K)	kcal/mol	cal/(mol*K)	kcal/mol	
4	0.000	17.248	-400.947	10.614	-403.846	Barin 77, JANAF 98
5	100.000	21.600	-398.993	16.671	-405.214	Barin 77, JANAF 98
6	200.000	24.797	-396.665	22.185	-407.162	Barin 77, JANAF 98
7	300.000	26.970	-394.068	27.157	-409.633	Barin 77, JANAF 98
8	400.000	28.161	-391.303	31.601	-412.576	Barin 77, JANAF 98
9	500.000	28.386	-388.468	35.527	-415.936	Barin 77, JANAF 98
10	600.000	29.168	-385.590	39.027	-419.666	Barin 77
11	700.000	29.709	-382.646	42.219	-423.731	Barin 77
12	800.000	30.166	-379.651	45.148	-428.101	Barin 77
13	900.000	30.564	-376.614	47.853	-432.753	Barin 77
14	1000.000	30.916	-373.540	50.368	-437.666	Barin 77
15						
16	Formula	FM	Conc.	Amount	Amount	Volume
17		g/mol	wt-%	mol	g	l or ml
18	Al2O3	101.961	100.000	1.000	101.961	25.715 ml
19		g/mol	wt-%	mol	g	l or ml
20						
21						

Fig. 2. Thermodynamic data of Al₂O₃ (alumina) displayed by the Reaction Equation option 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 those temperatures which you really want. Please follow these steps:

1. Write a chemical formula into the box, 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 21.2.
2. Select the lower limit, upper limit and temperature step.
3. Select the Temperature and Energy Units, by clicking the corresponding buttons.
4. Select the Format of the results.

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):

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

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

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

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

z = charge.

This format is used for example in the NBS Tables^{NBS 82}.

5. The **Collect to Sheet** option will collect several tables on the same spreadsheet.
 6. Select the **Show Transitions** option if you also want to see the data at the phase transformation temperatures, such as crystal structure changes and melting.
 7. Select the **Criss-Cobble** option if you want a Criss-Cobble extrapolation for the heat capacity of aqueous species, see Chapter 21.4.
 8. Press **Calculate** (or Enter) to get the results on the screen.
 9. Press **Print** to print the results, see Fig. 2. Note that you can collect several sets of results in the same sheet if you have selected the **Collect to Sheet** option in Fig. 1. You can clear the whole sheet by pressing **Clear**.
 10. Press **Copy All** to get all the results into the Clipboard, then you can easily paste the results to other Windows applications, for example, to MS-Excel, see Fig. 2. Using **Copy** it is possible to copy and paste contents of individual cells to other applications.
 11. If you want to save the formula and results in an ASCII-file press **Save**, see Fig. 2. You can read these files back to the Reaction module using **File Open**, see Fig. 1. Note that **Save** saves all the selections in Fig. 1, so you can return these using **File Open**. The **File Open HSC 2 File** button reads only old HSC 2.0 files which return only formula, but not the selections nor temperature range.
- Note:**
1. You can easily check the basic data from the database, which has been used in the reaction module calculations. In Fig. 1 select the formula in the Reaction Equation box and press **Peep Database**. The same procedure can be found in Fig. 2 by pressing the right mouse button or selecting **Edit** from the menu.
 2. The table in Fig. 2 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** (OwnDB5.HSC). If it does not find a species there, it will search from the **Main database** (MainDB5.HSC). 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 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 28.4.

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 the previous screen, Fig. 1, you will arrive in the results window, Fig. 2. From this results screen you can save and print the results:

1. Press **Save** if you wish to recalculate the results later. The **Save** button will also save the settings used in Fig. 1. You can read these files back to HSC using the **File Open** button, see Fig. 1.
2. Press **Print** if you want a paper copy. If you have selected the **Collect to Sheet** option in Fig. 1, then all results will be collected on the same sheet and can be printed together. **Clear** will clear the results sheet.
3. Press **Copy** to get the results of selected cells into the Clipboard, then you can easily paste the results, for example, to MS -Excel, see Fig. 2.
4. Press **Copy All** to get all the results of the sheet into the Clipboard, then you can easily paste the results, for example, to MS -Excel, see Fig. 2.
5. Press **OK** to return to the previous Window.

10.3 Reaction Equations

The screenshot shows the 'Reaction Equations' window in HSC Chemistry 6.0. The main input field contains the chemical equation: $\text{Ni} + 4\text{CO}(\text{g}) = \text{Ni}(\text{CO})_4(\text{g})$. Below this, the temperature range is set from 70 to 160 with a step of 10.000 C. The interface includes several control panels: 'Temperature Units' (Celsius selected), 'Energy Units' (Calories selected), 'Format of Results' (Normal selected), and a checkbox panel (Show Transitions and Criss-Cobble checked). At the bottom, there are buttons for 'Help', 'Exit', 'File Open HSC 2 File', 'File Open ...', 'Balance Equation' (with a value of 1), and 'Peep Database'. A 'Calculate' button is also present.

Reaction Equation or Chemical Formula:			
$\text{Ni} + 4\text{CO}(\text{g}) = \text{Ni}(\text{CO})_4(\text{g})$			
Temperature:	From	To	Step
	70	160	10.000 C

Temperature Units: <input checked="" type="radio"/> Celsius <input type="radio"/> Kelvins	Energy Units: <input checked="" type="radio"/> Calories <input type="radio"/> Joules	Format of Results: <input checked="" type="radio"/> Normal <input type="radio"/> Delta	<input type="checkbox"/> Collect to Sheet <input checked="" type="checkbox"/> Show Transitions <input checked="" type="checkbox"/> Criss-Cobble
--	---	---	---

Help	File Open HSC 2 File	Balance Equation	Peep Database
Exit	File Open ...	1	Calculate

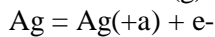
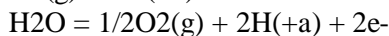
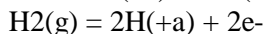
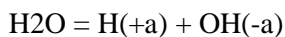
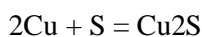
Fig. 3. Input data for Reaction Equation calculations.

HSC Results						
File Edit Format Help						
	T	Cp	H	S	G	Reference
1	Ni + 4CO(g) = Ni(CO)4(g)					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	C	kcal	cal/K	kcal		
4	70.000	-38.321	-97.649	-4.813	1.163E+003	3.065
5	80.000	-38.293	-97.569	-3.837	2.369E+002	2.375
6	90.000	-38.264	-97.487	-2.861	5.274E+001	1.722
7	100.000	-38.233	-97.404	-1.887	1.274E+001	1.105
8	110.000	-38.201	-97.318	-0.913	3.319E+000	0.521
9	120.000	-38.167	-97.232	0.059	9.267E-001	-0.033
10	130.000	-38.133	-97.145	1.031	2.760E-001	-0.559
11	140.000	-38.097	-97.057	2.002	8.724E-002	-1.059
12	150.000	-38.060	-96.969	2.972	2.915E-002	-1.535
13	160.000	-38.022	-96.881	3.942	1.026E-002	-1.989
14						
15	Formula	FM	Conc.	Amount	Amount	Volume
16		g/mol	wt-%	mol	g	l or ml
17	Ni	58.700	34.379	1.000	58.700	6.596 ml
18	CO(g)	28.010	65.621	4.000	112.042	89.654 l
19		g/mol	wt-%	mol	g	l or ml
20	Ni(CO)4(g)	170.742	100.000	1.000	170.742	22.414 l
21						

OK Help Print Clear Copy All Copy Save

Fig. 4. Results of Reaction Equation calculations.

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



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 Equation** for solving 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.

On the right side of the 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 Chapter 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 the 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. The reaction is exothermic (ΔH is negative) at all temperatures.

Vapor pressures p can be calculated by writing the reaction equation for the vaporization reaction concerned. For example, for pure magnesium the equilibrium is $\text{Mg} = \text{Mg(g)}$, Fig. 5. The activity a of pure magnesium is 1 and thus the vapor pressure in bar is equal to the equilibrium constant according to Eq. (10) in Chapter 8. *Introduction* and Eq. (1). See also Fig. 6.

$$K = p_{\text{Mg}} / a_{\text{Mg}} = p_{\text{Mg}} \quad [1]$$

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.

You 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 if electron (e^-) is used in the formula.

You can calculate mass balances in moles, grams and liters for any reaction. The species does not need to exist in the HSC databases.

HSC Reaction Equations

Reaction Equation or Chemical Formula:

Temperature: C

Temperature Units: Energy Units: Format of Results: Collect to Sheet
 Celsius Calories Normal Show Transitions
 Kelvins Joules Delta Criss-Cobble

Fig. 5. Input data for Reaction Equation calculations.

HSC Results

File Edit Format Help

	T	Cp	H	S	G	Reference
1	Mg = Mg(g)					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	C	kcal	cal/K	kcal		
4	500.000	34.389	26.299	14.056	1.063E-004	-3.974
5	600.000	34.148	26.006	11.441	1.368E-003	-2.864
6	700.000	31.827	23.492	8.966	9.689E-003	-2.014
7	800.000	31.503	23.176	6.633	4.458E-002	-1.351
8	900.000	31.180	22.887	4.330	1.561E-001	-0.807
9	1000.000	30.857	22.623	2.054	4.439E-001	-0.353
10	1100.000	30.533	22.378	-0.195	1.074E+000	0.031
11	1200.000	30.210	22.151	-2.422	2.287E+000	0.359
12	1300.000	29.886	21.938	-4.626	4.393E+000	0.643
13	1400.000	29.563	21.739	-6.810	7.755E+000	0.890
14	1500.000	29.239	21.551	-8.974	1.277E+001	1.106
15						
16	Formula	FM	Conc.	Amount	Amount	Volume
17		g/mol	wt-%	mol	g	l or ml
18	Mg	24.305	100.000	1.000	24.305	13.968 ml
19		g/mol	wt-%	mol	g	l or ml
20	Mg(g)	24.305	100.000	1.000	24.305	22.414 l
21						

Antti Roine

August 10, 2006

06120-ORC-T

Fig. 6. The equilibrium constant K is equal to the vapor pressure in atm 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 atm.

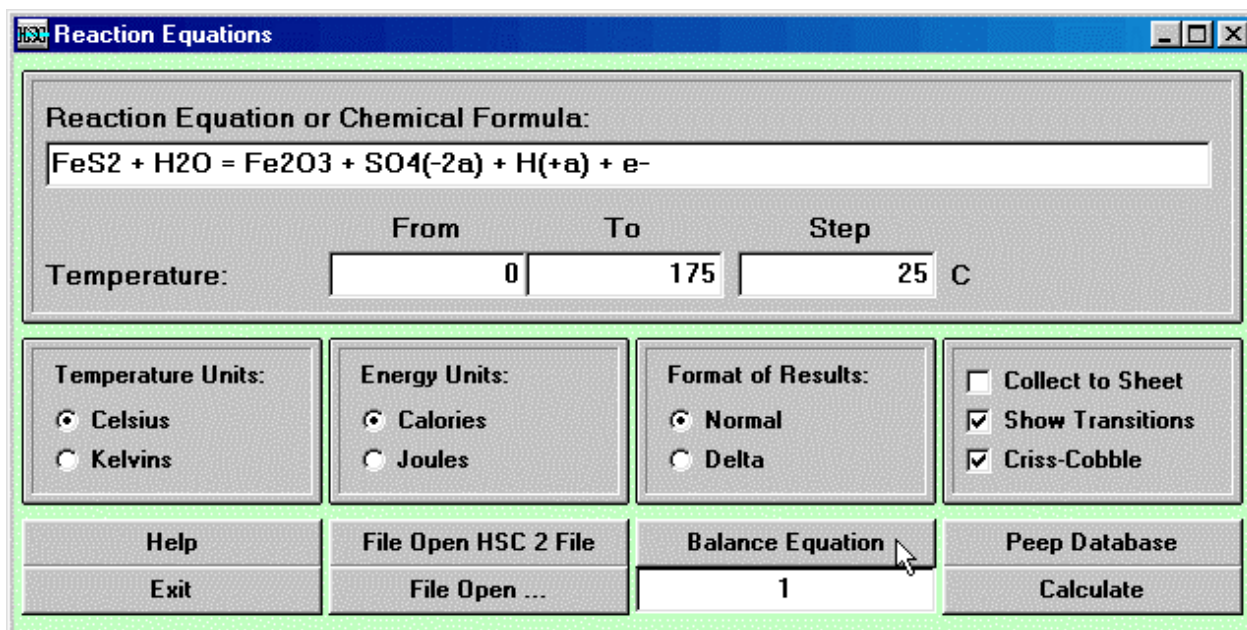


Fig. 7. Write the reaction equation without stoichiometric coefficients and press **Balance Equation**.

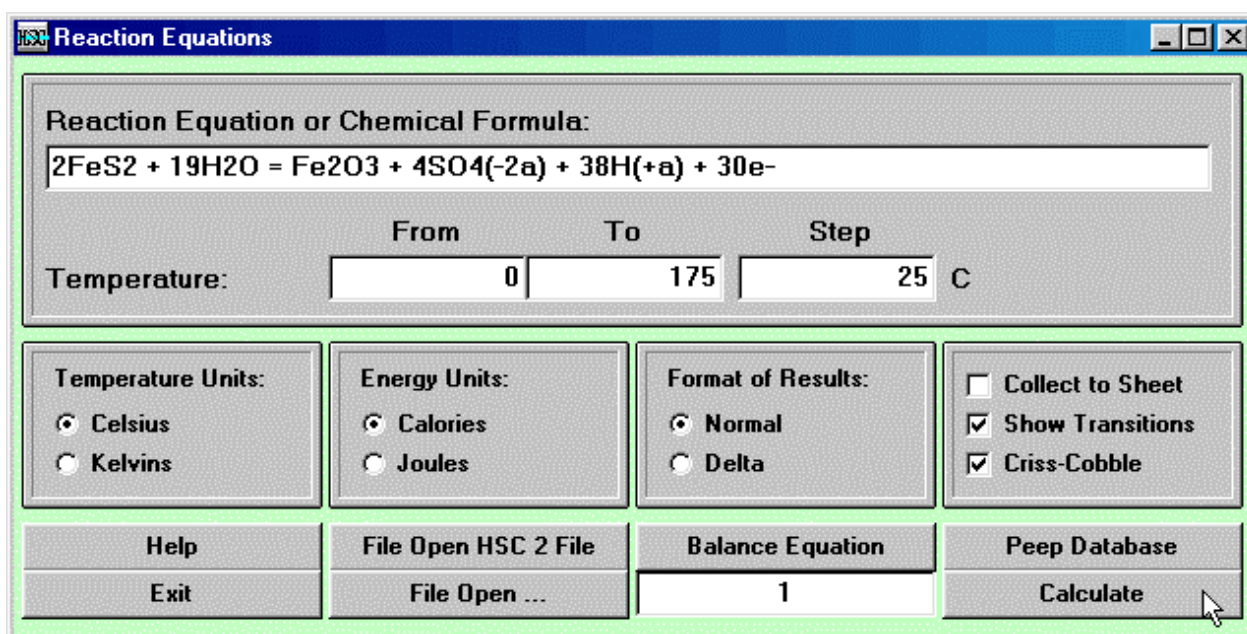


Fig. 8. Press **Calculate** to display the results.

HSC Results													
File Edit Format Help													
	T	Cp	H	S	G	Reference							
1	2FeS2 + 19H2O = Fe2O3 + 4SO4(-2a) + 38H(+a) + 30e-												
2	T	deltaH	deltaS	deltaG	K	E vs. SHE							
3	C	kcal	cal/K	kcal		Y							
4	0.000	354.839	315.127	268.762	8.768E-216	-0.389							
5	25.000	313.089	164.432	264.063	2.632E-194	-0.382							
6	50.000	301.399	126.758	260.437	7.067E-177	-0.377							
7	75.000	290.273	93.592	257.688	1.674E-162	-0.373							
8	100.000	278.971	62.250	255.743	1.592E-150	-0.370							
9	125.000	266.991	31.187	254.574	1.776E-140	-0.368							
10	150.000	253.803	-0.920	254.192	5.050E-132	-0.368							
11	175.000	238.836	-35.261	254.638	6.456E-125	-0.368							
12													
13	Formula	FM	Conc.	Amount	Amount	Volume							
14		g/mol	wt-%	mol	g	l or ml							
15	FeS2	119.967	41.210	2.000	239.934	47.796 ml							
16	H2O	18.015	58.790	19.000	342.289	373.270 ml							
17		g/mol	wt-%	mol	g	l or ml							
18	Fe2O3	159.692	27.427	1.000	159.692	30.476 ml							
19	SO4(-2a)	96.058	65.992	4.000	384.230	0.000 ml							
20	H(+a)	1.008	6.578	38.000	38.300	0.000 ml							
21													
<table border="1"> <tr> <td>OK</td> <td>Help</td> <td>Print</td> <td>Clear</td> <td>Copy All</td> <td>Copy</td> <td>Save</td> </tr> </table>							OK	Help	Print	Clear	Copy All	Copy	Save
OK	Help	Print	Clear	Copy All	Copy	Save							

Fig. 9. Results for an aqueous ionic reaction.

The data used to calculate the results can be displayed by selecting one substance in the **Reaction Equation** box, see Fig. 3 and pressing **Peep Database**. The same procedure can be found in the Results window, see Fig. 4, by pressing the right mouse button. The database content is shown in Fig. 10. **Insert** is available for inserting a selected formula into the Reaction Equation box. **Remove** will remove a selected formula from this same box. Note that the selections and editing in Fig. 10 do not have any effect on the HSC databases.

MainDB	1.	2.	3.
Formula	TiO2	TiO2	
Structural Formula	O2Ti	O2Ti	
Chemical Name	Titanium(IV) oxide; Titanium(IV) oxide		
Common Name	Rutile		
CAN	13463-67-7	13463-67-7	
Mol. Weight	79.90	79.90	
Melting p. K	2116.00	2116.00	
Boiling p. K	3000.00	3000.00	
T1 K	298.15	2143.00	
T2 K	2143.00	3000.00	
State	s	1	
H kcal/mol	-225.800	16.000	
S cal/(mol*K)	12.020	7.512	
A cal/(mol*K)	16.777	24.000	
B	1.810	0.000	
C	-3.690	0.000	
D	-0.364	0.000	
Density kg/l	4.230	0.000	
Color RGB	7.000	0.000	
Solubility	0.000	0.000	
Reference	Barin 93, Saxen	Barin 93	
Class	1	1	

Fig. 10. The database window.

10.4 Reaction Equations Results

The operation of the buttons in Fig. 3 are described in the previous chapter. The meaning of the results can be summarized as the following:

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. Negative Enthalpy H of the reaction means that the reaction is exothermic, i.e. heat is released, Equation 7 in 8. *Introduction*.
4. Positive Enthalpy H of the reaction means that the reaction is endothermic, i.e. heat is needed, 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.
7. Equilibrium constant K is calculated using Equation 11 in 8. *Introduction*.