Advanced features of Equilib

The Equilib module has many advanced features which are described here.

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A species or solution phase may be declared as a Target phase. There are several types of target phases:

1. **[F] - Formation target phase:** the T (P or <A>) is calculated when the species or phase first begins to form. The final T (P, <A>) must not be specified (blank column) and an estimate of the unspecified T (P, <A>) must be entered.

2. **[P] - Precipitate target phase:** the T (P or <A>) is calculated when another species or phase first starts to precipitate from this phase. The precipitate target phase must be a solution (for example FACT-SLAG or gas phase). The final T (P, <A>) must not be specified (blank column) and an estimate of the unspecified T (P, <A>) must be entered.

3. **[C] - Composition target phase:** the <A> is calculated for a given solution composition. The final T and P must also be specified and final <A> must not be specified (blank column).
The program calculates when this phase first forms (activity = 1, and generally zero mass). One of T, P or alpha must not be specified (i.e. blank) so that Equilib can calculate the limiting T (P or alpha) when the formation target phase first forms. The formation target phase may be a compound species (for example a pure solid or liquid) or a solution phase (gas phase or real solution such as FACT-SLAG).

Values of $<A>$ and $T$ used in the following example.
**Setting a FACT-SLAG formation target at a given composition**

1° **Right-click** on the + column to open the FACT-SLAG extended menu and **select F - formation target phase**.

2° **Enter** a value of \(<A\) (0.35) and leave a **blank** for the value of T(C) in the input boxes of the **Final Conditions** frame. This activates the **Formation Target** frame.

3° The **Formation Target** frame is **enabled**. **Enter** an estimate for the value of T(C). Here T(C) = 1000°C.

The program will calculate that temperature when FACT-SLAG first starts to form (0 mole).

---

**Equilib Advanced 2.1.1**

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Calculation of the FACT-SLAG formation target at a given composition

Note:
activity = 1.0
number of moles = 0
for the slag phase (liquid)
i.e. FACT-SLAG is just beginning to form.

<table>
<thead>
<tr>
<th>System component</th>
<th>Mole fraction</th>
<th>Mass fraction</th>
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<tbody>
<tr>
<td>Ca</td>
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<td>O</td>
<td>0.50401</td>
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</table>

Compositions and quantities of the solid oxides in equilibrium with FACT-SLAG.

Value of <A>, $X_{SiO_2} = 0.35$
Formation Target phase: specifying the target phase mass

In the **Menu-Equilb** window **Formation Target** frame, the target phase mass is set to **0.5 mole**.

Note: The slag-liquid composition is now: \( X_{\text{SiO}_2} = 0.36667 \)

and the temperature has increased to: \( T = 1922.80^\circ C \)

Value of \( <A> \), \( X_{\text{SiO}_2} = 0.35 \)

The cutoff concentration has been specified to \( 1.0000E-75 \)

Data on 6 product species identified with \( "T" \) have been extrapolated

\[
\begin{align*}
\text{H} & : 1.45531E+06 & \text{U} & : -1.0002E+06 & \text{S} & : 0.0000E+00 & \text{Cp} & : 1.64265E+02 & \text{Cp} & : 7.66105E+01 \\
\end{align*}
\]
Setting a **FACT-SLAG formation target** at a given temperature

1° **Right-click** on the + column to open the FACT-SLAG extended menu and **select F-formation target phase**.

2° **Enter** a value of \( T \) (1800 °C) and leave a **blank** for the value of \( <A> \) in the input boxes of the **Final Conditions** frame.

3° The **Formation Target** frame is **enabled**. Enter an estimate of the value of \( <A> \). Here \( <A> = 0.5 \).

The program will calculate that composition when FACT-SLAG first starts to form (0 mole).
Calculation of the FACT-SLAG formation target at a given temperature (1800°C)

Compositions and quantities of the solid phases in equilibrium (activity = 1) with FACT-SLAG.

Note: activity = 1.0 number of moles = 0 for the slag phase (liquid) i.e. FACT-SLAG is just beginning to form.

Calculated value of \(<A> = 0.3333\)
Precipitate target

The program calculates when a second phase first starts to precipitate (activity = 1, zero mass) from this target solution phase (activity = 1, 100% mass). One of T, P or alpha must not be specified (i.e. blank) so that Equilib can calculate the limiting T (P or alpha) when the second phase precipitates.

The precipitate target phase must be a solution phase for example gas or FACT-SLAG.

CaO - SiO₂

<\(A\) > = 0.35

T = 1800°C

Values of <\(A\) > and T used in the following example.
Setting a FACT-SLAG precipitate target at a given composition

1° Right-click on the + column to open the FACT-SLAG extended menu and select P – precipitate target phase.

2° Enter a value of \(<A> (0.35)\) and leave T(C) blank.

3° The Precipitate Target frame is enabled. Enter an estimate of the value of T(C). Here T(C) = 1000°C.
Calculation of the **FACT-SLAG precipitate target** at a given composition

Equilibrium at **2085.37 °C**

*Note:* activity = 1.0
number of moles = 1 (100%) for the first phase: the slag phase (liquid).

First precipitate to deposit from the slag phase
activity = 1.0
number of moles = 0.

Value of \( <A> \), \( X_{SiO_2} = 0.35 \)

The cutoff concentration has been specified to 1.0000E-75

Data on 6 product species identified with "T" have been extrapolated

<table>
<thead>
<tr>
<th>( H )</th>
<th>( G )</th>
<th>( V )</th>
<th>( S )</th>
<th>( Cp )</th>
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<td>(J)</td>
<td>(litre)</td>
<td>(J/K)</td>
<td>(J/K)</td>
</tr>
<tr>
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<td>0.00000E+00</td>
<td>1.70907E+02</td>
<td>6.93966E+01</td>
</tr>
</tbody>
</table>
1° Right-click on the + column to open the FACT-SLAG extended menu and select P – precipitate target phase.

2° Enter a value of T (1800°C) and leave <A> blank.

3° The Precipitate Target frame is enabled. Enter an estimate of the value of <A>. Here <A> = 0.5.
Calculation of a **FACT-SLAG precipitate target** at a given temperature.

Note:
activity = 1.0
number of moles = 1 (100%)
for the first phase:
the slag phase (liquid).

First precipitate to deposit from the slag phase
activity = 1.0
number of moles = 0.

Calculated value of \(<A>\), \(X_{\text{SiO}_2} = 0.3767\).
**Precipitate target phase** calculation for a more complex system

This is an example of a Slag-liquid precipitate target phase calculation in the CaO-SiO$_2$-Al$_2$O$_3$ ternary system.

In a precipitate target phase calculation, the temperature (or composition) is calculated when a second phase first starts to form (activity = 1, and zero mole) from the «precipitate target phase». The «precipitate target phase» must be a solution for example, gas, FACT-SLAG, etc. (this differs from the «formation target phase» that can be any type of phase).

In this example that temperature is calculated when the first solid precipitate starts to deposit when Slag-liquid (FACT-SLAG) is cooled. Such a calculation is extremely important for example in the pyrometallurgy and glass industries. In principle one could select the equilibrium «transitions» option and execute a normal calculation, but this may lead to lot of unwanted output, especially if the system is complex.

Red rimmed dot: for the 1$^{\text{st}}$ example
Teal line for $<\text{B}> = 25\%$ (2$^{\text{nd}}$ example)
Setting a ternary system in the *Equilib* Reactants Window

In the **Reactants Window** the reactants are \(<1-A-B>\) CaO + \(<A>\) SiO\(_2\) + \(<B>\) Al\(_2\)O\(_3\). This defines a CaO-SiO\(_2\)-Al\(_2\)O\(_3\) ternary system if \(<A> + <B>\) is in the range 0 to 1. The use of unit mass (g or lb) will give the compositions in weight %.

*All data taken from the FACT compound and solution databases.*
Setting the FACT-SLAG precipitate target at a given composition

1° Right-click on the + column to open the FACT-SLAG extended menu and select P - precipitate target phase.

2° Enter values for <A> (0.35) and <B> (0.25) (i.e. %wt CaO = 40%, %wt SiO₂ = 35%, %wt Al₂O₃ = 25%) and leave T(C) blank.

3° The Precipitate Target frame is enabled. Enter an estimate of the value of T(C). Here T(C) = 2000°C.

<A> is a variable, <B> is a constant (here, 25 wt.%) that must be defined.
**Precipitate target Results**

*Equilib* reports the temperature (1458.99 °C) where the second phase (Ca$_2$Al$_2$SiO$_7$(s1)) starts to precipitate from the target phase (Slag-liquid).

Notes: the composition of the first phase (Slag-liquid) is the same as the input values. activity = 1.0

number of grams = 1 (i.e. 100%)  

First precipitate to deposit from the slag phase
activity = 1.0
number of grams = 0.  

Value of $<A>$, wt% SiO$_2$ = 35%.
Performing a composition Precipitate Target calculation

As in the previous example on Formation Target calculations, it is possible to perform a composition Precipitate Target calculation on \(<A>\) (constant \(<B>\) remains unchanged).

For example, if in the Menu Window the composition \(<A>\) is now unspecified (blank), \(<B>\) is still 25% and now the temperature is set to 1600°C, an estimate of \(<A>\) is 50%.
In the Results Window Equilib now reports the silica (SiO$_2$) composition ($<A> = 13.371$ wt.%) at $1600^\circ$C where CaO(s1) first starts to precipitate (activity = 1, 0 gram).

In the ternary phase diagram at $1600^\circ$C (see slide 4.0), there are two liquidus lines intersecting the composition line for which $<B> = 25$wt.%. One on the CaO-rich side (calculated here) and one on the SiO$_2$-rich side.
In the **Results Window** **Equilib** now reports the silica (SiO$_2$) composition ($<A> = 68.303$ wt.%$)$ at 1600$^\circ$C where mullite Al$_6$Si$_2$O$_{13}$(s1) first starts to precipitate (activity $= 1$, 0 gram).

By setting (in the **Menu Window**) another estimate for ALPHA $<A>$ on the SiO$_2$-rich side, one can calculate the other value of $<A>$ for which a precipitate starts to form.
Transitions in the CaO-SiO$_2$ binary phase diagram

Liquid phase immiscibility – for example $X_{\text{SiO}_2} = 0.7783$ and 0.9707 at 1800°C.
Isothermal phase transitions in the **CaO-SiO₂** binary system

1° Binary system <1-A> CaO + <A> SiO₂.

2° Possible products:
- pure solid oxides
- liquid Slag (**FACT-SLAG**) with a possible 2-phase immiscibility (I)

3° <A> = 0.7, 0.75, ..., 1.0
T (°C) = 1800

4° Select transitions

The program will calculate the equilibrium at **1800°C** for mole fractions of SiO₂ varying from **0.7** to **1** in increments of **0.05** and will search for all phase transitions.
1° In the **Menu-Equilib** window **Compound species** frame, **right-click** on the **pure solids checkbox** to open the Species selection window.

**17 pure solid oxides**

2° **Click on Clear**, then on **Select/Clear…** and then **select all (solid) species containing... Oxygen.**

3° **Press OK** to return to the **Menu-Equilib window.** An asterisk (*) indicates **custom selection** for the **pure solids**.
Step 2°: Products Selection – solution species

1° In the Menu-Equilib window Solution species frame, right-click on the + column to open the FACT-SLAG extended menu.

2° In the FACT-SLAG extended menu, select option I.

3° The I indicates a possible 2-phase immiscible region.

- [I] - 2-phase Immiscibility: the solution phase may be immiscible. Use this option for FACT-SLAG when SiO$_2$ > 50%. If the phase is not immiscible the results of the calculation will be OK - the phase will appear twice with the same composition. **Note:** This option tends to slow down the speed of the calculation - you may wish to try I! (immiscible and dormant) to check if the phase is stable.
Compositions at the two ends of the 1800°C tie-line

2-phase transitions – the ends of the 1800°C tie-line.

Equilib reports two-phase stability within the composition range:

\[ 0.77829 < X_{\text{SiO}_2} < 0.97074 \]

and one-phase stability outside this range.
One-phase and two-phase stability at 1800°C

Example of two-phase stability at $X_{\text{SiO}_2} = 0.85$

Example of one-phase stability at $X_{\text{SiO}_2} = 0.75$

Slag-liquid#2 is close to forming – its activity is 0.98105.

In such systems, if option «I» is not selected, the results may be in error even when the second liquid (Slag-liquid#2) is not stable (as in the above example).
Constant composition in the CaO-SiO₂ binary system

The program will calculate all phase transitions at $X_{SiO_2} = 0.35$ in the temperature range 600 to 2600°C.
Transition Temperatures for $X_{SiO_2} = 0.35$ in CaO-SiO$_2$

In the **Results** Window, *Equilib* reports all phase transitions at $<A> = 0.35$ within the temperature range 600 to 2600°C. **Most transitions report both compositions on each side of the tie-line.** Such information is important in complex systems.

For example at 1436.85°C:

$\alpha'$-Ca$_2$SiO$_4$ to $\alpha$-Ca$_2$SiO$_4$

$<A> = X_{SiO_2} = 0.35$
Solution Properties: FACT-Salt in the NaCl-KCl binary system

1° The reactants are \(<1-A>\) NaCl + \(<A>\) KCl – i.e. the NaCl-KCl binary system where \(<A>\) varies from 0 to 1.

2° The only possible product is the solution phase:
   - Salt-liquid (FACT-SALT)

3° The final conditions

The program calculates the equilibrium in Salt-liquid at 850°C for mole fractions of KCl varying from 0 to 1 in increments of 0.1.

4° Calculate
**Solution Properties**: opening the window

1° **Right-click** on the + column to open the FACT-Salt extended menu and select solution properties...

1a° ...or point to FACT-SALT and **double-click**

This option lists the common partial and integral solution properties for the phase. The option is **only active** if the equilibrium has been calculated and the solution phase is stable.
Solution Properties Window and menus

Open spreadsheet to view the selected partial properties of the selected phase: FACT-SALT
In the **solution properties** window menu, select **Standard States > Change Standard States...** and click in the + column to select the new standard state.
### Solution Properties: Molar Partial Properties Spreadsheet

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<th>Component i</th>
<th>Page</th>
<th>$^\circ$C</th>
<th>P(atm)</th>
<th>X(NaCl)</th>
<th>X(KCl)</th>
<th>a(i)</th>
<th>gamma(i)</th>
<th>Delta_g(i)</th>
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<th>$^\circ$C</th>
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<th>X(KCl)</th>
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</tbody>
</table>
Solution Properties: Molar Integral Properties Spreadsheet

Open spreadsheet to view the selected integral properties of the selected phase: FACT-SALT
The FACT-CuLQ solution (Cu(liq) alloy) does not contain Cr. This example shows how to create a dilute Henrian solution of Cr and then merge it into the FACT-CuLQ solution phase.

1 Cu + 0.05 Fe + 0.10 Cr
that is, Cu may be considered as a solvent and Fe and Cr as solutes.
Include **dilute solution:** Cr in Cu-Fe alloy – Possible products

**Solution Phase** FACT-CuLQ - Cu-liqu or speiss (presence of Cu not essential), <50 mol% As, <15 mol% S, 300-1300 °C; <10 mol% O (good around 1250 °C).

FACT-CuLQ: 15 Cu, 16 Fe

**Possible products at 1200°C and 1 atm:**
- **Compound species:** pure liquids, pure solids
- **Solution species:** FACT-CuLQ

**Short description of the FACT-CuLQ Solution Phase.** It does not contain Cr.

**Right-click to open the pure liquids Species Window**
Creating an ideal Henrian solution of Cr(liq)

1° Right-click to open the Cr(liq) extended menu

2° Select Ideal Solution > Ideal solution #1...

3° Enter the values of A and B. Specify New mixing particles P = 1 (this is the default setting), and enter the solution name diluteCr.

4° Press OK

In an earlier example taken from the Equilib Slide Show – Regular Examples (slide 54), the Henrian activity coefficient of Cr(liq) in Cu(liq) was calculated from the binary Cu-Cr phase diagram and reported as:

$$\log_{10} \left[ \gamma_{\text{Cr(liq)}} \right] = \frac{5983.29}{T(K)} - 2.9522 = \frac{A}{TK} + B$$

Enter the values of A and B.
Merging the ideal solution diluteCr and FACT-CuLQ

# denotes species also used in ideal solution 1 and h indicates an henrian activity coefficient

5° Press OK to return to the Menu Window

6° Right-click in the + column of FACT-CuLQ to open its extended menu.

7° Select m - merge dilute solution from > Dilute Solution #1 - diluteCr
Recalling that the Henrian activity coefficient of Cr(liq) in Cu(liq) is:

$$\log_{10} [\gamma_{\text{Cr(liq)}}] = \frac{5983.29}{T(K)} - 2.9522$$

We have, at $1200^\circ\text{C}$ (1473.15 K), $\gamma_{\text{Cr(liq)}} = 12.86$

The dilute solute (Cr) is merged into the existing FACT-CuLQ solution.

Let's calculate the equilibrium and retrieve the calculated value of $\gamma_{\text{Cr(liq)}}$ at $1200^\circ\text{C}$.
Cr in Cu-Fe alloy – Results

With the m option you can merge almost any type of dilute solute into an existing real solution.

Hence, at 1200°C, the calculated activity coefficient is:

\[ \gamma_{\text{Cr(liq)}} = \frac{a_{\text{Cr(liq)}}}{X_{\text{Cr(liq)}}} = \frac{0.53979}{0.041963} = 12.86 \]

\[ a_{\text{Cr(liq)}} = 0.53979 \]

\[ X_{\text{Cr(liq)}} = 0.041963 \]
Include dilute solution: Tl₂O and HfO₂ in FACT-Slag

The FACT-SLAG (Slag-liquid) solution does not contain the components Tl₂O and HfO₂. This example shows how to merge Tl₂O and HfO₂ solutes into a FACT-SLAG containing SiO₂-CaO-Al₂O₃ taking into account the «New mixing particles» since HfO₂ dissolves as Hf⁴⁺ and 2 O²⁻, and Tl₂O dissolves as 2 Tl⁺ and O²⁻.

We wish to create a liquid slag solution which is an equimolar mixture of SiO₂-CaO-Al₂O₃ containing small amounts of Tl₂O and HfO₂.

It is assumed that the activity coefficients (defined as \( \gamma = a/X \) where \( a = \) activity and \( X = \) mole fraction) of the dilute constituents are independent of composition. That is, the dilute components obey Henry's Law. Also, for demonstration purposes let us assume that the activity coefficient of HfO₂ at 1000°C in the equimolar mixture is approximately: \( \gamma_{\text{HfO}_2} = 9.0 \) with respect to its pure solid standard state.

Finally, suppose that there is no information on the activity coefficient of Tl₂O and so ideal solution behavior (\( \gamma = 1 \)) is assumed for this component. In this case it is necessary to take into account the fact that a liquid slag is an ionic mixture and that Tl₂O dissociates in solution to form two independent Tl ions. That is, the formula «Tl₂O» really represents two moles of Tl ions dissolved in the slag. That is, it is actually the component TlO₀.₅ which follows ideal solution behaviour.
The reactants are: 0.3333 CaO + 0.3333 SiO$_2$ + 0.3333 Al$_2$O$_3$ + 0.01 Ti$_2$O + 0.05 HfO$_2$

The system is an equimolar mixture of CaO, SiO$_2$ and Al$_2$O$_3$... with Ti$_2$O and HfO$_2$ added as dilute components.
TI\textsubscript{2}O and HfO\textsubscript{2} in FACT-Slag – Possible products

Possible products at 1000°C and 1 atm:
- Solution species: FACT-SLAG
- Compound species: ideal gas

Short description of the FACT-Slag Solution Phase. It does not contain TI\textsubscript{2}O nor HfO\textsubscript{2}.

Right-click to open the pure solids Species Window.
Creating an ideal Henrian solution of $\text{HfO}_2(s)$

1° Right-click to open the $\text{HfO}_2(s2)$ extended menu

2° Select Ideal Solution > Ideal solution #1…
Creating an ideal Henrian solution of HfO$_2$(s) – setting γ

3° Enter $\log_{10} [\gamma_{\text{HfO}_2(s2)}] = 1214.9/T(\text{K}) + 0$

in order that $\gamma = 9.0$ when $T = 1273.15\text{K} (1000°C)$.

4° Specify New mixing particles $P = 1$

(this is the default setting).

5° Replace the default solution name «Ideal-1» by a new name «DilOxide».

6° Press OK to return to the Solid Species Window.

Notes:
1. In general, if $\gamma$ is known at only one temperature, it is better to assume that $RT \log \gamma = \text{constant}$ than to assume that $\log \gamma = \text{constant}$.
2. In this example note that $\gamma$ is the activity coefficient relative to SOLID HfO$_2$(s2) as standard state.
Adding \( \text{Tl}_2\text{O}(l) \) to the ideal solution

\# denotes species also used in ideal solution 1 and \( h \) indicates an henrian activity coefficient

7° Press OK to return in the Menu Window

8° Right-click to open the pure liquids Species Window
Adding $\text{Tl}_2\text{O}(\text{l})$ to the ideal solution – setting $\gamma$

9° Right-click to open the $\text{Tl}_2\text{O(l)}$ extended menu

10° Select Ideal Solution > Ideal solution #1…

11° Log $\gamma$ is set equal to 0 (i.e. $\gamma = 1$), Enter $A = B = 0$

12° Specify New mixing particles $P = 2$ to indicate that one mole of $\text{Tl}_2\text{O}$ dissociates into 2 independent particles ($2[\text{Tl}^+]$) in the oxide solution.
A dilute solute in an ideal solution may have a Henrian activity coefficient, $\gamma$, where:

$$\log_{10} \gamma = \frac{A}{TK} + B$$

You specify $A$ and $B$, and the number of new mixing particles $P$.

Examples:

1. Solute $Sn(s)$ dissolving in $Pb(s)$:
   
   $P = 1$ since $Sn$ is a new particle.

2. Solute $NaF(liq)$ dissolving in $LiCl(liq)$ (i.e. $Li^+$ and $Cl^-$):
   
   $P = 2$ since $NaF$ dissolves as new mixing particles $Na^+$ and $F^-$.

3. Solute $NaCl(liq)$ dissolving in $LiCl(liq)$ (i.e. $Li^+$ and $Cl^-$):
   
   $P = 1$ since $NaCl$ dissolves as $Na^+$ and $Cl^-$ but only $Na^+$ is a new particle.

4. Solute $S_2(liq)$ dissolving in $Fe(liq)$ as $S$:
   
   $P = 2$.

In the present example $P = 2$ because $Tl_2O$ dissociates in the slag as:

$$Tl_2O \rightarrow 2 Tl^+ + O^{2-}$$
Merging the ideal Henrian solution DilOxide and FACT-Slag

An ideal Henrian solution (DilOxide) of $\text{Tl}_2\text{O}$ and $\text{HfO}_2$ has now been created.

13° Press OK to return to the Menu Window

14° Right-click in the + column of FACT-Slag to open its extended menu.

15° Select - merge dilute solution from > Dilute Solution #1 - DilOxide
Calculation including a **dilute solution**: $\text{Tl}_2\text{O}$ and $\text{HfO}_2$ in $\text{CaO-SiO}_2-\text{Al}_2\text{O}_3$ slag

Click on **details** to display a summary of the ideal solution data entry.

The dilute solution (**DilOxide**) is merged into the existing **FACT-Slag** solution.

**Equilib Advanced 5.2.9**
**Results (FACT format)**

\[
X_{\text{HfO}_2} = \frac{0.047174}{0.31446 + 0.31446 + (2 \times 0.31446) + (2 \times 0.0094349) + 0.047174} = 0.035632
\]

...because Tl$_2$O dissociates into two Tl ions and also Al$_2$O$_3$ dissociates into two Al ions: $\text{Al}_2\text{O}_3 \rightarrow 2 \text{Al}^{3+} + 3 \text{O}^{2-}$

**Note:**
This information about Al$_2$O$_3$ is included in the FACT-SLAG database.

The calculated activity of HfO$_2$(s2) is:

\[
a_{\text{HfO}_2} = \gamma_{\text{HfO}_2} X_{\text{HfO}_2} = (9.0)(0.035632)
\]
\[
= 0.32070
\]

**Note:**
If we increase $\gamma_{\text{HfO}_2}$, the calculated activity would increase until solid HfO$_2$(s) would be calculated to precipitate when its activity = 1.0. If the solubility of HfO$_2$ were experimentally known for instance, then we could adjust $\gamma_{\text{HfO}_2}$ in this way in order to reproduce the measured solubility. That is, a measured solubility limit permits us to determine the value of the Henrian activity coefficient.
**Results**

\[
X_{\text{TI}_2\text{O}_{0.5}} = \frac{(2 \times 0.0094349)}{0.31446 + 0.31446 + (2 \times 0.31446) + (2 \times 0.0094349) + 0.047174} = 0.014253
\]

<table>
<thead>
<tr>
<th><strong>STREAM CONSTITUENTS</strong></th>
<th><strong>AMOUNT/mol</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>3.3330E-01</td>
</tr>
<tr>
<td>SiO2,quartz(s)</td>
<td>3.3300E-01</td>
</tr>
<tr>
<td>Al2O3,gamma(s)</td>
<td>3.3300E-01</td>
</tr>
<tr>
<td>Tl2O(s)</td>
<td>1.0000E-02</td>
</tr>
<tr>
<td>HfO2(s)</td>
<td>5.0000E-02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>PHASE: gas ideal</strong></th>
<th><strong>mole</strong></th>
<th><strong>FUGACITY</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>0.0000E+00</td>
<td>8.0000E-01</td>
</tr>
<tr>
<td>TOTAL</td>
<td>0.0000E+00</td>
<td>1.0000E+00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>PHASE: Slag-liquid+DilOxide</strong></th>
<th><strong>mole</strong></th>
<th><strong>ACTIVITY</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>3.3330E-01</td>
<td>3.1445E-01</td>
</tr>
<tr>
<td>CaO</td>
<td>3.3300E-01</td>
<td>2.0370E-01</td>
</tr>
<tr>
<td>Al2O3</td>
<td>3.3300E-01</td>
<td>3.1445E-01</td>
</tr>
<tr>
<td>Tl2O DilOxide</td>
<td>1.0000E-02</td>
<td>9.4349E-03</td>
</tr>
<tr>
<td>HfO2s2</td>
<td>5.0000E-02</td>
<td>4.7174E-02</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1.0699E+00</td>
<td>1.0000E+00</td>
</tr>
</tbody>
</table>

The calculated activity of Tl2O(liq) is:

\[
a_{\text{Tl}_2\text{O}} = \gamma_{\text{Tl}_2\text{O}} X_{\text{Tl}_2\text{O}} = \gamma_{\text{Tl}_2\text{O}} (X_{\text{TlO}_{0.5}})^2
\]

\[
= (1.0) (0.014253)^2 = 2.0315 \times 10^{-4}
\]

**Note:**
The calculated vapor pressure of Tl gas is 1.988 \times 10^{-4} atm.
If experimental vapor pressure data were available, then one could adjust \(\gamma_{\text{Tl}_2\text{O}}\) in order to reproduce these data. That is, a measured vapor pressure permits one to determine the value of the Henrian activity coefficient.
Limitations and restrictions of merging dilute solutes into solutions

1. Ions are not permitted as dilute species (ex: $\text{Na}^+$, $\text{AlClO}_3^-$ in 'diluteCr').
2. The resulting solution should be dilute in the solute(s) that are merged (ex: in the present case if the resulting solution phase is say $>10\%$ Cr then the validity of the results would be in question).
3. Try to avoid species that are already present in the existing database (ex: in the present case avoid adding dilute Fe(liq)).
4. You may create several different ideal Henrian solutions, each with one or more solutes, however:
   1. a given solute can only appear in one ideal solution (ex: in the present case Cr(liq) is a solute only in 'Ideal Solution #1 - diluteCr').
   2. each ideal Henrian solution can be merged only once into one real solution (ex: in the present case 'diluteCr' is merged into FACT-CuLQ and no other).
   3. each real solution can contain no more than one merged dilute solution (ex: in the present FACT-CuLQ contains only 'diluteCr').
5. Merging dilute solutions into complex solutions (ex: oxides into FACT-SLAG, salts into FACT-SALT) may require special consideration due to the number of "New mixing particles" (ex: please refer to the example on $\text{Tl}_2\text{O}$ and $\text{HfO}_2$ in FACT-SLAG).
6. Although the calculated solution phase composition is thermodynamically self-consistent, the results are an approximation only and only truly valid at infinite dilution.
Using Pseudonyms

The following two slides show how a user defined list of phase names of solution phases (pseudonyms) can be applied in order to give output tables a user-specific appearance.

NOTE that this feature is also available in the Phase Diagram module where the user defined phase names are used for labelling the phase fields.
Pseudonyms

This feature enables you to use your own description (that we call a 'pseudonym') for a solution phase. For example, you could replace '?Slag-liquid' by say 'slag', or 'FCC-A1' by 'Fe(fcc)', etc.

1° Click on the **List...** button to access the pseudonyms menu.

2° Select 'Edit...' or 'Add...' and then click on the phase to open the **Pseudonyms** dialog box.
Pseudonyms

If the 'apply' box is checked the pseudonyms will appear in the Equilib Results Window and Phase Diagram plotted Figure.

3° Enter a **pseudonym** for the selected phase and press OK.
For some stoichiometric condensed substances, e.g. SiO2 or C, molar volume data are stored in the database which permit the influence of high pressure on the phase equilibria to be calculated.

The following two slides show how the use of molar volume data is controlled from the Equilib Menu screen.

NOTE that the use of molar volume data must be executed with great care in order to avoid erroneous results.
Include molar volumes: graphite to diamond transition

Where available, density (i.e. molar volume) data for solids and liquids can be employed in Equilib (the “VdP” term) although their effect only becomes significant at high pressures. Note that (unlike Reaction) compressibility and expansivity data are also employed in Equilib.

1° Reactant: C

2° Possible products:
   - Graphite
   - Diamond

3° $T (K) = 1000 \text{ K}$
   $P (\text{atm}) = 1 \times 10^4 \text{ atm}$, $2 \times 10^4 \text{ atm}$, ..., $1 \times 10^5 \text{ atm}$

The program will calculate the equilibrium at $1000\text{K}$ for pressures varying from $1 \times 10^4 \text{ atm}$ to $1 \times 10^5 \text{ atm}$ in increments of $1 \times 10^4 \text{ atm}$ and will search for all phase transitions.
Graphite to diamond transition: equilibrium calculation

Hence, at high pressures, the "VdP" term creates a favorable negative contribution to the enthalpy change associated with the graphite to diamond transition.

The volume of diamond is smaller than graphite.

At 1000 K and 31488 atm, graphite and diamond are at equilibrium.

Note: If molar volumes are not included then no transitions are found.

Molar volume data are employed
Calculations with Equilib are usually Closed System calculations, i.e. calculations in which the amounts of all input substances are kept constant.

However, under certain conditions it is also possible to use Equilib for Open System calculations. In such cases it is assumed that all condensed substances/phases remain in the system while the gas phase is refresh in every calculational step.

The following slide explains the general procedure in more detail. In sections 9.1 and 9.2 two example applications are shown.
In many pyrometallurgical processes, for example copper converting (or steelmaking), the system is «open». Gas, typically in the form of air or oxygen, enters the furnace, reacts with the system, and then leaves the reactor as $SO_2(g)$ and $SO_3(g)$ (or as $CO(g)$ and $CO_2(g)$). These product gaseous species, being removed from the system, change the overall mass balance. An open process, with the gaseous products being continuously removed from the calculation, can be simulated by the Equilibrium command OPEN.

In the case of $Cu_2S$ converting eventually all the sulfur leaves the system and then $Cu_2O$ starts to form unless the converting is stopped.

The following figures demonstrate $Cu_2S$ desulphurisation by air in an OPEN process.

Air
($\approx 79\% N_2 + 21\% O_2$)

Furnace
$Cu_2S \rightarrow Cu \rightarrow Cu_2O$

$N_2(g) + S_2(g) + SO_2(g) + SO_3(g) + ...$
The following six slides show how the **Open command** is applied for the stepped (open) desulphurisation of Cu$_2$S with air.

Note how the variable **Alpha** is used to define the input amount of air (0.21 O$_2$ and 0.79 N$_2$) for use with the **Open command**.
Desulphurisation of $\text{Cu}_2\text{S}$ by air: setting the Reactants Window

The reactants are one mole of $\text{Cu}_2\text{S}$ with a variable amount $<A>$ moles of air.

In an OPEN system, $<A>$ moles of reactant are added at each step and then the gas species are removed after equilibration.
**Desulphurisation of Cu_2S by air: setting the Menu Window**

Possible products:
- Solution species: FACT-CuLQ, FACT-MATT
- Compound species: ideal gas, Cu_2O(s)

Setting the final conditions for a normal (i.e. closed system) equilibrium calculation at 1200°C and 1 atm for \(<A> = 5\)
Desulphurisation: Closed system equilibrium calculation

Air
(≈79% N\textsubscript{2} + 21% O\textsubscript{2})

N\textsubscript{2}(g) + S\textsubscript{2}(g) + SO\textsubscript{2}(g) + SO\textsubscript{3}(g) + ...

Furnace Cu\textsubscript{2}S \rightarrow Cu \rightarrow Cu\textsubscript{2}O

P_{SO_2} = 0.2019 \text{ atm}
in 4.9501 \text{ mol of gas}

A = 5.0, i.e. 5 moles of air

The cutoff concentration has been specified to 1.000E-04

Data on 1 solute identified with "C" have been extrapolated out of the suggested composition range

\begin{align*}
\begin{array}{cccc}
H & C & V & S \\
(J) & (J) & (l) & (J/K)
\end{array}
\end{align*}

\begin{align*}
4.33759E+03 & -2.18989E+06 & 5.98382E+02 & 1.48948E+03 & 2.59344E+02
\end{align*}
Desulphurisation of $\text{Cu}_2\text{S}$ by air: Open calculation

**Setting** the final conditions for an open (i.e., open system) equilibrium calculation at 1200°C and 1 atm for 50 steps of incremental $<A> = 0.1$

**Air**

($\approx 79\% \text{ N}_2 + 21\% \text{ O}_2$)

**Furnace**

$\text{Cu}_2\text{S} \rightarrow \text{Cu} \rightarrow \text{Cu}_2\text{O}$

$\text{N}_2(\text{g}) + \text{S}_2(\text{g}) + \text{SO}_2(\text{g}) + \text{SO}_3(\text{g}) + \ldots$

1° Select open in the Equilibrium frame to enable the steps’ Final Condition input box

2° Enter the number of steps (here, 50) and the amount $<A>$ (here, 0.1 mole of air) of reactant added to the system at each step at the end of which the gas phase is removed.
Desulphurisation: Open system equilibrium calculation

Air (≈79% N₂ + 21% O₂)

Furnace

Cu₂S → Cu → Cu₂O

N₂(g) + S₂(g) + SO₂(g) + SO₃(g) + ...

After 50 steps, A = 5.0, i.e. 5 moles of air were added to 1 mole of Cu₂S

\[ P_{SO_2} = 3.9905 \times 10^{-4} \text{ atm in 0.079037 mol of gas (mainly N}_2\text{)} \]

Note:
The simulation is improved by specifying a smaller value of \(<A>\) (and a correspondingly larger number of steps).
Because of its relatively high partial pressure Pb can be removed from Cu-Pb melts by way of vacuum refining.

The following six slides show how the Open command can be employed to simulate the process.

Note that «Vacuum» is established by setting a low total pressure and adding a small amount of Argon into each calculational step. The amount of argon is needed to establish a certain volume into which the lead can evaporate in each step.
Deleading of a Cu-1wt%Pb alloy by argon vacuum refining

The current example illustrates the concepts of normal (i.e. closed system) vs. open equilibrium calculations as applied to argon refining of a Cu-1wt%Pb alloy at reduced total pressures. It simulates deleading at 1200°C and 0.001 atm.

There are no chemical reactions involved in the process.

The reactants are 99 g of Cu, 1 g of Pb (this defines a Cu-1 wt% Pb alloy) with a variable amount $<A>$ g of Ar.

In an OPEN system, $<A>$ g of reactant are added at each step and then the gas species are removed after equilibration.
Deleading of a Cu-1wt%Pb alloy: setting the Menu Window

Possible products:
- Solution species: FACT-CuLQ
- Compound species: ideal gas

Setting the final conditions for a normal (i.e. closed system) equilibrium calculation at 1200°C and 0.001 atm for <A> = 10
Deleading of a Cu-1wt\%Pb alloy: Closed system equilibrium calculation

The concentration of Pb in Cu(liq) is $5.5876 \times 10^{-2}$ wt.\% in equilibrium with 30970 l of gas, mainly Ar.

A = 10.0, i.e. 10 g of Ar added to 100 g of alloy.
Deleading of a Cu-1wt%Pb alloy: Open calculation

Setting the final conditions for an open (i.e. open) system equilibrium calculation at 1200°C and 0.001 atm for 100 steps of incremental \(<A> = 0.1\)

1° Select open in the Equilibrium frame to enable the steps’ Final Condition input box

2° Enter the number of steps (here, 100) and the amount \(<A>\) (here, 0.1 g of Ar) of reactant added to the system at each step at the end of which the gas phase is removed.
**Deleading of a Cu-1wt%Pb alloy: Open system equilibrium calculation**

After 100 steps, $A = 10.0$, i.e. 10 grams of Ar were added to 100 grams of Cu-Pb alloy in equilibrium with 304.16 l of gas, mainly Ar.

The concentration of Pb in Cu(liq) is $1.4221 \times 10^{-7}$ wt.% in equilibrium with 304.16 l of gas, mainly Ar.

**Note:** The simulation is improved by specifying a smaller value of $<A>$ (and a correspondingly larger number of steps).
Deleading of Cu-1wt.%Pb alloy: Graphical Output

Deleading of Cu-1wt.%Pb by Argon Vacuum Refining

Example of «Open» Equilibrium Calculation: T=1200°C and P=0.001 atm.

![Graph showing weight % Pb in Cu(liq) vs. weight Ar (grams)]
In the Parameters menu the user is given information on certain overall parameter values, e.g. the dimensions of the major data arrays.

The user may also modify certain parameters which relate to output lists or which permit the interference with the execution of the calculations.

The following slide shows the Parameter screen as a whole. Further slides are used to give details on the use of the parameters.
Additional information and extended menus are available for many of the items. Point to a frame heading or input box and then click the mouse-right-button.
Parameters menu: Dimensions Frame

The following slide gives information on the Dimensions Frame. This part of the Parameters menu is strictly for information of the user. NO changes may be made.

- The dimensions table lists the current and maximum size of some commonly used variables. The maximum values are fixed during compilation and can not be modified without recompilation.
- Increasing a maximum value would increase the size of the program and reduce execution speed. Except for «Species selected for products», «Components», and «Total selected solutions», please contact us if you consider that a particular dimension is too small.
The following slides shows how Target limits may be changed and how the Stop/Kill button is activated/deactivated.

### Target Limits
- These values are the lower and upper limits of temperature, pressure, volume and alpha when these values are being calculated by Equilib. It is recommended that the default settings be used.
- Click on the «Target» frame in the Menu Window for details on how to specify a target.

### Stop and Kill Button
- When «checked» you are able to follow the progress of the equilibrium calculation and have the option to «stop» or «kill» the calculation should the program get hung up.
- This feature is only really useful for large and lengthy calculations, or those cases where the program is unable to converge.
Parameters menu: Predominant Species Frame

The following slide shows how the Predominant Species frame is made use of.

This input controls the execution of equilibrium calculations in which the number of species to be used exceeds the maximum number of species that may be used simultaneously.

<table>
<thead>
<tr>
<th>Predominant Species</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>gases (50 - 300):</td>
<td>100</td>
</tr>
<tr>
<td>solids + liqs (50 - 300):</td>
<td>100</td>
</tr>
</tbody>
</table>

- These are the number of predominant gaseous species (50 to 300) and pure solid and liquid species (50 to 300) that will be calculated when the Equilibrium option «Predominant» is selected.
- To improve the chances of convergence it is recommended that you use «300» in both cases. If you must reduce the number (for example because you have selected more than 100 solution species) then you should retain «300 gas» species and reduce only the number of solid and liquid species.
- The «log file» records the progress of the predominant calculation. If you get the message «- unable to calculate the standard state element(s)» it may be useful to consult this file. The log file will appear in the Results Window only if the «log file» box is checked.
This slide shows how use is made of the Dilute Extrapolation, the Print Cut-off and the Output Mass units frames.

- This value is used for extrapolating solute data outside its normal dilute concentration range stored in its solution database.
- The parameter is an advanced feature of the program and should not be modified from its default value (1.0e+6).

- In the Results Window, equilibrium products below this value are not printed.
- This is useful in large calculations where you want to limit unwanted output for insignificant species.
- The value must be in the range 1.0e-70 to 0.01
- The value has no effect upon the results of the calculation.

- Normally the input reactants and output results are both in moles and mole fractions, or grams and weight per cent.
- This option enables you to have input moles and output weight, or vice versa. The equilibrium results are still the same, just the method of presenting the results is changed.
- Note, the same effect can be obtained using the "gram" and "mole" formats in the List Window.
The following sixteen slides show how use is made of various options that can be found in the Reactants screen of the Equilib module.

The use of arbitrary species formulae is shown in the following slide.

Note that this option is very useful when only the input amount of the «arbitrary» species is important for the calculation. As soon as extensive property changes are to be calculated this kind of input is not permitted since the «arbitrary» species has a chemical formula but no thermodynamic properties. Thus the input cannot be used to calculate the state properties of the reactants.
Combining reactants into one composite chemical species

There are 6 reactants

The units are \( T \ (°C) \) and \( \text{Mass (mol)} \)

You can combine the 3 matte components, \( 42 \text{ Cu} + 25 \text{ Fe} + 33 \text{ S} \), into one composite species, \( \text{Cu}_{42}\text{Fe}_{25}\text{S}_{33} \).

Likewise \( 0.79 \text{ N}_2 + 0.21 \text{ O}_2 \) can become \( \text{N}_{1.58}\text{O}_{0.42} \).

Note: \( \text{N}_{1.5800.42} \) Make sure you do not mix up the letter «O» and the integer «0».

\(<A>\) is a variable corresponding to the number of moles of air, \(<B>\) is a constant amount of \( \text{SiO}_2 \) defined in the Menu Window.
The input of mass units in the Reactants screen is not fixed to the use of the unit that was chosen as default.

It is possible to «mix» mass units, i.e. to use the default for some and specific chosen units for others of the input substances.

The following two slides show how this is achieved.
**Converting reactant mass units (mol, g or lb)**

Point the arrow in the mass input box to view the mass conversion.

Point the arrow in the species input box to view the molecular weight.

For example you may wish to specify the matte component in grams.

1. **Right-click** on the **matte mass input box** to **open** the **mass menu**.
2. **Select**: Convert this reactant amount to > g

**Note** that no data are available for the composite chemical species.
**Mixing** reactant **mass** units of mol g and lb

You can mix the mass units by including a 'mol', 'g' or 'lb' in the reactant amount.

If the default mass units is mol, the following is equivalent to the above system:

Or if you like, you can always **explicitly** specify the mass units for each reactant amount to make your reactants data entry **independent** of the default mass units.

**Note:**
When creating a composite species (for example Cu$_{42}$Fe$_{25}$S$_{33}$ and N$_{1.58}$O$_{0.42}$)
- option «**initial conditions**» (Delta H, etc.) is **disabled** since there are no data for the species.
- the species is limited to 7 elements. For more than 7 elements use a mixture - refer to the **Mixture** module.
Importing a stream or mixture

In addition to entering input substances by name/formula in the Reactants screen it is also possible to enter «groups» of substances as a whole package.

Such groups can be either Mixtures or Streams. For the generation of Mixtures see the Slide Show on the Mixture Module. For the generation of Stream see below (slides 11.4.1 and 11.4.2).

The following five slides (11.4.3 to 11.4.7) show the details of making use of Streams and Mixture in the Equilib input.
Exporting and importing an equilibrated molten salt stream - CaCl$_2$-NaCl-KCl-MgCl$_2$

This example:
- **creates** and **saves** an equilibrated stream - CaCl$_2$-NaCl-KCl-MgCl$_2$ at 750°C.
- **imports** the stream into a new reaction
- **performs** various isothermal and adiabatic heat balances using the imported stream

The units are \( T \ (°C) \), \( P \ (\text{atm}) \) and \( \text{Mass} \ (\text{g}) \).

There are 4 reactants, total mass = 95g

Possible product: FACT-Salt

The final conditions are:
- \( T = 750°C \)
- \( P = 1 \ \text{atm} \)
Saving an equilibrated stream

Equilibrated molten salt

Save File
Saving file 12
Enter the name of the stream (upto 26 characters)
ex: Roaster Gas, Cu Matte, Slag
Mg-electrolyte
Importing the stream into a reaction

There are now 2 reactants:
\[ \text{MgCl}_2(\text{s,25°C}) + 95 \text{ [Mg-electrolyte]} \text{ (stream,750°C)} \]
i.e. \( \text{<A + 95>} \) grams total.

Note: You cannot change the initial \( T \) (750°C) or \( P \) (1 atm) of the [Mg-electrolyte] stream - these values, together with selected stream thermodynamic properties (\( H, S, G, C_p, V \)), are stored in the stream file (mixt12.dat) and are imported into the calculation when Initial Conditions (\( \Delta H, \text{etc.} \)) is checked.

You can change the amount of [Mg-electrolyte] from its default value (95 g)
In the **Menu Window** **FACT-Salt** is the only possible product. Set $<A> = '0 5'$ (i.e. $\alpha = 0$ and $5$), $T = 750^\circ\text{C}$ and $P = 1$ atm. The **Results** are:

- **Calculates** $\Delta H = 4415$ J – this is the total energy required to heat 5 g MgCl$_2$ from 25 to 750$^\circ\text{C}$ and dissolve it into the molten salt.

- **Calculated** $\Delta H = 0$ – imported and equilibrated streams are the same.
Adiabatic <5> MgCl₂ (solid, 25°C) + 95 g [Mg-electrolyte] stream

The output shows a calculated adiabatic temperature of 708.12°C.

Return to the Menu Window, set <A> = 5 and T(C) undefined ('blank') then specify an adiabatic reaction: ΔH = 0.
Adiabatic $<A>$ MgCl$_2$ (solid, 25°C) + 95 g [Mg-electrolyte] stream at 725°C

Return to the Menu Window, set $<A>$ undefined (‘blank’), set $T(C) = 725°C$, and specify an adiabatic reaction: $\Delta H = 0$.

The output shows:

From the previous Results we know that the value of $<A>$ should be 2 - 3 g. But Equilib requires that the calculated $<A>$ be no more than 1.0.
Adiabatic $<100A>$ MgCl$_2$ (solid, 25°C) + 95 g [Mg-electrolyte] stream at 725°C

The calculation now gives $A = 0.02939$, i.e. $100 \times 0.02939 = 2.939$ g MgCl$_2$ (solid, 25°C) are required to reduce the bath temperature to 725°C.

This is resolved by entering $<100A>$ MgCl$_2$ in the Reactants Window. Do not forget to check the Initial Conditions box.
In addition to the two «group input» methods outlined above it is also possible to employ Reaction Tables from which the input amounts are read.

Such Reaction Tables provide the opportunity to enter input amounts for cases in which non-linear changes of the amounts are needed. In the table each line contains for a given set of input substances the irregularly changing amounts.

In the calculations the line number (Page number) will be treated as the independent parameter in order to sort the result tables.

The Page number can also be used as an axis variable in the Result module.
In the **Reactants Window** you specify a set of reactant amounts, for example: 1 mol CH$_4$ + 2 mol C$_2$H$_6$ + 3 mol O$_2$:

With the **Reaction Table** you can specify many different sets of reactant amounts as well as their product temperatures and pressures - each resulting in a separate equilibrium calculation.

To open the Reaction Table: **click** on the Reaction Table button or **select Table > Reaction Table** from the Menu Bar.
Editing the Reaction Table

Each set (row in the Reaction Table) generates a page in the Results Window. There is no limit to the number of sets. The Reaction Table may be created and edited here, or imported via a simple text or Excel spreadsheet.

After creating the table, Close it and press Next >>
After the Reaction Table has been created, click on the Table check box in the Menu Window to activate it in the calculation.
The following three slides show how the various options in the Data Search menu are employed to select/deselect specific data entries in a database.

It is shown how the Gas Ions, Aqueous Species, Limited Data and CxHy options are made use of.
Data Search Menu: gas ions, aqueous species, limited data

- **Include gaseous ions (plasmas):**
  Gaseous ion concentrations are only significant at high temperatures and only meaningful in plasma calculations. Gaseous ions add a component (the electron) to the calculation and increase the total number of gaseous species. This increases slightly the calculation time. For most practical calculations gaseous ions have no effect and so it is safe not to include them in the data search.

  **Debye Shielding** is automatically taken into account for plasmas in *FactSage* versions 5.5 and higher.

- **Include aqueous species:**
  Including aqueous species is only meaningful in aqueous (hydrometallurgical) calculations at or near room temperature. If your calculations are above 300°C there is no point in including the aqueous species. This option has no effect upon gaseous ions (plasmas).

- **Include limited data compound (25°C/298K data only):**
  Some solid and liquid compound species only have limited data - typically the Gibbs energy of formation at 298.15 K but without Cp and enthalpy data. In Equilib these compounds are flagged as '25°C or 298 K only' in the List Window. Such species are automatically dropped from the calculation if the final temperature is above 25°C. In such a case the "activity" column in the List Window is blank. Since most of these species are unimportant and in most cases ignored anyway then there is little need to select this option.
**Reactants window – Data Search Menu: $C_xH_y$, databases**

- **Limit organic species $C_xH_y$:**
  
  The main compound substances database contains several hundred organic species $C_xH_y$... where the stoichiometric factor "x" can be large. These large organic molecules have little use in most inorganic calculations and are unlikely products in most equilibrium calculations. To drop large organic species from the data search you set "x" to the desired upper limit. For most calculations it is recommended you set $x = 2$, which means that organic molecules with 3 or more carbon atoms will be dropped from the data search.

- **Databases:**
  
  **Opens** the databases window.

  Databases may be added to or removed from the data search. For example private data entered through the Compound and Solution programs, or other commercial databases such as Thermo-Tech. If you have both FACT and SGTE databases then you use this option to tell the program to search both databases or search only one.

  Note: Clicking on the databases bar also opens the Databases window.

  **Refresh:**

  In the Data Search menu when you change a search option (gaseous ions, aqueous species, limited data) or database selection then Equilib will automatically 'refresh' the system with the new options and data. However, if changes to the databases are made via another program (for example Compound and Solution) you must click on “Refresh" to update the current system.
If 'coupled' is checked (this is the recommended setting) then compound and solution databases with the same nickname (for example FACT or SGSL) are treated as a group. For example, if you click on the '+' column in order to include the FACT compound database in the data search then the program automatically includes the FACT solution database. Likewise if you remove the SGSL solution database from the data search the program automatically excludes the SGSL intermetallic compound database.

If 'coupled' is NOT checked then the databases can be included or excluded independently. However this is not recommended since it can lead to misleading results.
The Equilib module enables you to perform cooling calculations and display the phase transitions and compositions during:

- Equilibrium cooling
- Scheil-Gulliver cooling
- Full annealing of cast alloys

### Cooling Calculations - Table of Contents

<table>
<thead>
<tr>
<th>Section 13.1</th>
<th>Table of Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section 13.2</td>
<td>Phase transitions: FeO-MnO</td>
</tr>
<tr>
<td>Section 13.3</td>
<td>Simple equilibrium cooling: FeO-MnO</td>
</tr>
<tr>
<td>Section 13.4</td>
<td>Simple Scheil-Gulliver cooling: FeO-MnO</td>
</tr>
<tr>
<td>Section 13.5</td>
<td>Equilibrium cooling, plots: Al-Mg-Zn</td>
</tr>
<tr>
<td>Section 13.6</td>
<td>Scheil-Gulliver cooling, annealing casted alloy: Al-Mg-Zn-Mn</td>
</tr>
</tbody>
</table>
FeO-MnO : Phase transitions - binary phase diagram

FeO-MnO binary phase diagram calculated by Phase Diagram

\[ <A> = X_{\text{MnO}} = 0.5 \]

\[ T_{\text{liquidus}} = 1620.23^\circ C \]

\[ T_{\text{solidus}} = 1529.1^\circ C \]

\[ T_{\text{FeO (melting point)}} = 1370.91^\circ C \]

Equilib Advanced 13.2.1
**FeO-MnO: Equilibrium phase transitions at** \( X_{\text{FeO}} = 0.5 \)

1° Binary system <1-A> MnO + <A> FeO.

2° Possible products:
- solid solution (MONO)
- liquid Slag (SLAG)

3° <A> = 0.5
\[ T \,(^\circ C) = 1500 \text{ and } 1700 \]

Equilib will calculate the equilibrium at \( X_{\text{FeO}} = 0.5 \) for temperatures varying from 1500°C to 1700°C and will search for All phase transitions.
FeO-MnO : Phase transitions showing liquidus and solidus

**Equilibrium liquidus**

- $\text{FeO} + \text{MnO} = 1.0000 \text{ mol Slag-liquid}$
  - $71.392 \text{ gram, } 1.0000 \text{ mol}$
  - $(1620.23 \text{ C, } 1 \text{ atm, } a=1.0000)$
  - $0.50000 \text{ FeO}$
  - $0.50000 \text{ MnO}$

**Equilibrium solidus**

- $\text{MnO} + \text{FeO} = 1.0000 \text{ mol Monoxide}$
  - $(71.392 \text{ gram, } 1.0000 \text{ mol})$
  - $(1529.11 \text{ C, } 1 \text{ atm, } a=1.0000)$
  - $0.50000 \text{ FeO}$
  - $0.50000 \text{ MnO}$

where "A" on the reactant side is 0.50000

The cutoff concentration has been specified to $1.0000E-75$
FeO-MnO: Simple equilibrium cooling – L-Option

1° **Right-click** on the ‘+’ column to open the **SLAG** extended menu and **select** L-cooling calculation to open the **Cooling Calculation Window**.

2° **Cooling Calculation Window**

- **select** equilibrium cooling
- **check** √ transitions + summary
- **click** **OK** to close.
FeO-MnO : Simple equilibrium cooling – step, T-auto and stop

Equilibrium Cooling of SLAG

- **cooling step** ‘5’ (0.1 – 250)
- **T-auto** ✓ automatically calculates the starting T
- **final mass** ‘0’ (i.e. stops after complete solidification)

In **equilibrium cooling** the **cooling step** ('5') defines the pages displayed in the **Results Window**. (i.e. every 5 degrees).

The **cooling step** has no effect on the transitions or when 100% solidification is attained.

Enter default starting temperature ‘1650’ – applied when **T-auto** is not used
FeO-MnO: Equilibrium cooling – Summary and Transitions

### Summary

- Temperature of final disappearance of Slag-liquid: 1529.11°C
- Temperature of transition: 1620.23°C

### Transitions

#### Temperature of transition: 1620.23°C

**EQUILIBRIUM COMPOSITION OF PHASES**

<table>
<thead>
<tr>
<th>Phase</th>
<th>MOLE FRACTION</th>
<th>MASS FRACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.5000E-01</td>
<td>3.9112E-01</td>
</tr>
<tr>
<td>Mn</td>
<td>2.5000E-01</td>
<td>3.8477E-01</td>
</tr>
<tr>
<td>O</td>
<td>5.0000E-01</td>
<td>2.2411E-01</td>
</tr>
<tr>
<td>TOTAL</td>
<td>2.0000E+00</td>
<td>7.1391E+01</td>
</tr>
</tbody>
</table>

#### Temperature of final disappearance of Slag-liquid: 1529.11°C

**EQUILIBRIUM COMPOSITION OF PHASES**

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<tr>
<td>TOTAL</td>
<td>2.0000E+00</td>
<td>7.1391E+01</td>
</tr>
</tbody>
</table>

**AVERAGE COMPOSITION OF ALL PRODUCT PHASES TAKEN TOGETHER**

<table>
<thead>
<tr>
<th>Phase</th>
<th>MOLE FRACTION</th>
<th>MASS FRACTION</th>
</tr>
</thead>
<tbody>
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<tr>
<td>O</td>
<td>5.0000E-01</td>
<td>2.2411E-01</td>
</tr>
</tbody>
</table>
FeO-MnO: Equilibrium cooling - Liquidus and Solidus

Liquidus

1.0000 mol Slag-liquid
(71.391 gram, 1.0000 mol)
(1620.23°C, 1 atm, a=1.0000)
(0.50000 FeO
+ 0.50000 MnO)

Solidus

1.0000 mol Monoxide
(71.391 gram, 1.0000 mol)
(1529.11°C, 1 atm, a=1.0000)
(0.50000 FeO
+ 0.50000 MnO)
The program performs a **Gulliver-Scheil cooling** calculation. That is, as phases precipitate from the **Scheil target phase** they are dropped from the total mass balance.

Generally a value of $T$ (the initial temperature) and a cooling step must be specified in the **Final Conditions** frame. Normally, the Scheil calculation is repeated until the Scheil Target phase disappears. However, it is possible to stop the calculation by either specifying a second temperature in the Final Conditions frame, or by specifying a target mass.

The **Scheil target phase** must be the gas phase or a real solution. If it is a liquid phase (such as FToxid-SLAG and Ftsalt-liquid) then the precipitates are generally solids - it would be unusual in this case to select and include other liquids or the gas phase in the calculation.

If the **Scheil target phase** is the **gas phase** then the precipitates could be any or all of the other compound and solution phases. To activate a Scheil target gas phase, first select the gas species in the usual way. Then with the mouse-right-button click on the gas '+' check box in the compound species frame of the Menu Window - this will open the Species Selection window. Point to the '+' column of any selected gas species and then click with the mouse-right-button and then select «Scheil cooling gas phase».
FeO-MnO: Scheil-Gulliver cooling – L-Option

1° Right-click on the ‘+’ column to open the FACT-SLAG extended menu and select **L-cooling calculation** to open the **Cooling Calculation Window**.

2° **Cooling Calculation Window**
- select Scheil-Gulliver cooling
- check √ transitions + summary.
- click OK to close.
FeO-MnO: Scheil-Gulliver cooling – step, T-auto and stop

Scheil-Gulliver Cooling of SLAG

- **cooling step** ‘5’ (0.1 – 250)
- **T-auto** `√` automatically calculates the starting T
- **final mass** ‘0’ (i.e. stops after complete solidification)

In Scheil-Gulliver cooling the **cooling step** (‘5’) defines the calculation step (i.e. every 5 degrees). After each calculation any phase that precipitates from the **solution phase** is dropped from the total mass balance.

The size of the step effects the calculated results. The smaller the step, the more precise the calculation and the longer the calculation time.

Enter default starting temperature ‘1650’ – this is applied when **T-auto** is not used
FeO-MnO: Scheil cooling – Summary and Transitions

Summary

Transitions

Equilib Advanced 13.3.3
The size of the cooling step effects the calculated results. Here the step 5°C gives 1376.68°C. The end of Scheil solidification should be at 1370.91°C – the melting point of FeO. With a much smaller step, 0.1°C, one obtains ~ 1370.9°C.
FeO-MnO: Scheil cooling – incremental vs. accumulated

Incremental Scheil solidification at 1500°C

Accumulated Scheil solidification at 1500°C
**Al-Mg-Zn** : Equilibrium cooling $X_{Mg}=0.8 \quad X_{Al}=0.15 \quad X_{Zn}=0.05$

**Al-Mg-Zn** polythermal liquidus projection calculated by **Phase Diagram** with data taken from FTlite – FACT light alloy databases

Four-Phase Intersection Points with Liquid

1. AlMgZn_Tau / FCC_A1# / Laves_C14#1
2. AlMgZn_Tau / Beta_ALMg / Gamma
3. AlMgZn_Tau / Beta_ALMg / FCC_A1#1
4. AlMgZn_Tau / Laves_C14#1 / MgZn3
5. AlMgZn_Tau / Gamma / Phi
6. Gamma / HCP_A3#1 / Phi
7. FCC_A1#1 / Laves_C14#1 / MgZn11
8. AlMgZn_Tau / MgZn3 / MgZn
9. FCC_A1#1 / HCP_Zn / MgZn11
10. HCP_A3#1 / Mg51Zn20 _<mg7z3>_0i1 / MgZn
11. AlMgZn_Tau / FCC_A3#1 / Phi
12. AlMgZn_Tau / HCP_A3#1 / MgZn

A = Zn, B = Mg, C = Al

X(A) X(B) X(C) °C
1: 0.35365 0.18471 0.46164 467.78
2: 0.04094 0.37786 0.58120 447.57
3: 0.04248 0.36009 0.59743 446.26
4: 0.33110 0.60810 0.06080 428.12
5: 0.16236 0.66052 0.17502 385.07
6: 0.16267 0.69979 0.13755 364.35
7: 0.80148 0.07683 0.12168 360.17
8: 0.29899 0.69007 0.05094 353.59
9: 0.85034 0.05789 0.09177 347.54
10: 0.28328 0.71522 0.00150 345.23
11: 0.23357 0.70211 0.06432 342.67
12: 0.24168 0.70263 0.05570 340.89

**Equilib Advanced** 13.4

www.factsage.com
**Equilibrium Cooling of Liquid Al-Mg-Zn**

- Cooling step ‘10’
- T-auto √
- Final mass ‘0’
Microstructural constituents, and the phases in them

**Liquidus temperature** = 497.61°C

**Constituent 1** is primary hcp formed between 497.61°C and 404.48°C

**Constituent 2** is a binary eutectic formed between 404.48°C and 364.35°C

---

**Summary of Results**

Constituent 1

- 497.61 to 404.48°C (Delta H = -5.8385E+05 J)
- Liquid -> HCP_A3

Constituent 2

- 404.48 to 364.35°C (Delta H = -4.2933E+05 J)
- Liquid -> HCP_A3 + Gamma

Constituent 3

- 364.35°C (isothermal) (Delta H = -9.9422E+04 J)
- Liquid + Gamma -> HCP_A3 + Phi

**Composition of Phases in Constituents at 364.35°C**

<table>
<thead>
<tr>
<th>Component</th>
<th>Moi Fraction</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.65E-02</td>
<td>4.29E-02</td>
</tr>
<tr>
<td>Al</td>
<td>5.97E-02</td>
<td>6.41E-02</td>
</tr>
<tr>
<td>Mg</td>
<td>9.23E-01</td>
<td>8.92E-01</td>
</tr>
<tr>
<td>TOTAL AMT/mol</td>
<td>TOTAL AMT/gram</td>
<td></td>
</tr>
</tbody>
</table>
Al-Mg-Zn: Equilibrium cooling – Plot Results

Equilib Advanced 13.4.3
Selection of species to be plotted
- select all solids and elements for which Gram (max) > 0
**Al-Mg-Zn: Equilibrium Cooling – Plot Results**

- **Liquidus temperature** = **497.61°C**

- **Constituent 1** is primary hcp formed between **497.61°C** and **404.48°C**

- **Constituent 2** is a binary eutectic formed between **404.48°C** and **364.35°C**
Al-Mg-Zn polythermal liquidus projection calculated by *Phase Diagram* with data taken from FTlite – FACT light alloy databases.

Al-Mg-Zn: Scheil cooling $X_{Mg} = 0.8$ $X_{Al} = 0.15$ $X_{Zn} = 0.05$

Equilib Advanced 13.5
Al-Mg-Zn: Scheil-Gulliver cooling – L-Option

Scheil Cooling of Liquid Al-Mg-Zn
- cooling step ‘10’
- check T-auto √
- enter final mass ‘0’
Calculation ends at temperature of final disappearance of liquid. Graph shows phase distribution.

80 Mg + 15 Al + 5 Zn

T(C)

gram
Al-Mg-Zn-Mn: Scheil cooling AZ91 + 0.25 wt.% Mn alloy

Scheil Cooling of Liquid Al-Mg-Zn-Mn
- cooling step ‘10’
- check T-auto √
- enter final mass ‘0’
Al-Mg-Zn-Mn : Scheil cooling – Summary and Transitions

AZ91 + 0.25 wt.% Mn alloy:
89.75Al-9Mg-Zn-0.25Mg (wt%)
Final disappearance of liquid at 340.89°C
Scheil cooling and post equilibration (annealing) of Scheil microstructure: **AZ91 alloy + 0.25 wt.% Mn**

Tracking microstructure constituents

Output: Solidification temperature of 340.89°C

<table>
<thead>
<tr>
<th>CONS. PHASE</th>
<th>TOTAL AMT/gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 'Al8Mn5'</td>
</tr>
<tr>
<td>2</td>
<td>1 HCP</td>
</tr>
<tr>
<td>2</td>
<td>2 'Al8Mn5'</td>
</tr>
<tr>
<td>3</td>
<td>1 HCP</td>
</tr>
<tr>
<td>3</td>
<td>2 Al11Mn4</td>
</tr>
<tr>
<td>4</td>
<td>1 HCP</td>
</tr>
<tr>
<td>4</td>
<td>2 'Al4Mn'</td>
</tr>
<tr>
<td>5</td>
<td>1 HCP</td>
</tr>
<tr>
<td>5</td>
<td>2 'Al12Mg17'</td>
</tr>
<tr>
<td>5</td>
<td>3 'Al4Mn'</td>
</tr>
<tr>
<td>6</td>
<td>1 HCP</td>
</tr>
<tr>
<td>6</td>
<td>2 Phi</td>
</tr>
<tr>
<td>6</td>
<td>3 'Al4Mn'</td>
</tr>
<tr>
<td>6</td>
<td>4 Al11Mn4</td>
</tr>
<tr>
<td>7</td>
<td>1 HCP</td>
</tr>
<tr>
<td>7</td>
<td>2 Tau</td>
</tr>
<tr>
<td>7</td>
<td>3 Al11Mn4</td>
</tr>
<tr>
<td>8</td>
<td>1 HCP</td>
</tr>
<tr>
<td>8</td>
<td>2 MgZn</td>
</tr>
<tr>
<td>8</td>
<td>3 Tau</td>
</tr>
<tr>
<td>8</td>
<td>4 Al11Mn4</td>
</tr>
</tbody>
</table>

Amount & Average Composition of the HCP phase

<table>
<thead>
<tr>
<th></th>
<th>wt. %</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>64.599</td>
<td>96.19</td>
<td>3.67</td>
<td>0.125</td>
<td>195 ppm</td>
</tr>
<tr>
<td>3</td>
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<td>92.25</td>
<td>7.45</td>
<td>0.298</td>
<td>14.7 ppm</td>
</tr>
<tr>
<td>4</td>
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<td>0.1 ppm</td>
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<td>90.55</td>
<td>2.93</td>
<td>6.519</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>8</td>
<td>0.042</td>
<td>90.57</td>
<td>2.90</td>
<td>6.538</td>
<td>0.2 ppm</td>
</tr>
</tbody>
</table>
1° Point mouse to constituent 2 HCP_A3 and double-click

2° Click OK to recycle HCP_A3
Change mass from 100% => 100 g

List of components in HCP phase
Al-Mg-Zn-Mn: Equilibrium calculation – full annealing of HCP

Anneal at 150 to 500 °C
Al-Mg-Zn-Mn: Plotting fully annealed HCP phase
Al-Mg-Zn-Mn : Graph of fully annealed HCP phase

Equilibrium phase distribution in HCP phase of constituent 2 after annealing (HCP + precipitates)
Equilibrium phase distribution in HCP phase of constituent 2 after annealing (HCP + precipitates)
Scheil cooling and post equilibration (annealing) of Scheil microstructure: AZ91 alloy + 0.25 wt.% Mn

Tracking microstructure constituents

Annealing: Phases vs T for HCP in the different microstructural constituents

Amount & Average Composition of the HCP phase at 340.89°C

<table>
<thead>
<tr>
<th></th>
<th>wt. %</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>64.599</td>
<td>96.19</td>
<td>3.67</td>
<td>0.125</td>
<td>195 ppm</td>
</tr>
<tr>
<td>3</td>
<td>15.644</td>
<td>92.25</td>
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</table>

Equilib Advanced 13.6.8
Paraequilibrium and minimum Gibbs energy calculations

- In certain solid systems, some elements diffuse much faster than others. Hence, if an initially homogeneous single-phase system at high temperature is quenched rapidly and then held at a lower temperature, a temporary paraequilibrium state may result in which the rapidly diffusing elements have reached equilibrium, but the more slowly diffusing elements have remained essentially immobile.

- The best known, and most industrially important, example occurs when homogeneous austenite is quenched and annealed. Interstitial elements such as C and N are much more mobile than the metallic elements.

- At paraequilibrium, the ratios of the slowly diffusing elements in all phases are the same and are equal to their ratios in the initial single-phase alloy. The algorithm used to calculate paraequilibrium in FactSage is based upon this fact. That is, the algorithm minimizes the Gibbs energy of the system under this constraint.

- If a paraequilibrium calculation is performed specifying that no elements diffuse quickly, then the ratios of all elements are the same as in the initial homogeneous state. In other words, such a calculation will simply yield the single homogeneous phase with the minimum Gibbs energy at the temperature of the calculation. Such a calculation may be of practical interest in physical vapour deposition where deposition from the vapour phase is so rapid that phase separation cannot occur, resulting in a single-phase solid deposit.

- Paraequilibrium phase diagrams and minimum Gibbs energy diagrams may be calculated with the Phase Diagram Module. See the Phase Diagram slide show.
Paraequilibrium and minimum Gibbs energy calculations

Fe-Cr-C-N system at 900K

For comparison purposes, our first calculation is a normal (full) equilibrium calculation.

Equimolar Fe-Cr with C/(Fe + Cr) = 2 mol% and N/(Fe + Cr) = 2 mol%

Select all solids and solutions from FSstel database

T = 900K
Paraequilibrium and minimum Gibbs energy calculations

Output for a normal (full) equilibrium calculation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Amount</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Fe + 0.5 Cr + 0.02 C + 0.02 N =</td>
<td>7.4396E-02 mol</td>
<td>BCC_A2#1 (4.0866 gram, 7.4396E-02 mol)</td>
</tr>
<tr>
<td></td>
<td>(900 K, 1 atm, a=1.0000)</td>
<td>(9.6768E-07 Cr1C3 + 3.1056E-06 Fe1C3 + 5.0286E-07 Cr1N3 + 1.6138E-06 Fe1N3 + 0.23757 Cr1Va3 + 0.76243 Fe1Va3)</td>
</tr>
<tr>
<td></td>
<td>+ 2.6944E-02 mol</td>
<td>SIGMA (43.703 gram, 2.6944E-02 mol)</td>
</tr>
<tr>
<td></td>
<td>(900 K, 1 atm, a=1.0000)</td>
<td>(0.54775 Fe8Cr4Cr18 + 0.45225 Fe8Cr4Fe18)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.1157E-02 mol)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(900 K, 1 atm, a=1.0000)</td>
</tr>
<tr>
<td></td>
<td>+ 3.2602E-03 mol</td>
<td>M23C6 (4.1658 gram, 3.2602E-03 mol)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(900 K, 1 atm, a=1.0000)</td>
</tr>
</tbody>
</table>

4 phases are formed at full equilibrium
Paraequilibrium and minimum Gibbs energy calculations

Fe-Cr-C-N system at 900K
when only C and N are permitted to diffuse

1° Click here
2° Click on « edit »
3° Click here
4° Enter elements that can diffuse
5° calculate
Output when only C and N are permitted to diffuse

\[ \begin{align*}
0.5 \text{ Fe} + 0.5 \text{ Cr} + 0.02 \text{ C} + 0.02 \text{ N} &= \\
0.14857 \text{ mol FCC_A1}\#1 \\
(8.2952 \text{ gram, 0.14857 mol}) \multirow{9}{*}{(900 K, 1 atm, \quad a=1.0000)} & \multirow{9}{*}{(1.1737E-03 \text{ Cr1C1} + 6.7310E-02 \text{ Cr1N1} + 0.43152 \text{ Cr1Va1} + 0.43152 \text{ Fe1Va1})} \\
& + 2.5870E-02 \text{ mol SIGMA} \\
(41.848 \text{ gram, 2.5870E-02 mol}) & + 0.61111 \text{ Fe8Cr4Cr18} + 0.38889 \text{ Fe8Cr4Fe18}) \\
& \multirow{9}{*}{\begin{array}{l}
\text{System component} \\
\text{Fe} \\
\text{Cr} \\
\text{N} \\
\text{C} \\
\text{Mole fraction} \\
0.43977 \\
0.43977 \\
0.11840 \\
2.0646E-03 \\
\text{Mass fraction} \\
0.50010 \\
0.46563 \\
3.3771E-02 \\
5.0496E-04 \\
\end{array}} \\
& \quad \begin{array}{l}
\text{Mole fraction} \\
0.50000 \\
0.50000 \\
0.11840 \\
2.0646E-03 \\
\text{Mass fraction} \\
0.51785 \\
0.48215 \\
3.3771E-02 \\
5.0496E-04 \\
\end{array}
\end{align*} \]

\[ \begin{align*}
+ 3.2752E-03 \text{ mol M23C6} \\
(4.2978 \text{ gram, 3.2752E-03 mol}) \multirow{9}{*}{(900 K, 1 atm, \quad a=1.0000)} & \multirow{9}{*}{(0.25000 \text{ Cr20C3C6} + 0.25000 \text{ Cr20Fe3C6} + 0.25000 \text{ Fe20C3C6} + 0.25000 \text{ Fe20Fe3C6})} \\
& \multirow{9}{*}{\begin{array}{l}
\text{System component} \\
\text{Fe} \\
\text{Cr} \\
\text{Mole fraction} \\
0.25000 \\
0.25000 \\
\text{Mass fraction} \\
0.25000 \\
0.25000 \\
\end{array}} \\
& \quad \begin{array}{l}
\text{Mole fraction} \\
0.25000 \\
0.25000 \\
\text{Mass fraction} \\
0.25000 \\
0.25000 \\
\end{array}
\end{align*} \]

Fe/Cr molar ratio = 1/1 in all phases

3 phases are formed at paraequilibrium when only C and N are permitted to diffuse
Paraequilibrium and minimum Gibbs energy calculations

- **Input when only C is permitted to diffuse**

- **Input when only N is permitted to diffuse**

- **Input when no elements are permitted to diffuse (minimum Gibbs energy calculation)**
Output when only C is permitted to diffuse

0.5 Fe + 0.5 Cr + 0.02 C + 0.02 N =

0.94732 mol BCC_A2#1
(51.387 gram, 0.94732 mol)
(900 K, 1 atm, a=1.0000)
(6.1460E-04 Cr1C3
+ 6.1460E-04 Fe1C3
+ 3.3333E-03 Cr1N3
+ 3.3333E-03 Fe1N3
+ 0.49605 Cr1Va3
+ 0.49605 Fe1Va3)

System component | Mole fraction | Mass fraction |
--- | --- | --- |
Fe | 0.48843 | 0.51475 |
Cr | 0.48843 | 0.47927 |
N | 1.9537E-02 | 5.1642E-03 |
C | 3.6023E-03 | 8.1649E-04 |

+ 1.7560E-02 mol CEMENTITE
(3.0536 gram, 1.7560E-02 mol)
(900 K, 1 atm, a=1.0000)
(0.47000 Cr3C1
+ 0.47000 Fe3C1
+ 3.0000E-02 Cr3N1
+ 3.0000E-02 Fe3N1)

System component | Mole fraction | Mass fraction |
--- | --- | --- |
Fe | 0.37500 | 0.48172 |
Cr | 0.37500 | 0.44852 |
N | 1.5000E-02 | 4.8329E-03 |
C | 0.23500 | 6.4926E-02 |

Fe/Cr molar ratio = 1/1 in all phases
N/(Fe+Cr) molar ratio = 0.02 in all phases

2 phases are formed at paraequilibrium
Output when only N is permitted to diffuse

FactSage 6.4

0.5 Fe + 0.5 Cr + 0.02 C + 0.02 N =

0.81037 mol  BCC_A2#1
(43.892 gram, 0.81037 mol)
(900 K, 1 atm,  a=1.0000)
( 3.3333E-03  Cr1C3
+ 3.3333E-03  Fe1C3
+ 2.4375E-05  Cr1N3
+ 2.4375E-05  Fe1N3
+ 0.49664  Cr1Va3
+ 0.49664  Fe1Va3)

System component  Mole fraction  Mass fraction
Fe               0.49013       0.51553
Cr               0.49013       0.48000
N               1.4336E-04       3.7820E-05
C               1.9605E-02       4.4350E-03

+ 0.18963 mol  FCC_A1#1
(10.549 gram, 0.18963 mol)
(900 K, 1 atm,  a=1.0000)
( 1.0000E-02  Cr1C1
+ 1.0000E-02  Fe1C1
+ 5.2423E-02  Cr1N1
+ 5.2423E-02  Fe1N1
+ 0.43758  Cr1Va1
+ 0.43758  Fe1Va1)

System component  Mole fraction  Mass fraction
Fe               0.44451       0.50194
Cr               0.44451       0.46734
N               9.3209E-02       2.6399E-02
C               1.7780E-02       4.3181E-03

Fe/Cr molar ratio = 1/1 in all phases
C/(Fe+Cr) molar ratio = 0.02 in all phases

2 phases are formed at paraequilibrium
Minimum Gibbs energy calculation (no elements permitted to diffuse)

0.5 Fe + 0.5 Cr + 0.02 C + 0.02 N =

1.0000 mol BCC_A2#1
(54.441 gram, 1.0000 mol)
(900 K, 1 atm, a=1.0000)
(3.333E-03 Cr1C3
+ 3.333E-03 Fe1C3
+ 3.333E-03 Cr1N3
+ 3.333E-03 Fe1N3
+ 0.49333 Cr1Va3
+ 0.49333 Fe1Va3)

<table>
<thead>
<tr>
<th>System component</th>
<th>Mole fraction</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.48077</td>
<td>0.51290</td>
</tr>
<tr>
<td>Cr</td>
<td>0.48077</td>
<td>0.47755</td>
</tr>
<tr>
<td>N</td>
<td>1.9231E-02</td>
<td>5.1457E-03</td>
</tr>
<tr>
<td>C</td>
<td>1.9231E-02</td>
<td>4.4124E-03</td>
</tr>
</tbody>
</table>

The phase with the lowest Gibbs energy of this composition at 900K is the bcc phase.