Alloy Design
Basics and Advanced

Mg-Sn alloy

Mg-Sn + Si alloy

Mg-Sn + Si + Sb alloy
All materials processes involve “Thermodynamics” and “Kinetics”.

Thermodynamics (Equilibrium) tells where we go. Kinetics tells how fast we can go.

FactSage can provide Thermodynamic calculations for:
- Multicomponent (< 48 elements) Chemical reaction equilibria
- Phase diagrams up to 8 component systems
- Thermodynamic properties such as heat balance, G, H, S, etc.
Alloy Design Concept using FactSage Calculations

- Gas, Oxide, Salt and Alloy databases

- Equilibrium Calculation
  - Equilibrium reactions as annealed microstructure
  - Scheil Cooling Calculation as cast microstructure

- Data mining program (FactOptimal)
  - Phase diagram
    - Multicomponent phase diagram section

- Alloy design
# Material Processing and FactSage

<table>
<thead>
<tr>
<th>Process</th>
<th>What can we do with FactSage</th>
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<tbody>
<tr>
<td>Extraction / Refining / Recycling</td>
<td>Gas/Slag/Matte/Salt/Metal/Refractory reactions</td>
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<tr>
<td>Casting</td>
<td>Scheil cooling calculation (as-cast microstructure)</td>
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<tr>
<td></td>
<td>Solidification software</td>
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<tr>
<td>Annealing / Homogenization</td>
<td>Multicomponent equilibrium calculations</td>
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<td>Secondary phase precipitation</td>
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<td>Solidification software</td>
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<td>TMP / Forming</td>
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<tr>
<td>Final treatment: Oxidation / Corrosion</td>
<td>Oxidation phase diagram, E-pH diagram, Gas corrosion reactions</td>
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<td>/ Surface treatment</td>
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<tr>
<td>Thermodynamic properties</td>
<td>All kinds of thermodynamic properties:</td>
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<tr>
<td></td>
<td>Heat balance, G, H, S, activity, partial pressure of gases, etc..</td>
</tr>
</tbody>
</table>
Alloy design (I): Phase diagram calculation to find out final target composition

Mg - Al - 1%Zn - 0.3%Mn

wt% Al

Temperature, °C

L + Mg + Al8Mn5

L + Mg + Mn4Al11

L + Mg + Mg17Al12 + MnAl4

L + Mg + Mg17Al12 + Al99Mn23

Liquid (L)

Mg + Al8Mn5

Mg + Mn4Al11

Mg + MnAl4

Mg + Mg17Al12 + Al99Mn23
Alloy design (II): Estimating of as-cast microstructure to find out whether solidification can be reasonable.
Scheil cooling calculation of AZ31 alloy

Alloy Design Basics 6

www.factsage.com
Scheil cooling calculations tell us the solidification path:

- Primary phase, precipitation, and eutectic reaction.
- Dendrite boundary (eutectics, segregation)

-> Estimation of as-cast microstructure
Scheil cooling calculation: as cast microstructure

Corning effect of Mg dendrite: AZ31

- Change of composition in dendrite & boundary
- Mg dendrite
- Boundary

Liquid - Al
Liquid - Zn
alpha Mg - Al
alpha Mg - Zn

Temperature, °C
Weight percent

Corning effect of Mg dendrite: AZ31

In dendrite & boundary
Alloy design (III): Calculate the final target microstructure AZ31

![Phase Diagram](image)

Temperature, °C

Phase Distribution (wt%)

- Mg$_{17}$Al$_{12}$
- Al$_{8}$Mn$_{5}$
- Al$_{11}$Mn$_{4}$
- Al$_{4}$Mn
- Mg

Liquid
FTlite database

Thermodynamic data & parameters for:

* 114 solution phases

- **HCP(HCP_A3)** Ag, Al, Be, Ca, Ce, Cr, Cu, Fe, In, Li, Mg, Mn, Mo, Na, Ni, Sb, Sc, Si, Sn, Sr, Ta, Ti, Y, Zn, Zr, RE
- Liquid: As HCP + hydrogen, carbon, boron
- BCC & FCC: Similar list as HCP
- **Gamma (β-Al₁₂Mg₁₇)** Mg, Al, Zn, Li
- Al₈Mn₅: Al, Cu, Fe, Mn, Si
- AlₓMnᵧ with Fe (x=4 & y=1;  x=11 & y =4)
- **Tau- & Phi-** ternary Mg-Al-Zn phases
  - Laves C14, C15, C36: Al, Ba, Ca, Mg, Sr, Zn, (RE) (being updated)
    - **LC14: Laves_C14**: MgZn, Mg₂Y, CaLi₂, Mg₂Ca, Mg₂Sr, Mg₂Ba
    - **LC15: Laves_C15**: MgCu₂, Mg₂Ce, Mn₂Y, Al₂Y, Al₂Ce, Al₂Ca, Al₂Sc, Al₂Sr
    - **LC36: Laves_C36**: MgNi₂
  - Mg₂X (X = Si,Sn,Ge,Pb): Mg₂Si, Mg₂Sn, Mg₂Ge, Mg₂Pb
    - ...

* 488 pure compounds

* Thousands of **gaseous species** (from the FACT53 Database)

- **Volumetric data & parameters**
  - For the Mg-Al-Zn-Mn-(Fe) system
The elements included in the FactSage FSstel steel database are:

Al, B, Bi, C, Ca, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, N, O, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ti, V, W, Zr

FCC: Fe / Carbide / Nitride are all treated as FCC phase
- > Fe with N and C should use J option (3-miscibility gaps).
- > Fe with N or C should use I option (2-miscibility gaps).
- > Also recommend to use I option for BCC phase
   For example, Fe-Ti-Nb-C-N calculations.

FCC ordered phase (FCC_L12) and BCC ordered phase (BCC_B2) significantly slow down the calculations. If you are not really interested in order/disorder transition, we recommend not to select this phase. (these ordered phases are necessary in Al-Ni rich system)

Carbon: When C content is lower than ~ 1%, Fe3C (metastable) phase normally forms instead of C (stable). So, in the selection for solid phase, unselect “C” solid phase.
Alloy database: Others

• **FSCopp**: Copper alloy development (all binary Cu-X systems)

• **FSlite**: Old database for FTlite

• **FSupsi**: High purity Si database for solar cell grade Si production

• **FSnobl**: Noble alloy database for Ag, Au, Ir, Os, Pd, Pt, Rh, Ru refining

• **SGnobl**: Similar to FSnobl

• **SGsold**: Solder alloy database

• **SGTE 2007**: developed by SGTE ([www.sgte.org](http://www.sgte.org)): Applicable to all general alloy system. But less accurate than other dedicated databases for specific region.
Calculation examples for Alloy design

EX1. Binary phase diagram: Mg-Al (how to read the phase diagram)
EX2. Target (Transition, Formation, Precipitation): Mg-Al
EX3. Equilibrium phase fraction / phase fraction vs temperature diagram: Mg-Al
EX4. Simple as-cast microstructure simulation / Scheil cooling calculation: Mg-Al
EX5. I option (miscibility gap): Al-Zn phase diagram
EX6. Isothermal Ternary phase diagram: Mg-Al-Zn
EX7. Projection calculation (Liquidus projection): Mg-Al-Zn
EX8. Scheil cooling calculation for AZ31 alloy (Mg-3Al-1Zn-0.3Mn)
EX9. Equilibrium calculation for AZ31 alloy (Mg-3Al-1Zn-0.3Mn)
EX10. Complex phase diagram: AZ31 – Sr rectangular phase diagram
EX11. Complex phase diagram: AZ31 – Sr – Ca rectangular isothermal section
EX12-1. Complex phase diagram: Mg-Al-Zn + 1% Sr triangle isothermal section
EX12-2. Complex phase diagram: Mg-Al-Zn + 1% Sr rectangular isothermal section
EX13. Metastable phase: Fe-C binary phase diagram with/without C (Fe3C)
EX14. J option (3 possible miscibility gap): Fe-Nb-Ti-C-N system
EX15-1. Phase diagram PO2 – T: oxidation of pure Fe
EX15-2. Phase diagram PO2 – X: oxidation of Fe-Cr
EX15-3. Phase diagram PO2 – T: oxidation of Fe-1%Mn-1%Si
EX16. <A> option: Simple counter-cross inter-diffusion calculation <A>Al-Mg // <1-A>Mg-Al-Zn
EX17. Oxidation of AHSS in tunnel furnace: Dew point control, stream, primary/secondary oxidation
EX19. Composition target: carburization and decarburization of steel
EX20. Open calculation: Refining of B and P for High purity Si production
EX21. Heat balance (ΔH): Initial condition, heat evolution (T evolution) during fluxing, alloying, heating, casting
EX23. Solidus projection
EX24. Precipitation during the solidification: Non-metallic inclusions
EX1. Binary phase diagram: Mg-Al binary system

1. Entering elements/components
2. Database selection
3. Phases (compounds and solutions) selection
4. Calculation conditions (T, X, P, etc.)
The diagram represents the Mg-Al phase diagram, showing the liquidus and solidus lines, as well as various phase regions such as Liquid, Gamma, HCP_A3, FCC_A1, and Beta_AlMg. The eutectic reaction is indicated, and the lever rule is used to determine compositions at tie-lines. The phase region of Eutectic rxn is highlighted, and the mole fraction of Al/(Mg+Al) is shown on the x-axis, with temperature (°C) on the y-axis.
EX2. Target calculations

(a) Transitions (EX2-1):
do calculation between initial and final temperature and find all phase transition between them

(b) Precipitation target (EX2-2): find temperature at which any other phase begins to precipitate out from the targeted phase

(c) Formation target (EX-2-3): find the temperature at which the targeted phase begin to form

To learn more, go to ??
EX2-1. Transition calculation

(1) Select the compositions
(2) Select “transitions” instead of “normal”

Range of temperature: “initial final interval”
Calculate Initial (0 °C) to final (700°C) temperature with interval of 10 °C
Calculation results at every 100°C intervals

What is this complex thing?
-> model structure in database
-> output for modeling people

Elemental composition of gamma phase

Input composition
**Phase transition happens at this temperature**

Although the amount of Gamma phase is zero, the activity \( a = 1 \) tells Gamma phase begins to form at this temperature.

Activity \( a \) of this phase = 0.45598

\( a = 1 \): stable phase, \( a < 1 \): unstable
EX2-2. Precipitation target calculation

Liquid is selected as precipitation target phase (P). Then, FactSage will calculate liquidus temperature of a given composition.

For target calculation, this temperature should remain blank.

Automatic default estimated value.
EX2-3. Formation target calculation

Liquid is selected as formation target phase (F). Then, FactSage will calculate solidus temperature of a given composition.

For target calculation, this temperature should remain blank.

automatic default estimated value
EX3. Variation of phase fraction with temperature (equilibrium)

Transition calculation from 700°C to 200°C with 10°C interval
Click to plot the results

Click to select X, Y axes

Click to setup axes

Select the phase to plot

Selection of phases
Special care is required for the phase selection.

### Pure compounds such as Mg, Al, intermetallic compounds

<table>
<thead>
<tr>
<th>Species</th>
<th>Mole</th>
<th>Mole</th>
<th>Fract. min</th>
<th>Fract. max</th>
<th>Act. min</th>
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</table>

### Solutions such as liquid, hcp, fcc, gamma phases

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</table>

Tip for “phase fraction vs. temperature diagram”

All phases which have amount > 0 in “Pure Solids” and “SOLUTIONS” should be selected.
If we want to plot the compositional variation inside of solution phases, we have to select the elements in this "ELEMENTS" section.

For example, if we want to plot the variation of Al and Mg concentrations in liquid phase with temperature, we have to select Al_Liq#1 and Mg_Liq#1.
EX4. Variation of phase fraction with temperature (Scheil cooling)

Cooling step: In most of cases, 5 degree is enough to simulate solidification process.

This cooling step is not directly related to solidification rate (cooling speed).

Temperature:
(i) starting temperature and final temperature
(ii) starting temperature: program will automatically calculate the final solidification temperature.
Equilibrium calc.

Scheil cooling calc.

Scheil cooling calculation is terminated when liquid phase disappears

Alloy Design Basics 28
“I” Option: when the phase has a miscibility gap (solid state or liquid state phase separation), I option should be selected to do more accurate calculations. For example, fcc phase in Al-Zn system has a solid state miscibility gap as in this example. Liquid oxide slag has a miscibility gap in high SiO2 region.
The diagram represents the phase diagram for the Al - Zn alloy system. It shows the miscibility gap where two phases, FCC_A1 + FCC_A1#2, coexist with a liquid phase. The temperature ($T$) is plotted on the y-axis, ranging from 0°C to 700°C, and the mole fraction of Zn/($Al+Zn$) is plotted on the x-axis. The diagram illustrates different phases and their stability regions.
EX6. Isothermal Ternary phase diagram: Mg-Al-Zn

Alloy Design Basics 31
EX7. Projection calculation (Liquidus projection): Mg-Al-Zn

“O” option for the target projection phase (Liquid in most of cases)
Al - Mg - Zn
Data from FTlite - FACT light alloy databases

T(min) = 340.89 °C, T(max) = 660.31 °C

Four-Phase Intersection Points with Liquid

1: AlMgZn_Tau / FCC_A1#1 / Laves_C14#1
2: AlMgZn_Tau / Beta_AlMg / Gamma
3: AlMgZn_Tau / Beta_AlMg / FCC_A1#1
4: AlMgZn_Tau / Laves_C14#1 / Mg2Zn3
5: AlMgZn_Tau / Gamma / Phi
6: Gamma / FCC_A1#1 / Phi
7: FCC_A1#1 / Laves_C14#1 / Mg2Zn11
8: AlMgZn_Tau / Mg2Zn3 / MgZn
9: FCC_A1#1 / FCC_A1#1 / Phi
10: HCP_A3#1 / Mg15Zn20<_mg7zn3>_oi1 / MgZn
11: AlMgZn_Tau / HCP_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 0.57720 447.57
3: 0.04248 0.36009 0.59743 446.26
4: 0.33110 0.60810 0.06080 428.12
5: 0.16296 0.66052 0.17652 385.07
6: 0.16267 0.69979 0.13755 364.35
7: 0.80148 0.07683 0.12168 360.17
8: 0.25899 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
EX8. Scheil cooling calculation for AZ31 alloy (Mg-3Al-1Zn-0.3Mn)
Close-up view

95.7 Mg + 3 Al + Zn + 0.3 Mn

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Alloy Design Basics 36
EX9. Equilibrium calculation for AZ31 alloy (Mg-3Al-1Zn-0.3Mn)

### Reactants (4)

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<tr>
<th>Component</th>
<th>Amount</th>
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<tr>
<td>Zn</td>
<td>1</td>
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<tr>
<td>Mn</td>
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### Products

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<tr>
<th>Compound Species</th>
<th>Solution Species</th>
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<tbody>
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<td>FTIt a-LO</td>
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</table>

### Final Conditions

- **A**: 700
- **B**: 100
- **T(C)**: 100
- **P(atm)**: 1

### Equilibrium

- Normal
- Predominant
- Open

### Calculations

1. **Calculate**

### Results

- **Composition Table**
  - Mg: 2.9708E-03, 9.6683E-03
  - Al: 2.7166E-03, 6.1122E-03
  - Zn: 7.6645E-03, 6.7994E-03
  - Mn: 0.5851E-03, 0.9835E-03

- **Mole fraction of sublattice constituents**:
  - Mg: 2.9708E-03, Stoichiometry = 24.000
  - Al: 2.1199E-03, Stoichiometry = 24.000
  - Zn: 9.6683E-03, Stoichiometry = 24.000
  - Mn: 0.5851E-03, Stoichiometry = 24.000

### FactSage

Alloy Design Advanced 37
MnAl$_4$(s) Mn$_4$Al$_{11}$(s)

95.7 Mg + 3 Al + Zn + 0.3 Mn

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T(C)

gram

100 200 300 400 500 600 700

0

0.50

1.00

1.50

2.00

Close-up view
In FactSage, all the input is in molar formula. Thus, in order to add AZ31 (97wt%Mg-3wt%Al-1wt%Zn), we have to do conversion of the composition into molar fraction first. Then, add this molar formula as input:

97wt%Mg-3wt%Al-1wt%Zn \rightarrow 0.96897Mg-0.027277Al-0.0037517Zn
EX11. Phase diagram: AZ31 – Sr – Ca isothermal section
For the triangle phase diagram of more than 4 component system, special care is needed to set correct composition.
Mg - Al - Zn - Sr

500°C, mass Sr/(Mg+Al+Zn) = 0.010101
EX12-2. Mg-Al-Zn + 1% Sr triangle /rectangular isothermal section
Mg - Al - Zn - Sr

500°C, mass Sr/(Mg+Al+Zn+Sr) = 0.01

Liquid + HCP_A3

Liquid + HCP_A3 + Al₄Sr(s)

HCP_A3 + Al₄Sr(s)

HCP_A3 + Mg₁₇Sr₂(s)

mass Zn/(Mg+Al+Zn+Sr)

mass Al/(Mg+Al+Zn+Sr)

mass Zn/(Mg+Al+Zn+Sr)
Although C (carbon) is thermodynamically stable phase than Fe3C, C is not appearing in most of low carbon steel. Thus, in order to do proper calculations, C should be removed from above compound list in particular in steel.

In the same way, if a certain phase is not readily formed (sluggish to form), we can unselect the phase to simulate the system more realistically.
Stable phase diagram with C

Metastable phase diagram without C
“J” option is needed for a phase which has more than 2 possible miscibility gaps. Most well known example is Fe FCC phase in steel with (Ti,Nb)(C,N) phase formation. Since Ti(C,N) and Nb(C,N) have FCC crystal structure, we describe both FCC metallic phase and carbonitride phase using the same FCC phase model. Thus, in order to do proper calculations, J option should be applied to FCC phase in this case.
Austenite phase

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<th>Phase</th>
<th>Composition</th>
<th>Stoechiometry</th>
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<tr>
<td>Ti(C,N)</td>
<td>Ti: N = 0.57</td>
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</tr>
<tr>
<td>Nb(C,N)</td>
<td>Nb: C = 0.54</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

**Mole fraction of sublattice constituents:**

- Fe: 0.3099
- Nb: 0.5400
- Ti: 0.1500
- C: 0.0300
- N: 0.0700

**System component**

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<th>Component</th>
<th>Mole fraction</th>
<th>Mass fraction</th>
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</tbody>
</table>

**Mole fraction of sublattice constituents:**

- Fe: 0.1970
- Nb: 0.3770
- Ti: 0.2000
- C: 0.0800
- N: 0.3500

**System component**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>0.0274</td>
<td>0.0274</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0300</td>
<td>0.0300</td>
</tr>
<tr>
<td>C</td>
<td>0.0700</td>
<td>0.0700</td>
</tr>
<tr>
<td>N</td>
<td>0.2300</td>
<td>0.2300</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2400</td>
<td>0.2400</td>
</tr>
</tbody>
</table>
99.875 Fe + 0.018 Ti + 0.068 Nb + 0.039 C +

c:\Workshop\Equi0.res 30Apr10

Alloy Design Advanced 51
EX15-1. Phase diagram PO2 – T: Oxidation of pure Fe

Oxidation of steel requires multiple databases
(a) FSStel: steel phases
(b) FToxid: oxide phases
(c) Fact53: gases and others
When we select multiple databases, this “suppress duplicate” option help to remove duplicate based on ‘database priority’ given by user.
Oxygen partial pressure can be selected by this option.
If we want to use oxygen as one of axes, O2 should be added as input component.
Any kind of counter-cross inter-diffusion reaction at interface can be simulated with <A> option in Equilib. This assume the diffusivity of all components in both materials are the same.
Joining of Al-Mg // AZ31
\texttt{<A> Al0.97Mg0.03 + \langle1-A\rangle Mg0.965Al0.03Zn0.005}

c:\Workshop\Equi0.res 30Apr10
EX17. Oxygen partial pressure control for oxidation of metals

- Ice(H$_2$O(s)), $T = -30^\circ$C
- Dew point

- $N_2 - 5\%H_2$

- Annealing $T = 800^\circ$C
- $H_2 + \frac{1}{2}O_2 = H_2O$
- $PO_2 = ?$

- Hot Dip Galvanizing

- Cold worked at $300^\circ$C
We should select real gas to obtain accurate Gibbs energy and volume fraction of gas at low temperature and high pressure.
We will heat this gas at 800°C using stream file.
EX17-1. Oxygen partial pressure control using Dew-point concept
EX17-1. Oxygen partial pressure control using Dew-point concept
EX17-1. Oxygen partial pressure control using Dew-point concept
EX17-1. Oxygen partial pressure control using Dew-point concept

<table>
<thead>
<tr>
<th>PHASE: gas_real</th>
<th>EQUIL AMOUNT (mol)</th>
<th>MOLE FRACTION</th>
<th>FUGACITY (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>9.5000E+01</td>
<td>9.4965E-01</td>
<td>9.5000E-01</td>
</tr>
<tr>
<td>H2</td>
<td>4.9994E+00</td>
<td>4.9975E-02</td>
<td>4.9991E-02</td>
</tr>
<tr>
<td>H2O</td>
<td>3.7523E-02</td>
<td>3.7509E-04</td>
<td>3.7510E-04</td>
</tr>
<tr>
<td>NH3</td>
<td>4.0450E-04</td>
<td>4.0435E-06</td>
<td>4.0442E-06</td>
</tr>
<tr>
<td>H</td>
<td>3.1448E-07</td>
<td>3.1437E-09</td>
<td>3.1448E-09</td>
</tr>
<tr>
<td>OH</td>
<td>9.1648E-12</td>
<td>9.1614E-14</td>
<td>9.1647E-14</td>
</tr>
<tr>
<td>NO</td>
<td>8.8497E-14</td>
<td>8.8465E-16</td>
<td>8.8494E-16</td>
</tr>
<tr>
<td>HNNH</td>
<td>3.0707E-16</td>
<td>3.0695E-18</td>
<td>3.0706E-18</td>
</tr>
<tr>
<td>NH</td>
<td>1.1411E-16</td>
<td>1.1407E-18</td>
<td>1.1411E-18</td>
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<tr>
<td>N2O</td>
<td>6.2969E-18</td>
<td>6.2946E-20</td>
<td>6.2963E-20</td>
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<tr>
<td>HNO</td>
<td>5.8273E-18</td>
<td>5.8252E-20</td>
<td>5.8273E-20</td>
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<tr>
<td>N</td>
<td>1.4359E-18</td>
<td>1.4354E-20</td>
<td>1.4359E-20</td>
</tr>
<tr>
<td>HOOH</td>
<td>1.2268E-21</td>
<td>1.2261E-23</td>
<td>1.2265E-23</td>
</tr>
<tr>
<td>HONO (g2)</td>
<td>2.0473E-24</td>
<td>2.0466E-26</td>
<td>2.0473E-26</td>
</tr>
<tr>
<td>HOO</td>
<td>1.9844E-24</td>
<td>1.9837E-26</td>
<td>1.9844E-26</td>
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<tr>
<td>HONO (g)</td>
<td>1.5885E-24</td>
<td>1.5879E-26</td>
<td>1.5885E-26</td>
</tr>
<tr>
<td>NO2</td>
<td>3.1410E-26</td>
<td>3.1398E-28</td>
<td>3.1410E-28</td>
</tr>
<tr>
<td>N2H5OH</td>
<td>T 7.1401E-27</td>
<td>7.1374E-29</td>
<td>7.1400E-29</td>
</tr>
<tr>
<td>HONO2</td>
<td>1.5179E-37</td>
<td>1.5172E-39</td>
<td>1.5178E-39</td>
</tr>
<tr>
<td>O3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>1.6943E-18</td>
<td>1.6926E-20</td>
<td>1.6932E-20</td>
</tr>
<tr>
<td>N2O3</td>
<td>1.4364E-18</td>
<td>1.4349E-20</td>
<td>1.4354E-20</td>
</tr>
<tr>
<td>O2</td>
<td>1.8361E-20</td>
<td>1.8343E-22</td>
<td>1.8348E-22</td>
</tr>
<tr>
<td>HONO (g2)</td>
<td>1.5058E-23</td>
<td>1.5043E-25</td>
<td>1.5049E-25</td>
</tr>
</tbody>
</table>

Final partial pressure of oxygen when the temperature of ice is -20°C
EX17-2. phase diagram $\text{PO}_2$ – $\text{T}$: Oxidation of Fe-1%Mn-1%Si
$O_2 - Fe - Mn - Si$

mass $\frac{Mn}{(Fe+Mn+Si)} = 0.01$, mass $\frac{Si}{(Fe+Mn+Si)} = 0.01$

\[ T(C) \]

\[ \log_{10}(p(O_2)) \text{ (atm)} \]

500 600 700 800 900 1000

-40
-36
-32
-28
-24
-20

Alloy Design Advanced 69

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EX17-3. Primary oxide formation diagram

Fe - C - Mn - Si - O₂
800° C, p(O₂) = 10⁻²⁷.₅ bar, C = 0.1%

Drawing of the diagram:
1) Collect all blue/red/green lines at different PO2 and superimpose them in one diagram.
2) The boundary of each color line (different phase) is the phase boundary of the primary oxide phase in the diagram.
Fe-Mn-Si at $PO_2=10^{-28}$ atm, $T=800^\circ$C
**EX17-3. Primary oxide formation diagram**

**Fe - Mn - Si - O₂**

\[ p(O_2) = 10^{-25} \text{ atm}, \ 800^\circ\text{C}, \ 1 \text{ atm} \]

**Boundaries for oxide phase**

**Fe - Mn - Si - O₂**

\[ p(O_2) = 10^{-27} \text{ atm}, \ 800^\circ\text{C}, \ 1 \text{ atm} \]

Superimpose the figures of the lines calculated at different partial pressure of oxygens.
EX17-4. Primary and Secondary Oxidations

Concept of primary and secondary oxidations

SiO_2 formation

Mn = 0.5
Si = 1.5

Primary oxidation

SiO_2 + MnSiO_3 formation

Mn = 0.5
Si = 1.0

Secondary oxidation

Concept of primary and secondary oxidations
Oxidation phase diagram of the Fe-0.002%C-Mn-Si steel at 800°C
EX18. Remelting and oxidation of Zn galvanized steel

1. L/S Interfacial reaction
   - Reheating (900 °C)

2. Oxidation reaction
   - Air
   - Zn (liquid)

Oxidation Calculation

By controlling the partial pressure, different layer oxides can be calculated. But the partial pressure is not linearly decreasing with depth of oxide layer. So this type of calculation shows quantitative oxidation behavior.
EX18-1. Interface reaction between liquid Zn and steel

FTlite database contains reasonable Zn bath data for Zn-galvanizing. So, this is chosen instead of FSStel.
EX18-1. Interface reaction between liquid Zn and steel

Original steel: Fe-1%Mn-0.5%Cr

Reaction products: Zn-rich Liquid

Reaction products: BCC + FCC

We need this liquid Zn for the oxidation reaction
→ Save it as stream
EX18-2. Oxidation reaction of liquid Zn

(1) Setting oxygen partial pressure: activity or log activity can be fixed

(2) Remove duplicate compounds
   Give a priority in database
   Typically “FToxid > any metallic database > FactPS”
EX18-2. Oxidation reaction of liquid Zn

**Diagram:**

- **Setting X-axis:**

**Output:**

- **Results - Equilib a=1.00E-30 (page 1/61)**

**Species Selection - EQUILIB Results: gram vs log10(activity)**

- **Y-axis: gram**
  - Maximum: 55
  - Minimum: 0
  - Tick every: 5

- **X-axis: log10(activity)**
  - Maximum: 0
  - Minimum: -30
  - Tick every: 5

**System component:**

- **Mole fraction:**
  - Zn: 0.8803
  - Fe: 0.0913
  - Mn: 0.0857
  - Cr: 0.0857
  - O: 0.2374

**Gram Liquid#2:**

- **(900 C, 1 atm, a=1.0000)**
- **0.20374**
- **9.1514**
- **0.46556**
- **8.9787E-25**
- **90.179**

**Calculations:**

1. **Gas (g)**
   - **O_2(g)**
     - **0**
     - **1.00E+03**

2. **Liquid (l)**
   - **Zn**
     - **0**
     - **100**
   - **Fe**
     - **0.210796**
   - **Mn**
     - **0.020359**
   - **Cr**
     - **0.020359**
   - **O**
     - **8.9787E-25**
   - **Zn**
     - **35.391**
   - **Fe**
     - **1.00E+03**
   - **Mn**
     - **1.00E+03**
   - **Cr**
     - **1.00E+03**

3. **FCC+**
   - **Zn**
     - **1.111E+03**
   - **Fe**
     - **5.143E+03**
   - **Mn**
     - **5.143E+03**
   - **Cr**
     - **5.143E+03**

**Activity (min) and max):**

- **O_2(g):** 1.00E-30 to 1.00E+00
- **Zn:** 1.00E-30 to 1.00E+00
- **Fe:** 4.9988E-13 to 6.90E+00
- **Mn:** 6.90E-13 to 1.24E+00
- **Cr:** 6.90E-13 to 1.24E+00
- **O:** 2.528E-22 to 1.27E+02
- **Zn:** 1.00E-30 to 1.00E+00
- **Fe:** 4.9988E-13 to 6.90E+00
- **Mn:** 6.90E-13 to 1.24E+00
- **Cr:** 6.90E-13 to 1.24E+00
EX18-2. Oxidation reaction of liquid Zn

It is hard to expect the thickness of each layer
EX19. Carburization and Decarburization of Steel

CO / CO₂ is variable
EX19. Carburization and Decarburization of Steel
EX19. Carburization and Decarburization of Steel

99.62 Fe + 0.08 C + 0.2 Mn + 0.1 Si + (1-A)mol CO + A mol CO₂

An amount of carbon in FCC phase (Fe)
Composition Target: “How to calculate optimum amount of CO₂ to reduce C in steel to a targeted composition”
EX19. Carburization and Decarburization: Composition target

99.62 Fe + 0.08 C + 0.2 Mn + 0.1 Si + (1-A) mol CO + A mol CO₂
EX20-1. P reduction in high purity Si using vacuum

FactSage ultrapure silicon database
This is special database for high purity Si production
EX20-1. P reduction in high purity Si using vacuum
EX20-1. P reduction in high purity Si using vacuum
EX20-2. B reduction in high purity Si using H$_2$-H$_2$O mixture

Fig. 1. B concentration changes in H$_2$-H$_2$O blowing determined by the resistivity meter

[B] = 49.6Exp(-0.015t)

[B] = 57.8Exp(-0.024t)

JOM, JOURNAL OF THE MINERALS, METALS AND MATERIALS SOCIETY
Volume 64, Number 8 (2012), 952-956
EX20-2. B reduction in high purity Si using $\text{H}_2-\text{H}_2\text{O}$ mixture

Open calculations:
Simple reactor module with off-gas removal

“Open” menu
Addition of $<A>$ amount of gas and make chemical reaction
→ Remove the gas as off gas
→ Add another $<A>$ gas for chemical reaction
→ Remove the gas as off gas
→ Do this iteration until reaching “10” step
EX20-2. B reduction in high purity Si using H$_2$-H$_2$O mixture

B product in gas phase

B reduction in liquid Si
EX20-2. B reduction in high purity Si using $\text{H}_2$-$\text{H}_2\text{O}$ mixture

B content in liquid Si

$98\text{ Si} + \text{B} + \text{P} + <\text{xA}>\text{H}_2 + <(1-\text{x})\text{A}>\text{H}_2\text{O}$

1600°C

B content can be reduced with decreasing T

“page” in x-axis is amount of gas injected (or considered as the degassing time)
1) How much heat is required to increase temperature from T1 to T2?
2) If we add or remove a certain amount of H from mixtures of materials, what would be the final temperature?

→ Good for
a) Furnace capacity design
b) Heat balance calculation for alloying or fluxing of materials to melt bath
c) Calculate exothermic or endothermic heat generated during explosion
d) Process simulation for temperature change

Heat of formation + T increase

Heat of Dissolution
EX21-1. Heat balance: Addition of Ferro-Mn into Liquid steel

1. Heat balance:
   - Addition of Ferro-Mn into Liquid steel
   - Final Temperature?

2. 65% Mn - 35% Fe
   - 25°C

1. 1600 °C, Liquid
   - Fe - 1 wt.% Al - 0.8 wt.% C

Use two stream

1. gram 98.2 Fe + Al + 0.8 C =
   - mol gas_ideal
   - (1600 °C, 1 atm, a=1.426E-06)
   - (1.4261E-06 Al)
   - 10.00 gram LIQUID
     - (100.00 gram, 1.8621 mol)
     - (1600 °C, 1 atm, a=1.0000)
     - (98.200 wt.% Fe
     + 0.80000 wt.% C
     + 1.00000 wt.% Al)
   - System component Mole fraction Mass fraction
     - Fe 0.94433 0.98200
     - Al 1.9905E-02 1.00000E-02
     - C 0.57762E-02 0.00000E-03

2. (gram) 65 Mn + 35 Fe =
   - 79.546 gram CBCG_A1
     - (79.546 gram, 1.4436 mol)
     - (25 °C, 1 atm, a=1.0000)
     - (18.409 wt.% FeV
     + 81.581 wt.% MnV)
   - System component Mole fraction Mass fraction
     - Fe 0.18409 0.18409
     - Mn 0.81591 0.81591
   - + 20.454 gram BCC A2
     - (20.454 gram, 0.36630 mol)
     - (25 °C, 1 atm, a=1.0000)
     - (93.521 wt.% FeV
     + 6.47860 wt.% MnV)
   - System component Mole fraction Mass fraction
     - Fe 0.93521 0.93521
     - Mn 4.8646E-03 4.7870E-03
If we know the heat loss of the ladle we can setup this here for the final Temperature prediction.
EX21-1. Heat balance: Addition of Ferro-Mn into Liquid steel
EX21-2. Heat balance: Cooling of AZ91 from 600 to 300°C

Stream: AZ31 alloy at 600 °C
EX21-2. Heat balance: Cooling of AZ91 from 600 to 300°C
EX22-1. Thermodynamic properties: Activity, $\Delta G$, $\Delta H$, $\Delta S$ etc.
EX22-1. Thermodynamic properties: Activity, $\Delta G$, $\Delta H$, $\Delta S$ etc.
EX22-1. Thermodynamic properties: Activity, $\Delta G$, $\Delta H$, $\Delta S$ etc.
EX22-1. Thermodynamic properties: Activity, ΔG, ΔH, ΔS etc.

$\langle 1-A \rangle$ Mg + $\langle A \rangle$ Si

Delta H (kJ)

Delta S (J)

Alpha
Calculation of iso-activity line of Mg(l) in the Mg-Si-Sn system at T=1350 K
EX22-2. Iso-activity line in ternary system

(1) Click mouth right button on “pure liquids” →
(2) Click “+” button to (3) setup activity of element (this case is for Mg)

scan $X_{\text{Mg}} = 0.3$ from left to right of this triangle and ask FactSage to find out composition for activity of Mg(l) = 0.1
EX22-2. Iso-activity line in ternary system

Save results in excel or spread sheet form
EX22-2. Iso-activity line in ternary system

Plot the results in triangle diagram
- Prepare the triangle frame
- Plot the A,B,C coordinate numbers in triangle diagram

“Cont+C” → “Cont+V” or “copy” and “paste”.

Sometimes, “Cont+V” is not working due to the setting of values in Excel software, then use “paste” in “Edit” menu.
EX23. Calculation for Solidus lines (Solidus projection)

Calculating a polythermal projection – the first melting surface

This is a new feature in Phase diagram.
- Liquidus projection: plotting Liquidus in the temperature range with a certain interval ("O" option should be required for Liquid phase)
- Solidus projection: plotting Solidus in the same way as liquidus projection ("F" option should be required for Liquid phase)
EX23. Calculation for Solidus lines (Solidus projection)

Solidus projection

Liquidus projection
Table 3 — Chemical Test Summary

<table>
<thead>
<tr>
<th>Weld</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Ni</th>
<th>Ti</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-aluminum</td>
<td>0.234</td>
<td>&lt;0.003</td>
<td>0.011</td>
<td>0.50</td>
<td>0.28</td>
<td>1.70</td>
<td>0.02</td>
<td>0.003</td>
<td>0.006</td>
<td>0.064</td>
</tr>
<tr>
<td>E70T-4</td>
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<td></td>
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<td></td>
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<tr>
<td>Low-aluminum</td>
<td>0.149</td>
<td>&lt;0.003</td>
<td>0.005</td>
<td>0.64</td>
<td>0.30</td>
<td>0.53</td>
<td>0.01</td>
<td>0.058</td>
<td>0.030</td>
<td>0.033</td>
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<td>E71T-8</td>
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</table>

AWS 80th Annual Meeting, April 12–15, 1999, St. Louis, Mo. Page 98-s to 105-s
EX24. Non-metallic Inclusion formation during metal solidification

Table 3 — Chemical Test Summary

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Ni</th>
<th>Ti</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-aluminum</td>
<td>0.234</td>
<td>&lt;0.003</td>
<td>0.011</td>
<td>0.50</td>
<td>0.28</td>
<td>1.70</td>
<td>0.02</td>
<td>0.003</td>
<td>0.006</td>
<td>0.064</td>
</tr>
<tr>
<td>E70T-4</td>
<td>0.149</td>
<td>&lt;0.003</td>
<td>0.005</td>
<td>0.64</td>
<td>0.30</td>
<td>0.53</td>
<td>0.01</td>
<td>0.058</td>
<td>0.030</td>
<td>0.033</td>
</tr>
</tbody>
</table>
EX24. Non-metallic Inclusion formation during metal solidification

98.255 Fe + 0.149 C + 0.02 S + 0.005 P +

To zoom-up the small part of the calculated results, the axis of the figure should be changed.
EX24. Non-metallic Inclusion formation during metal solidification

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>Ni</th>
<th>S</th>
<th>Ti</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>0.20</td>
<td>1.31</td>
<td>0.006</td>
<td>1.82</td>
<td>0.006</td>
<td>0.023</td>
<td>351ppm</td>
<td>115ppm</td>
</tr>
</tbody>
</table>
EX24. Non-metallic Inclusion formation during metal solidification

96.109 Fe + 0.06 C + 0.2 Si + 1.31 Mn +

Zoom-up