

Thermo-Calc Software

Thermo-Calc: For All Kinds of Thermodynamic Calculations!

*Some Applications for Calculating
Complex Heterogeneous Interactions*

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- **Metal-Slag-Gas Interactions**
- Metal-Gas Interactions (Redox Reactions, Coatings, CVD, ...)
- Combustion/Sintering/Incineration/Remelting/Recycling
& Environmental Issues
- Dew Points
- Ellingham Diagrams
- *and more ...*

Making Life Better or Worse?

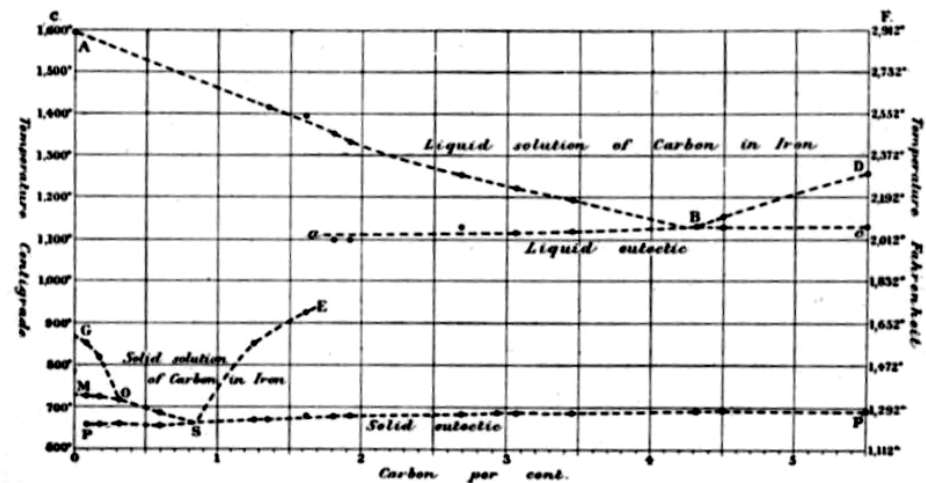
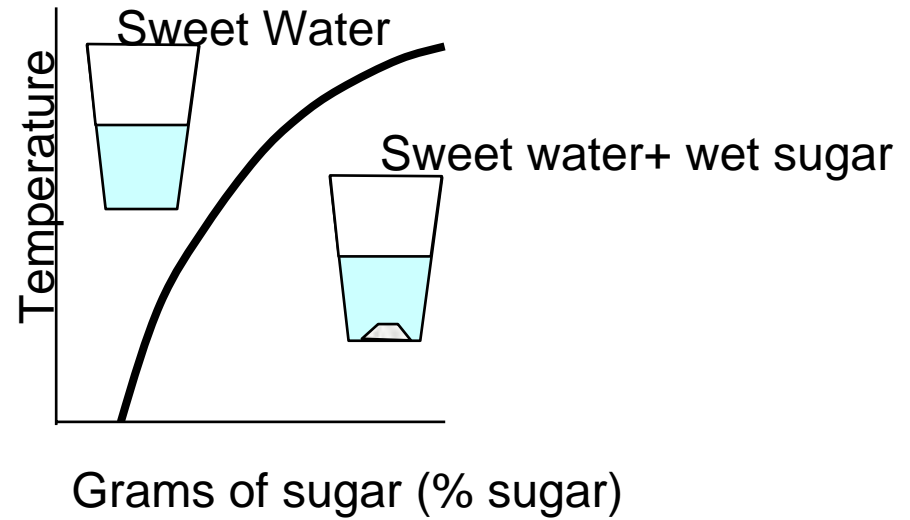
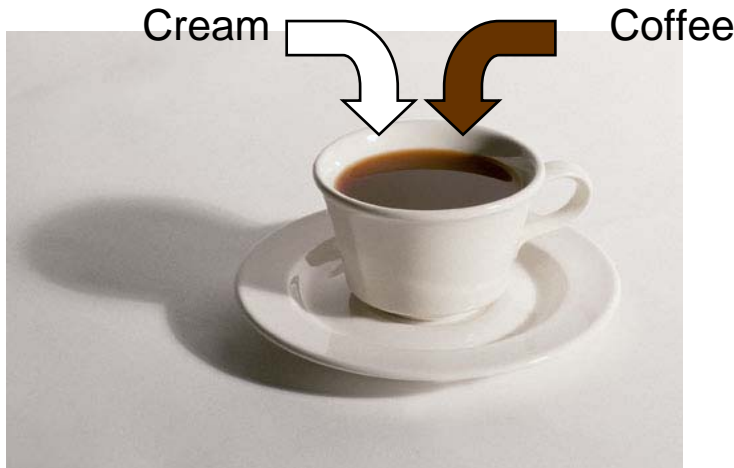
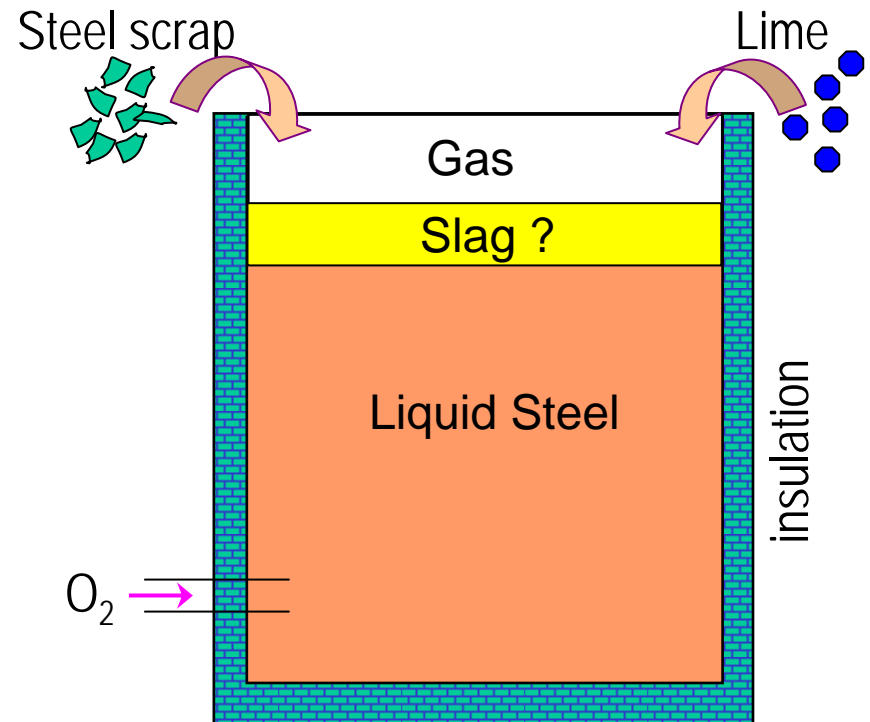
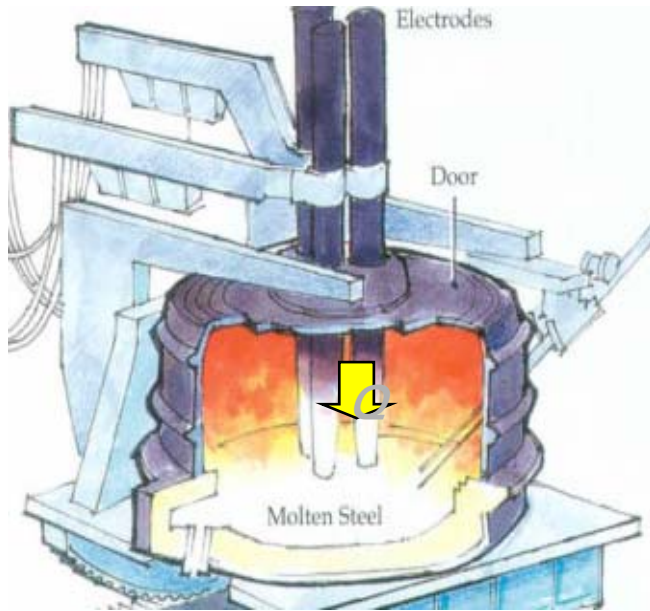


Fig. 401. — Roberts-Austen's first equilibrium diagram (1897).

Requirements from metallurgical industries



- ✓ Liquid Slag Formation and Solid Inclusions in Steels
- ✓ Slag Formation in Refractory Converter
- ✓ Slag-Removal During Hot/Cold Rolling (*Clean Steelmaking*)
- ✓ Solubility/Activity of Oxygen in Liquid Steel
- ✓ Metallurgical Extraction
- ✓ Casting in Production Lines
- ✓ ... *more* ...

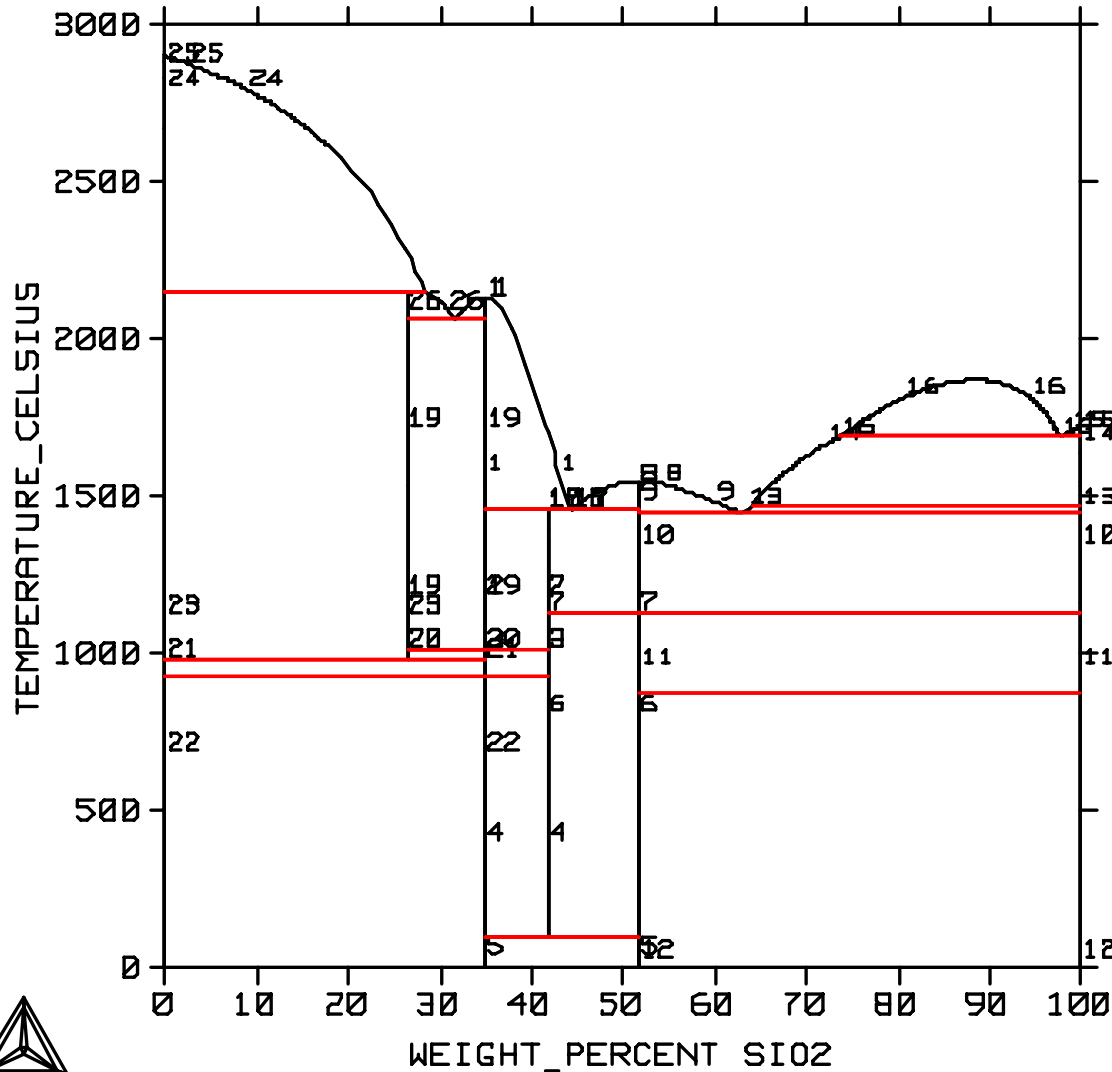
Typical Thermo-Calc Calculations

Using the TCC/TCW software, it is possible to make various calculations for heterogeneous systems involving complex metal-slag interactions:

- Liquid slag phase alone;
- Alloy phases in equilibrium with slag phases (liquid slag + oxide solids);
- Alloy+slag+gas phases.

The MACRO feature of TCC software is especially useful and efficient in making complicated calculations of complex metal-slag interactions in heterogeneous systems, while to some extent it may be time-consuming and experience-demanding.

Design of Slag Compositions: Pseudo-Binary



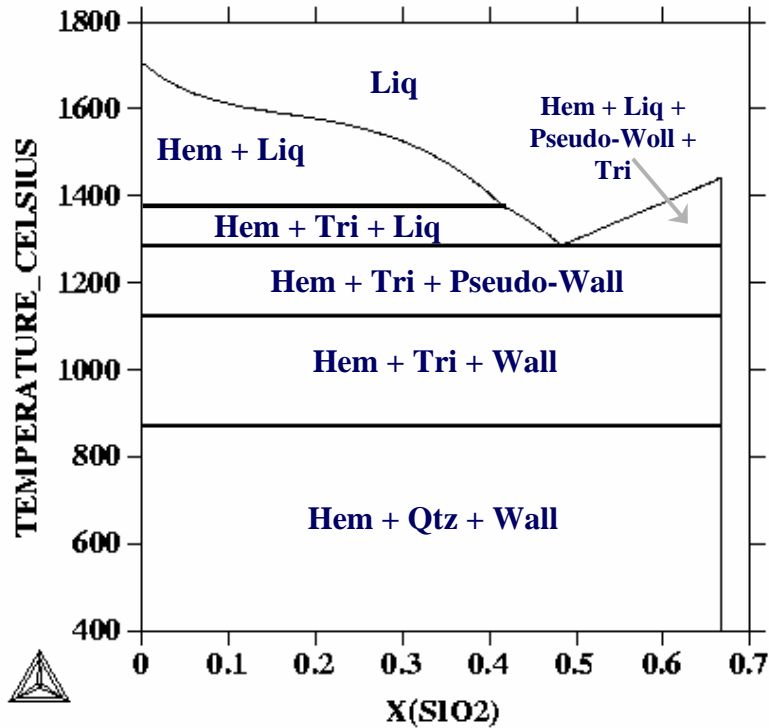
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- 2: *ALPHA_CA2SI04 RANKINITE
- 3: *LARNITE RANKINITE
- 4: *OLIVINE RANKINITE
- 5: *OLIVINE WOLLASTONITE
- 6: *WOLLASTONITE RANKINITE
- 7: *PSEUDO_WOLLASTONITE RANKINITE
- 8: *IONIC_LIQ PSEUDO_WOLLASTONITE
- 9: *PSEUDO_WOLLASTONITE IONIC_LIQ
- 10: *PSEUDO_WOLLASTONITE TRIDYMITE
- 11: *WOLLASTONITE TRIDYMITE
- 12: *QUARTZ WOLLASTONITE
- 13: *TRIDYMITE IONIC_LIQ
- 14: *CRISTOBALITE IONIC_LIQ
- 15: *IONIC_LIQ#2 CRISTOBALITE
- 16: *IONIC_LIQ#2 IONIC_LIQ
- 17: *IONIC_LIQ RANKINITE
- 18: *RANKINITE IONIC_LIQ
- 19: *ALPHA_CA2SI04 HATRURITE
- 20: *LARNITE HATRURITE
- 21: *HALITE LARNITE
- 22: *HALITE OLIVINE
- 23: *HALITE HATRURITE
- 24: *IONIC_LIQ HALITE
- 25: *HALITE IONIC_LIQ
- 26: *IONIC_LIQ HATRURITE



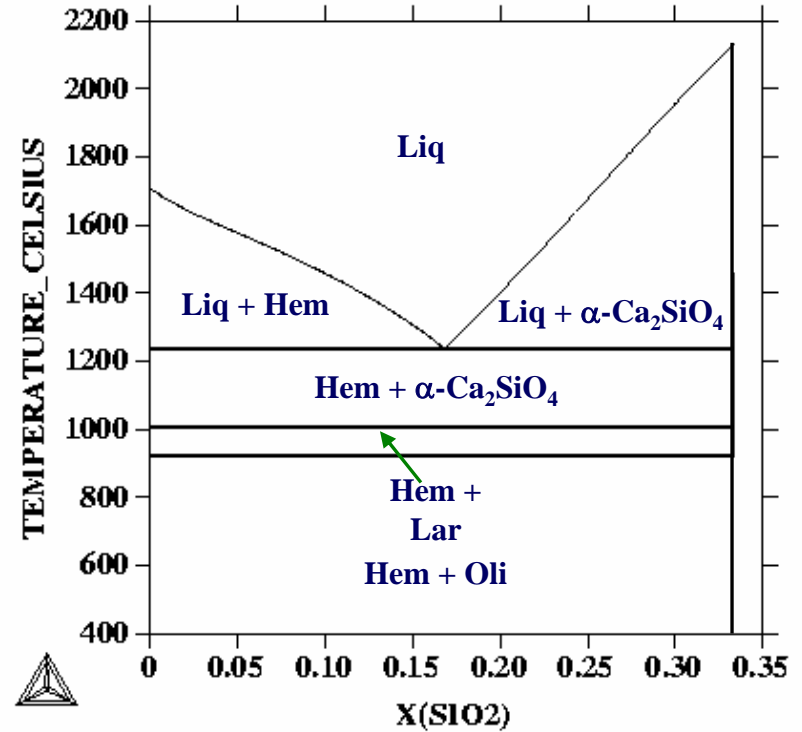
Phase diagram of the CaO-SiO₂ pseudo-binary system

Design of Slag Compositions: Pseudo-Ternary

THERMO-CALC (2002.04.25:09.45) :Pseudo-Ternary System
CaO-FeO-SiO₂ at 2*X(CaO)-X(SiO₂)=0



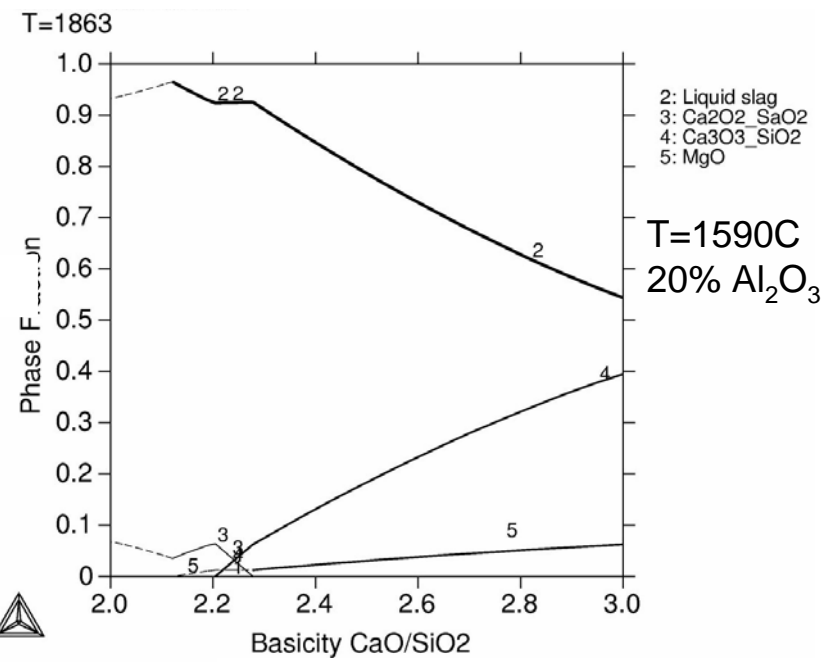
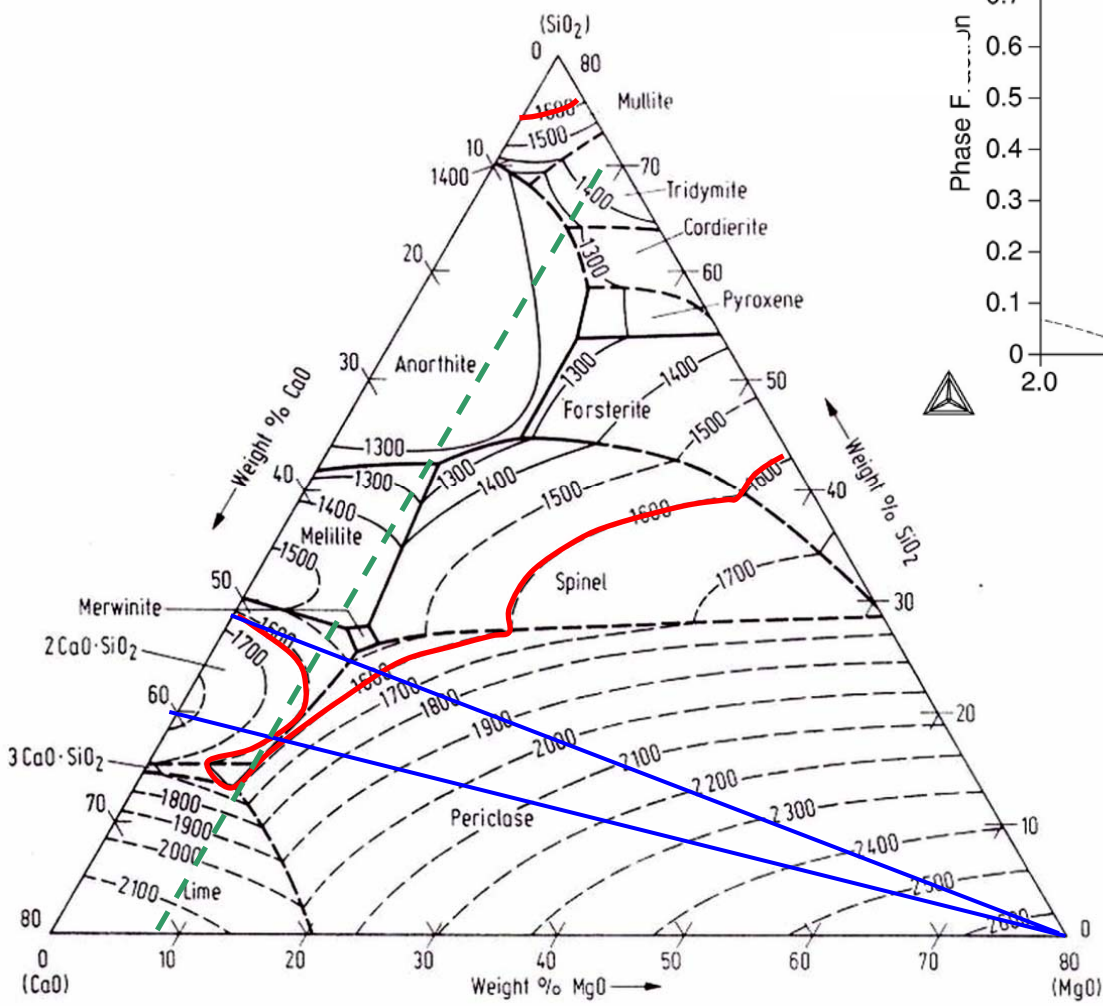
THERMO-CALC (2002.04.25:10.44) :Pseudo-Ternary System
CaO-FeO-SiO₂ at X(CaO)-2*X(SiO₂)=0



Phase diagrams of the CaO-FeO-SiO₂ pseudo-ternary system

Design of Slag Compositions: Pseudo-Quaternary

CaO-MgO-SiO₂ (at 20% Al₂O₃)

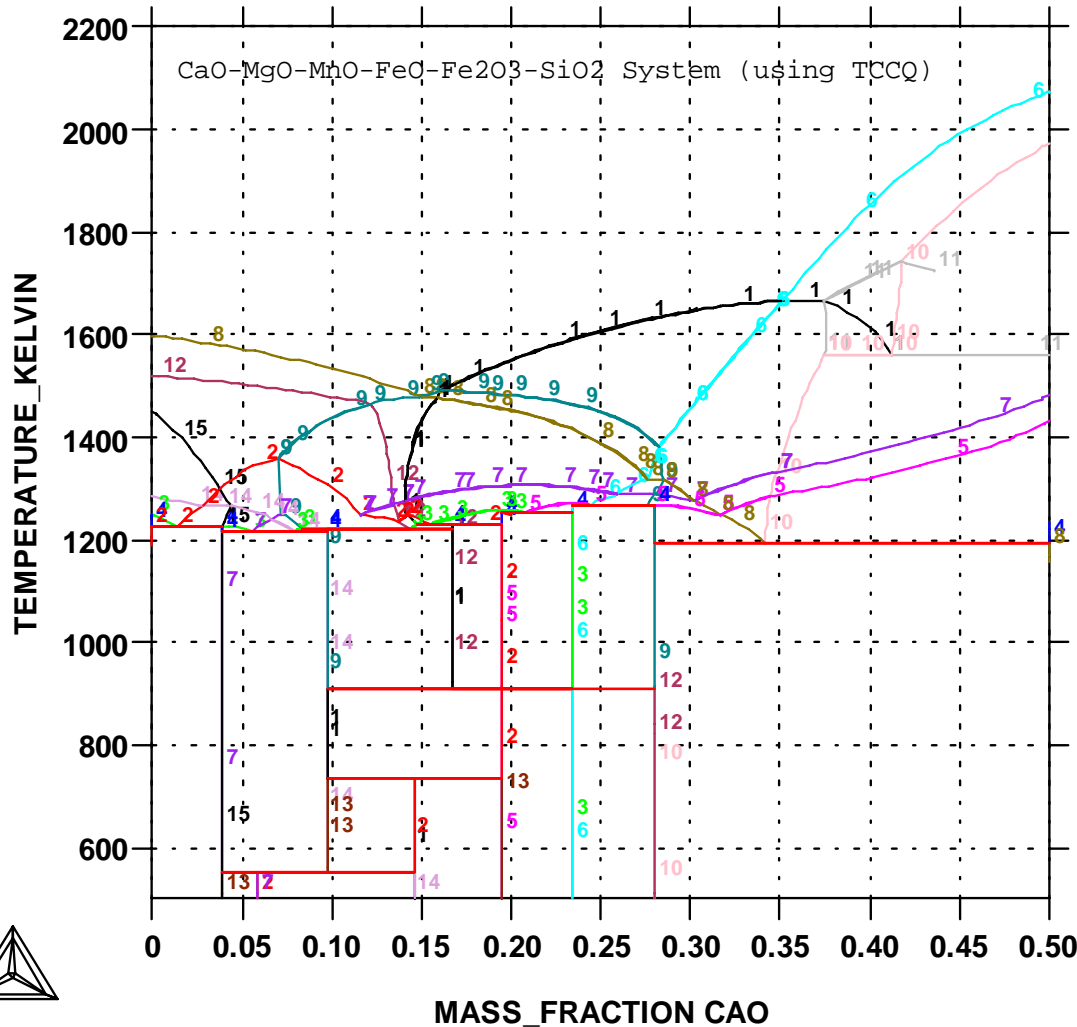


T ≈ 1600 °C
Basicity = 2-3
MgO ≈ 9
20% Al₂O₃

Design of Slag Compositions: Multi-Component

DATABASE:SLAG2

P=1E5, N=1., W(FeO)=0.15, W(SiO2)=0.2, W(MgO)=0.1, W(MnO)=5E-2;



Bulk Composition (wt%):

CaO = 0 – 0.50

MgO = 0.1

MnO = 0.05

SiO₂ = 0.2

FeO = 0.15

Fe₂O₃ = remaining

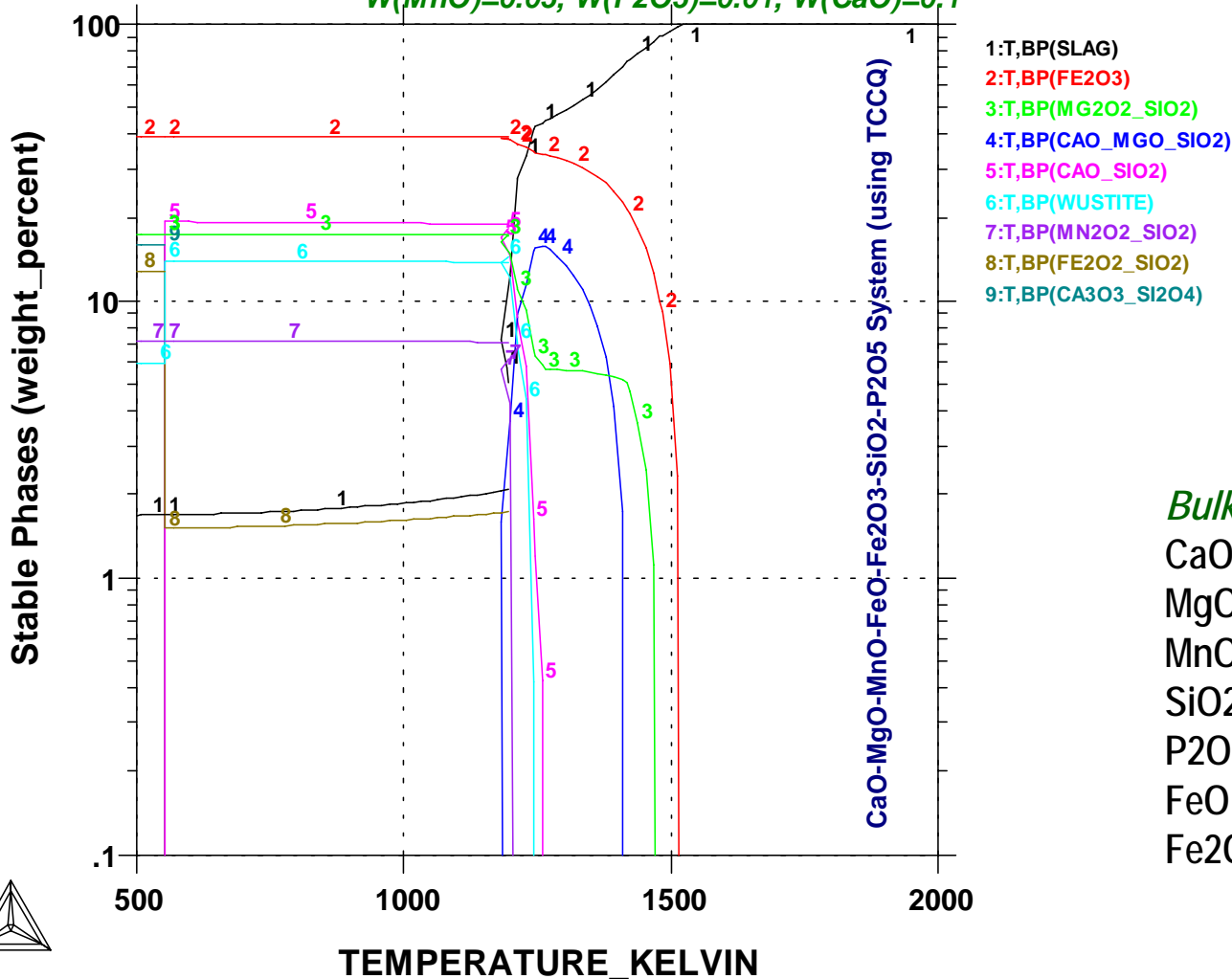


Phase diagrams of the CaO-MgO-MnO-FeO-Fe₂O₃-SiO₂ system

Design of Slag Compositions: Multi-Component

DATABASE: SLAG2

$P=100000$, $B=100$, $W(\text{FeO})=0.15$, $W(\text{SiO}_2)=0.2$, $W(\text{MgO})=0.1$,
 $W(\text{MnO})=0.05$, $W(\text{P}_2\text{O}_5)=0.01$, $W(\text{CaO})=0.1$



Bulk Composition (wt%):

CaO = 0.1

MgO = 0.1

MnO = 0.05

SiO₂ = 0.2

P₂O₅ = 0.01

FeO = 0.15

Fe₂O₃ = remaining

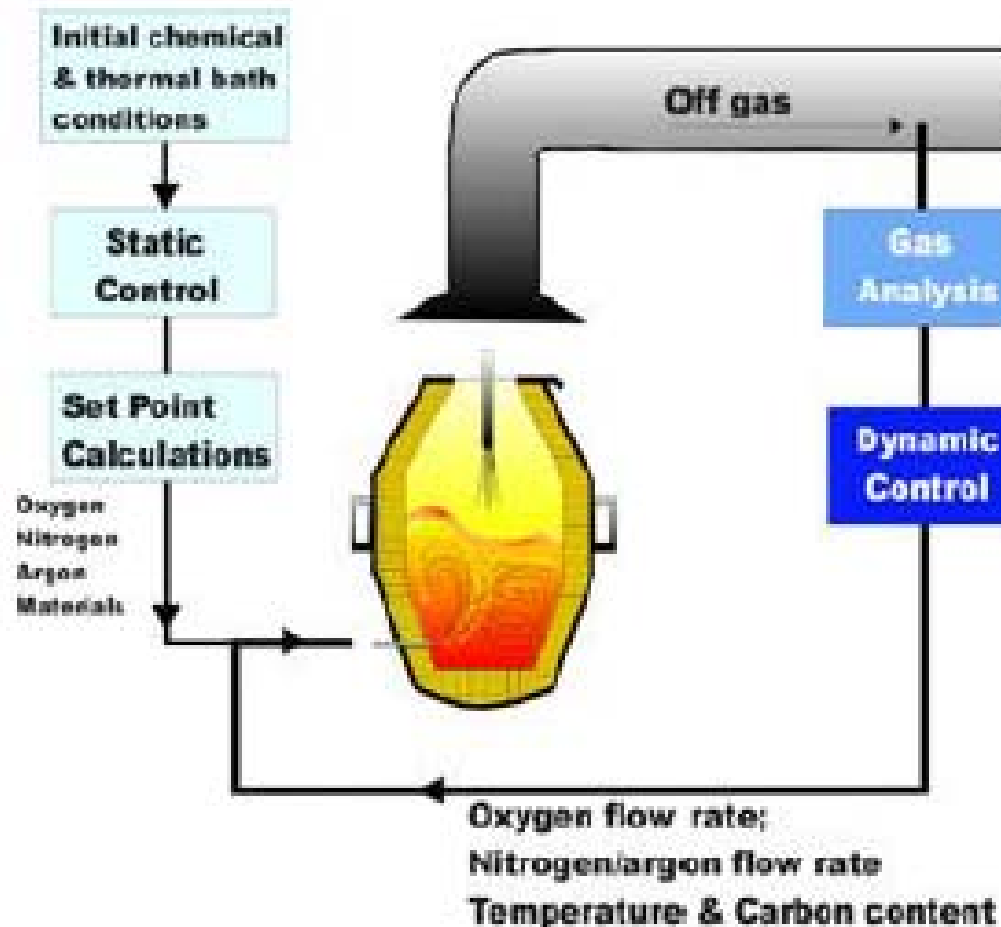


Property diagrams of the CaO-MgO-MnO-FeO-Fe₂O₃-SiO₂-P₂O₅ system

Successful Application (Example)

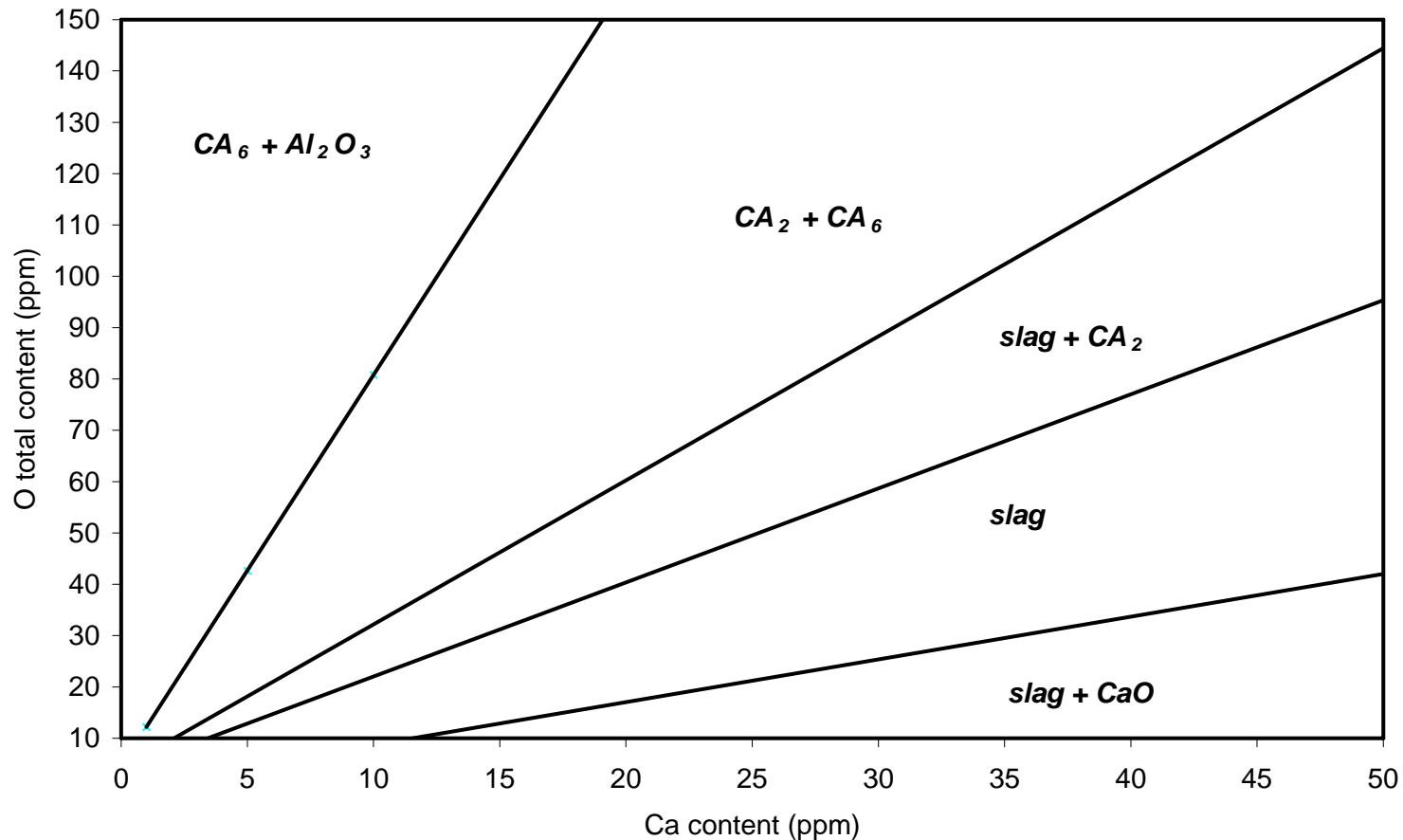
Liquid Slag Formation & Solid Inclusions in Refractory Converter

AOD Converter at TK AST



Liquid Slag Formation & Solid Inclusions

Inclusion modification by Ca treatment: Case 1

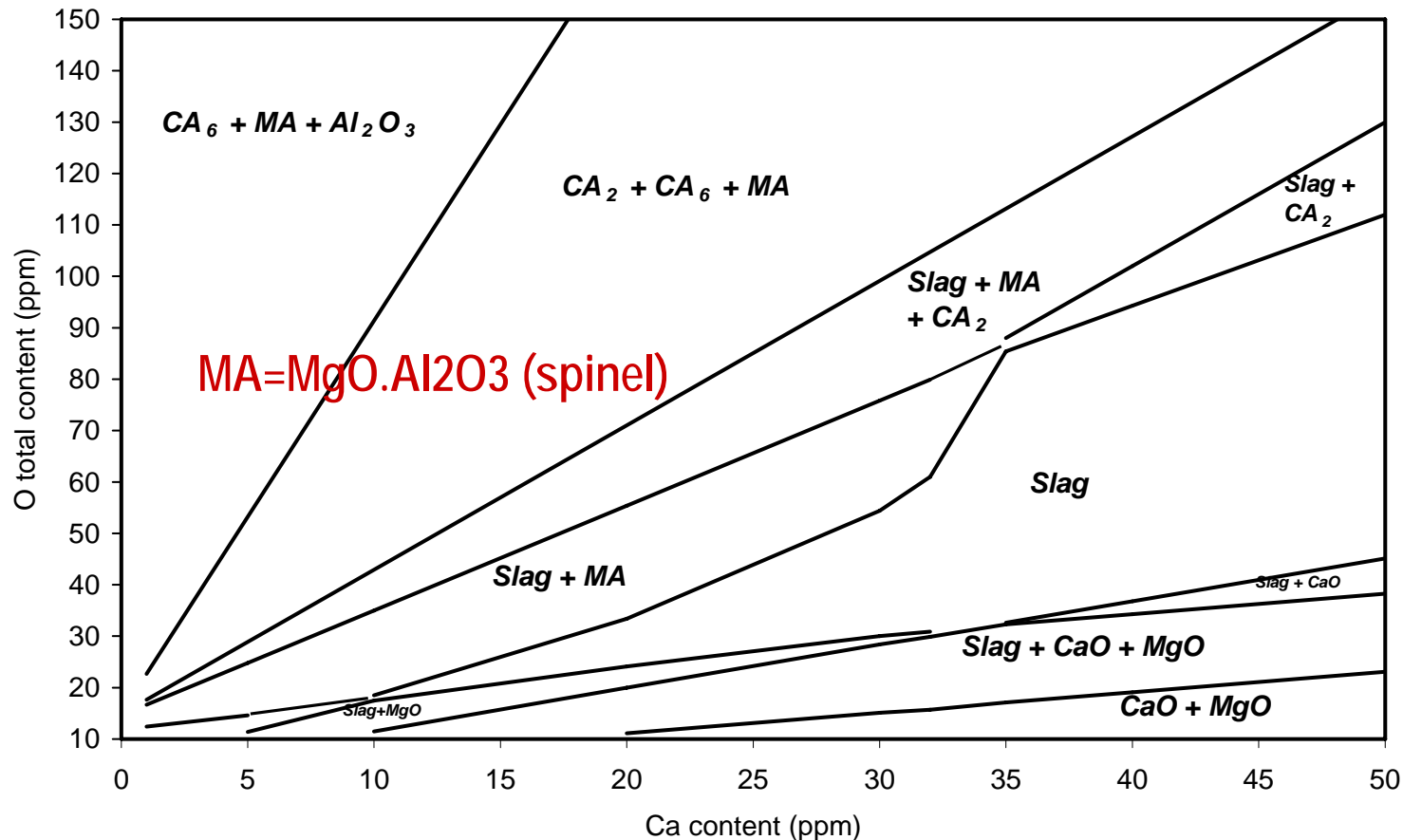


Phases present in inclusions in equilibrium with steel as a function of Ca & O content.

*Steel composition: Al = 400 ppm, Si = 100 ppm and Mn = 2500 ppm;
T = 1600°C*

Liquid Slag Formation & Solid Inclusions

Inclusion modification by Ca treatment: Case 2



Phases present in inclusions in equilibrium with steel as a function of Ca & O content.

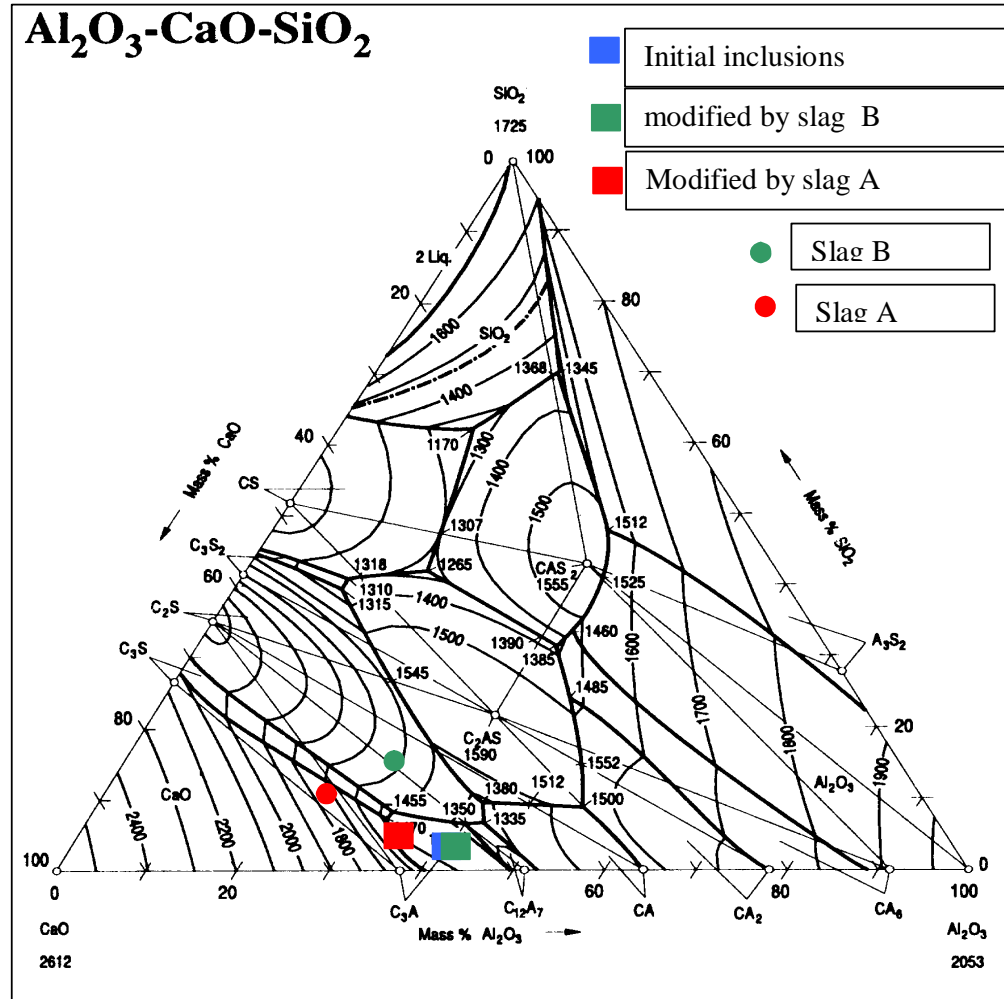
Steel composition: Al = 400 ppm, Si = 100 ppm, Mn = 2500 ppm and Mg = 4 ppm;
 $T = 1600^\circ C$

Liquid Slag Formation & Solid Inclusions

Slag emulsification

Composition of original inclusions and inclusions modified by two slags at different compositions

species	composition of original inclusions (mass %)	composition of inclusions after interaction with slag A (mass %)	composition of inclusions after interaction with slag B (mass %)
SiO ₂	2,15	2,13	2,84
Al ₂ O ₃	42,41	43,17	36,13
CaO	55,29	54,55	60,94
MnO	0,02	0,05	0,03
Cr ₂ O ₃	0,05	0,05	0,03
FeO	0,05	0,05	0,03



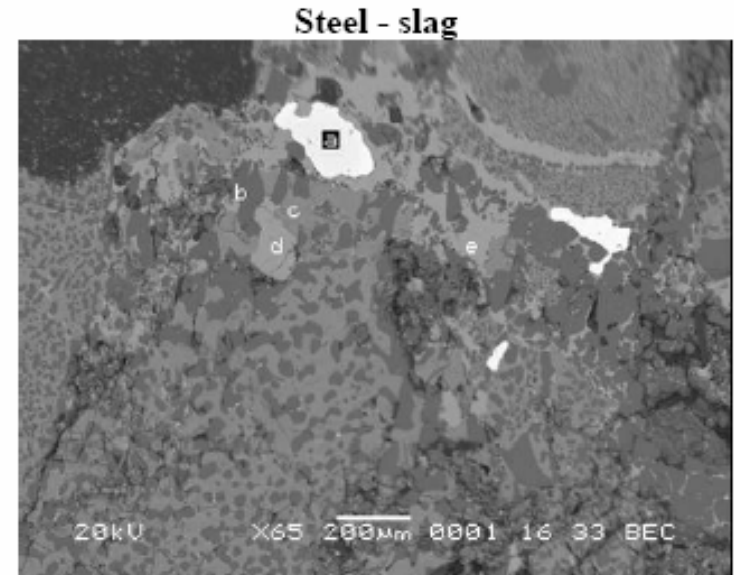
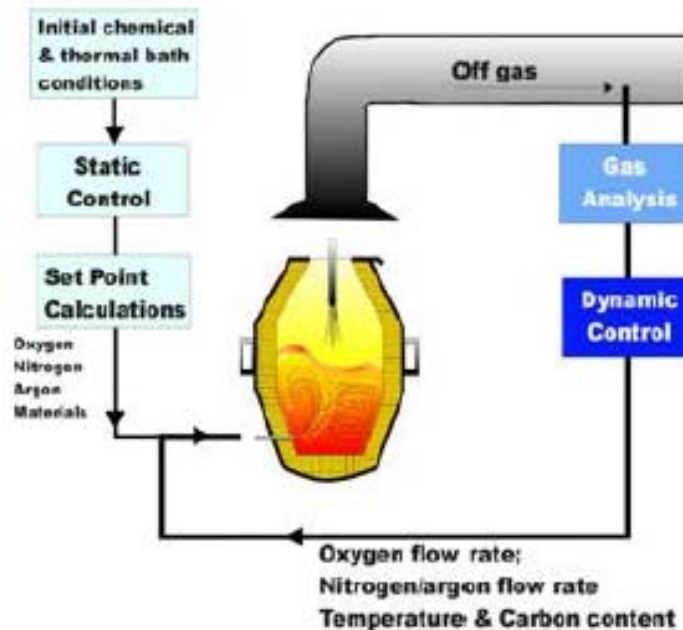
Modification of inclusions due to interactions with two slag phases at different compositions.

Slag A: CaO 55% SiO₂ 15% Al₂O₃ 30%

Slag B: CaO 65% SiO₂ 10% Al₂O₃ 25%

Liquid Slag Formation & Solid Inclusions in Refractory Converter

AOD Converter at TK AST



Refractory
a: Steel, b: MgO, c: CaO, d and e: C3S

Tuyeres area: texture of reaction zone

Experiments
+ Calculations

Improved AOD Process Control System:

1. the system steel-slag-refractory is close to equilibrium after the reduction phase, but not during the oxidation;
2. the interaction of the refractory with the steel-slag system produces three main new phases: $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$ and $2\cdot\text{CaO}\cdot\text{Fe}_2\text{O}_3$;
3. the use of the model has allowed to identify the operating changes leading to an increase of the average refractory campaign at TK AST AOD n. 2 from 85 to 98 heats.

Liquid Slag Formation & Solid Inclusions in Refractory Converter

AOD Converter at TK AST

The SEM analysis of the used bricks has shown the presence of 2 different wear situations in the different areas of the refractory (tuyeres and slag line). This result has been confirmed by the calculations at the equilibrium, both qualitatively and in terms of compositions of the compounds found (see tab. VI and VII).

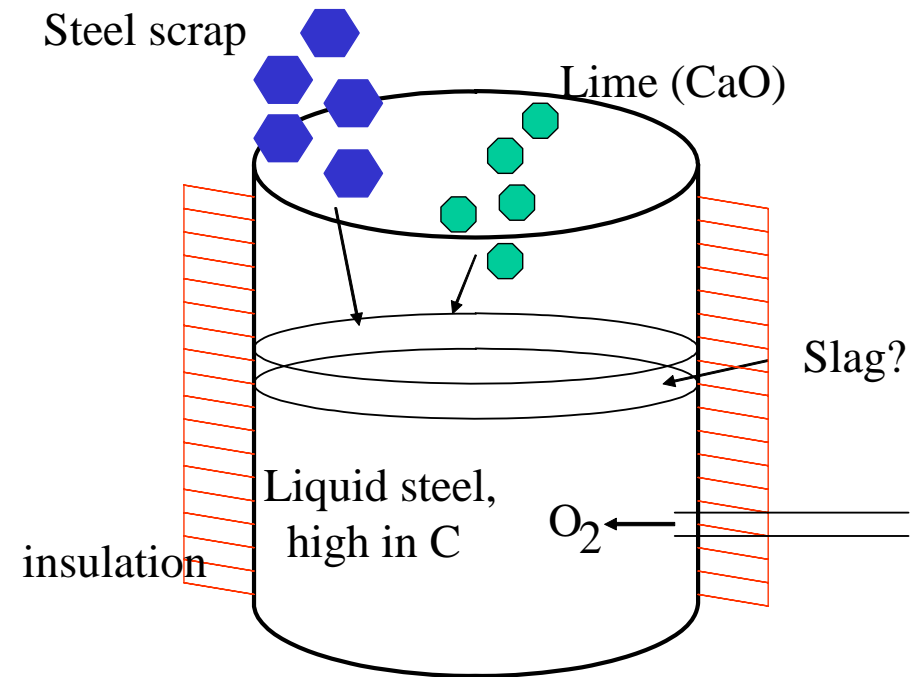
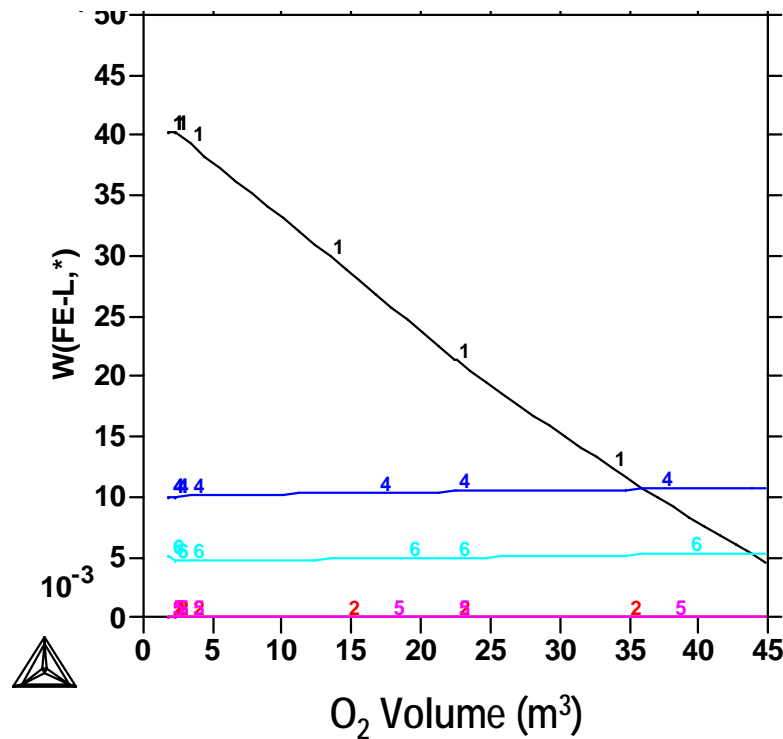
n.	Phase	Source	% CaO	% MgO	% SiO ₂	% Cr ₂ O ₃	% FeO
1	Reduction	SEM analysis	71	2	26	-	-
2	Reduction	SEM analysis	64	2	32	1	-
3	Reduction	Model	73	-	26	-	-
4	Oxidation	Model	53	22	0	13	9

Table VI - New phase composition generated after reduction at the equilibrium in the tuyeres brick

n.	Phase	Source	% CaO	% MgO	% SiO ₂	% Cr ₂ O ₃	% FeO
5	Oxidation	SEM analysis	47	2	1	2	47
6	Oxidation	Model	38	8	1	14	38
7	Reduction	SEM analysis	64	1	32	-	-
8	Reduction	Model	55	10	24	7	3
9	Reduction	SEM analysis	70	2	28	-	-
10	Reduction	Model	73	-	26	-	-

Table VII – New phase composition generated after reduction at the equilibrium in the slag line

Steel Refining



- ✓ Liquid steel with 4%C, 1%Mn, 0.6%Si (wt%).
- ✓ Oxygen and lime added.
- ✓ Assume no heat loss to environment. Starting $T=1673$ K.
- ✓ Scrap will also be added during the oxygen blowing.

Oxygen Solubility/Activity in Liquid Steel

Formation of liquid slag and solid inclusions
under certain temperature conditions (and partial CO₂ pressures)

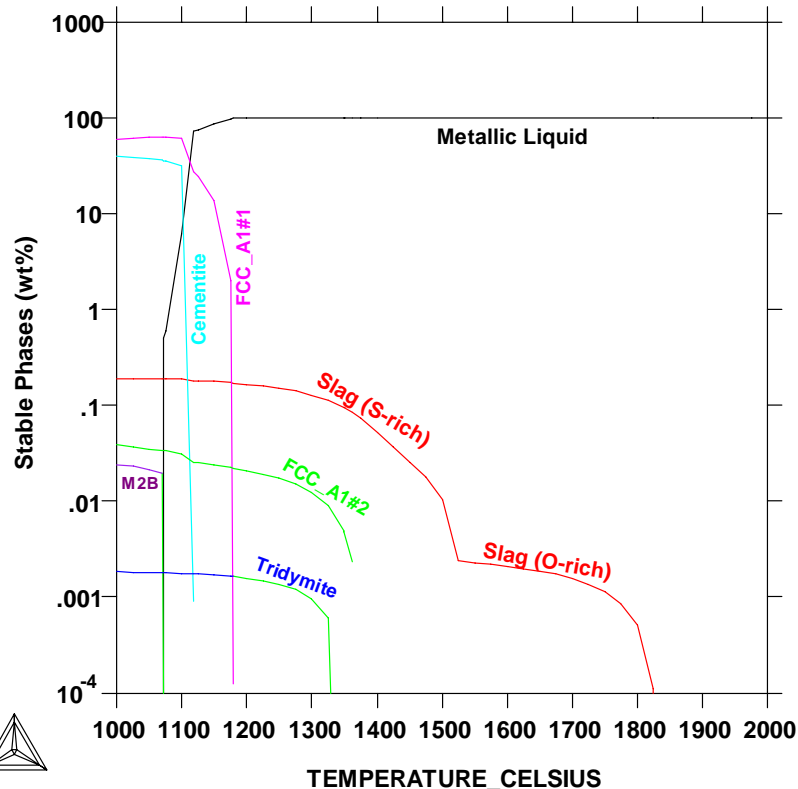
Bulk Composition (wt%)

Fe	C	Si	Mn	Cr	Al	Cu	Mo	Ni	Co	Nb
<i>remaining</i>	3.45	1.91	0.66	0.29	0.3	0.635	0.167	0.034	0.012	0.0126
	Ti	Mg	V	P	B	N	S	O		
	0.0158	<0.002	0.055	0.036	0.024	0.01	0.09	0.03		

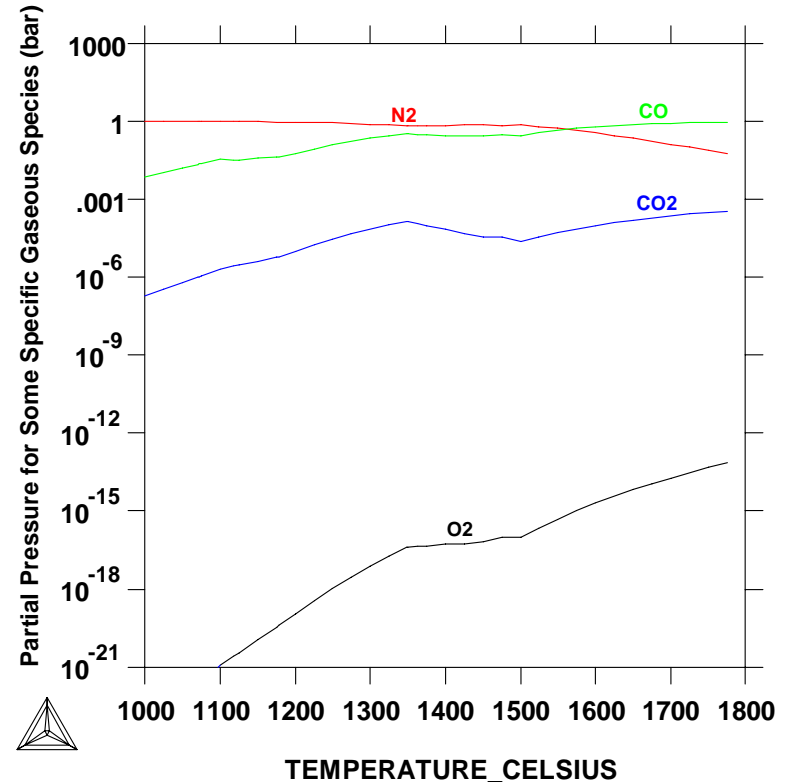
Oxygen Solubility/Activity in Liquid Steel

Formation of liquid slag and solid inclusions

THERMO-CALC (2006.03.10:12.12) :
Databases: TCFE3 + SLAG2



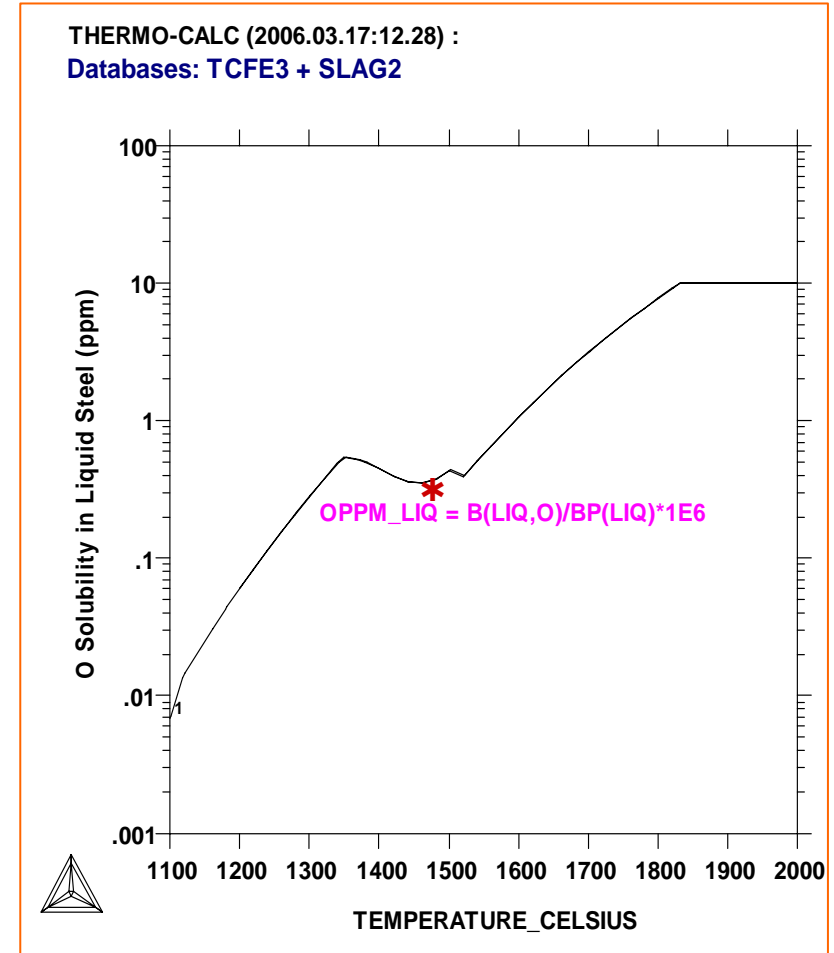
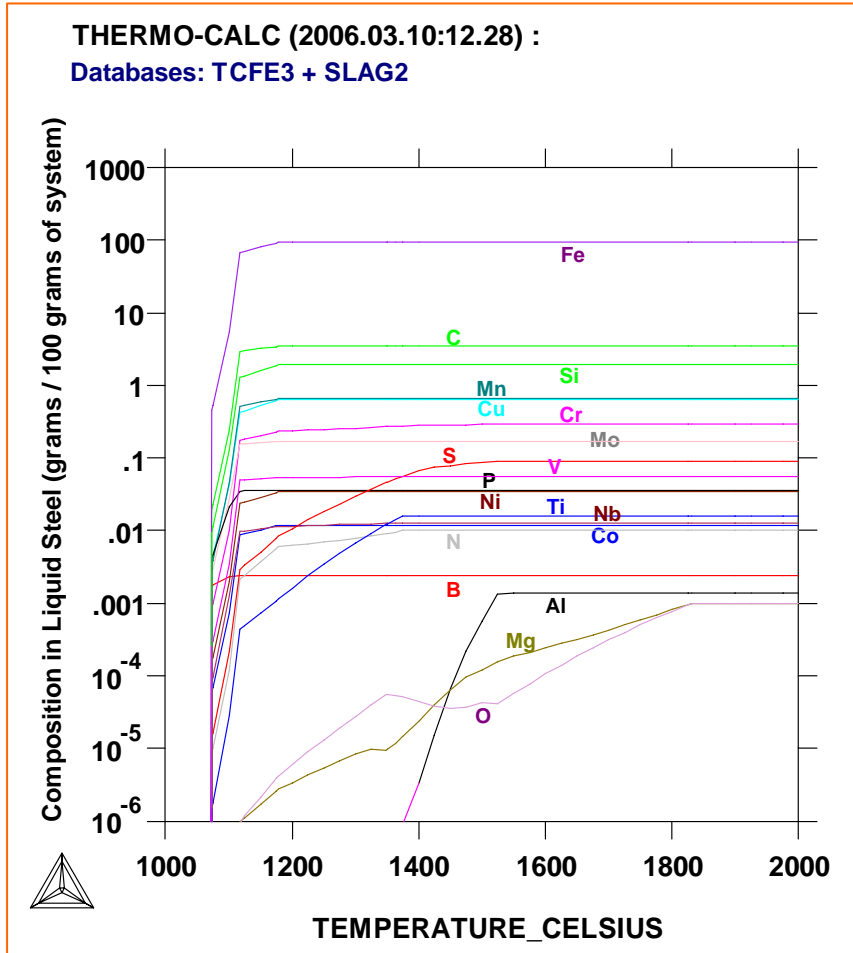
THERMO-CALC (2006.03.17:12.56) :
Databases: TCFE3 + SLAG2



Stable phase assemblages and partial pressures of some saturated gaseous species in the system over the temperature range from 1000 to 2000°C.

Oxygen Solubility/Activity in Liquid Steel

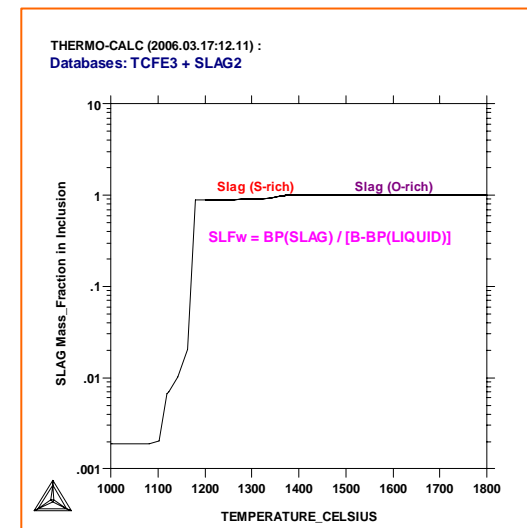
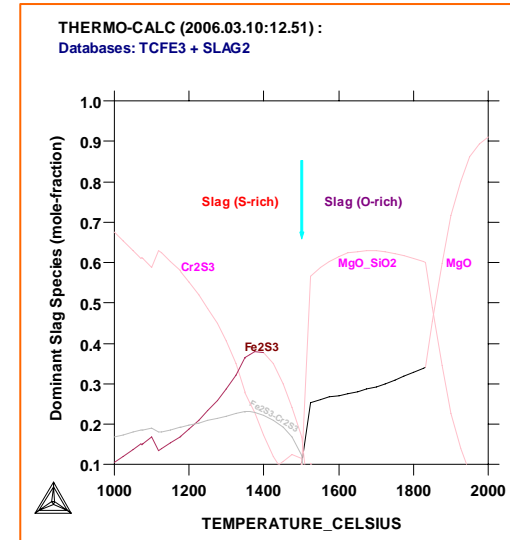
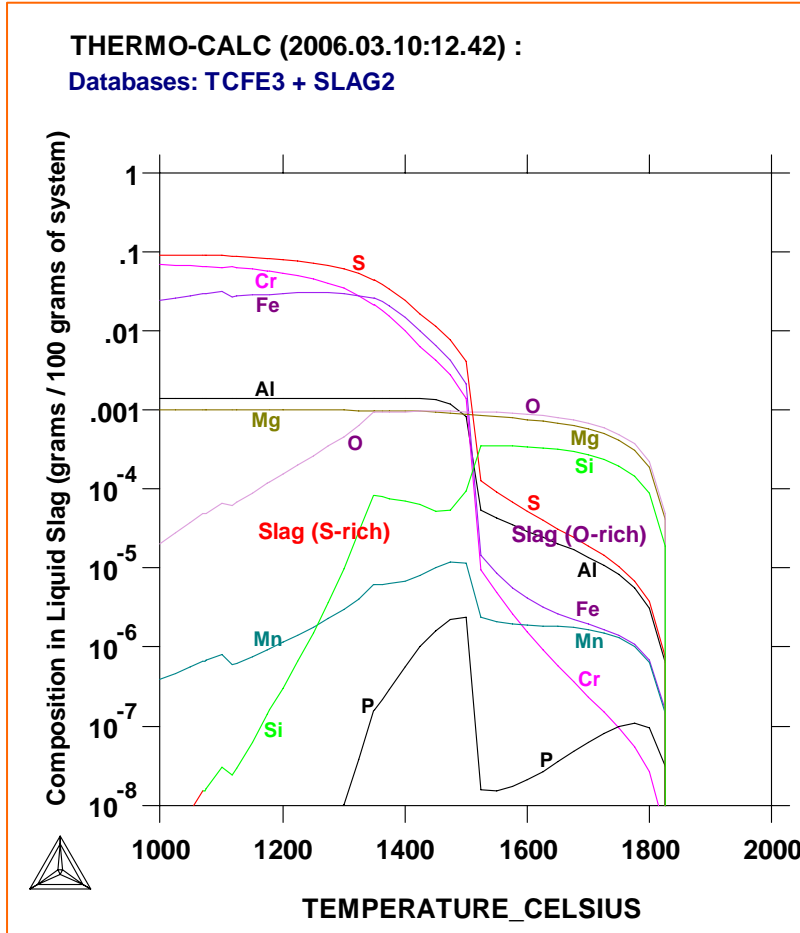
Formation of liquid slag and solid inclusions



Equilibrated composition of the metallic liquid phase, and variation of oxygen solubility in liquid steel, over its stable temperature range.

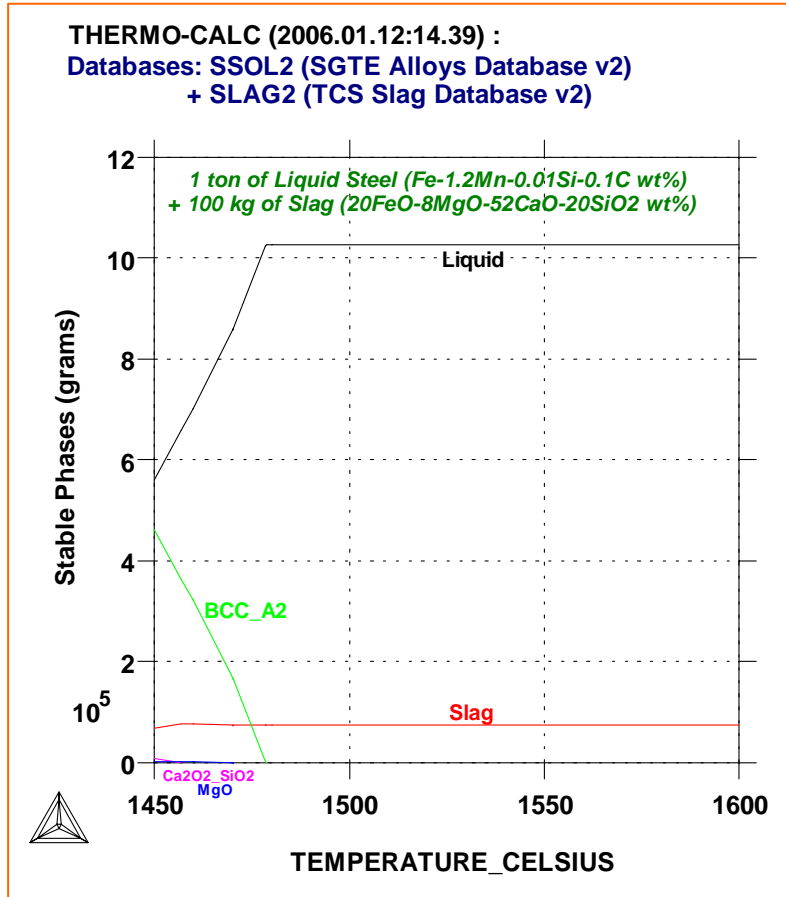
Oxygen Solubility/Activity in Liquid Steel

Formation of liquid slag and solid inclusions

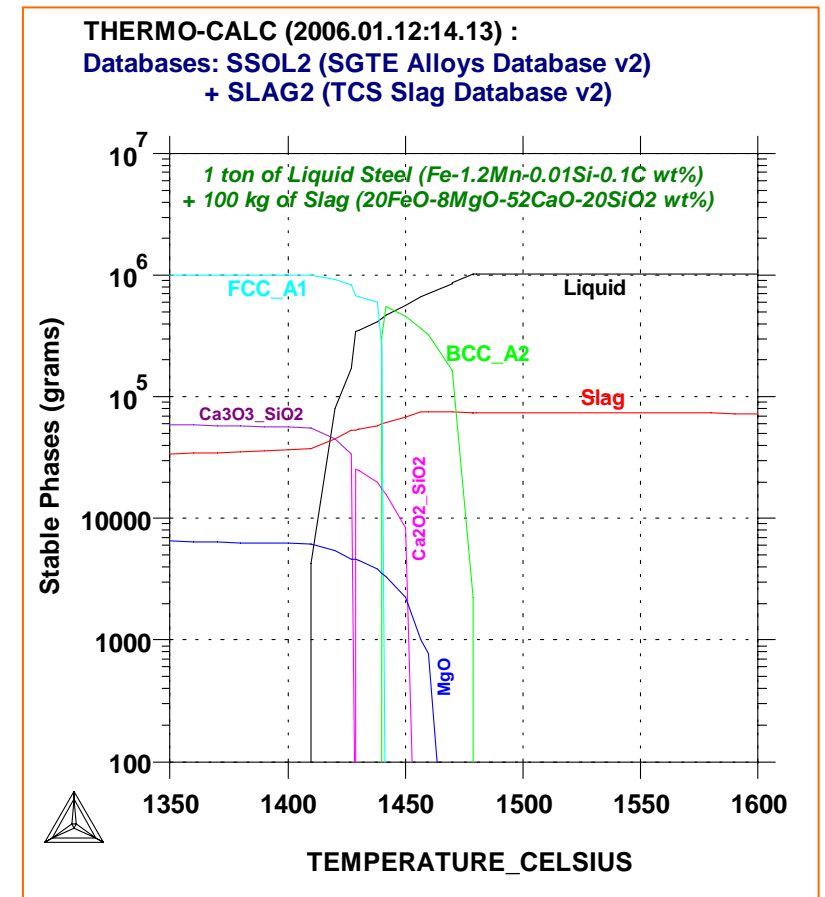


Equilibrated composition of the liquid slag phase, over its stable temperature range.

Interaction between Liquid Steel and Slag



Equilibrated phase assemblages in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO2 wt%) over the temperature range from 1600 to 1450°C.

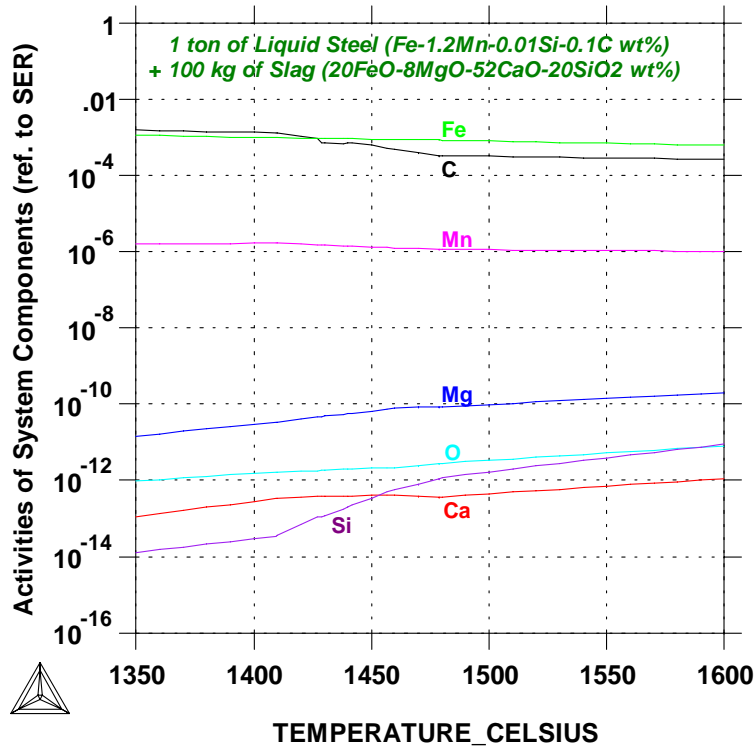


Equilibrated phase assemblages in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO2 wt%) over the temperature range from 1600 to 1350°C.

Interaction between Liquid Steel and Slag

THERMO-CALC (2006.01.12:14.23) :

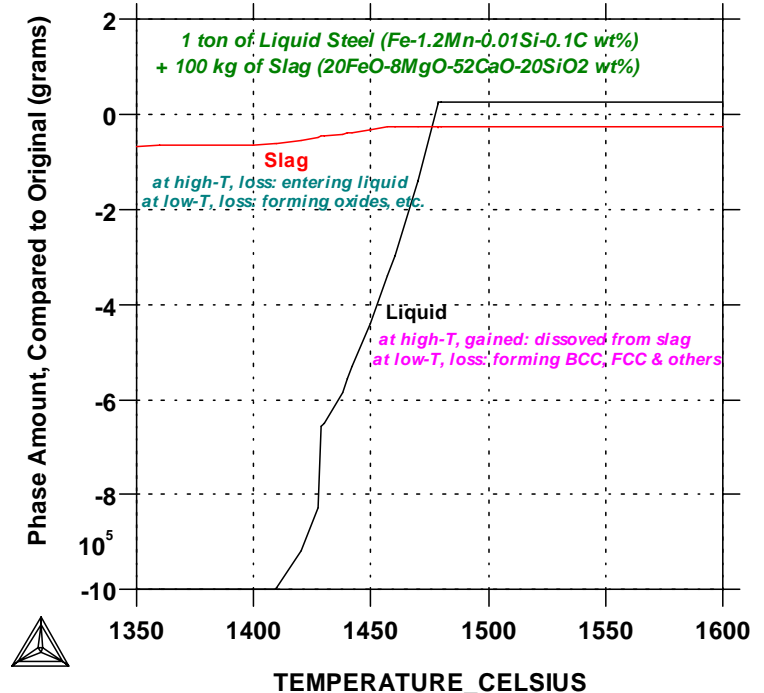
Databases: SSOL2 (SGTE Alloys Database v2)
+ SLAG2 (TCS Slag Database v2)



Activities of components in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO₂ wt%) over the temperature range from 1600 to 1350°C.

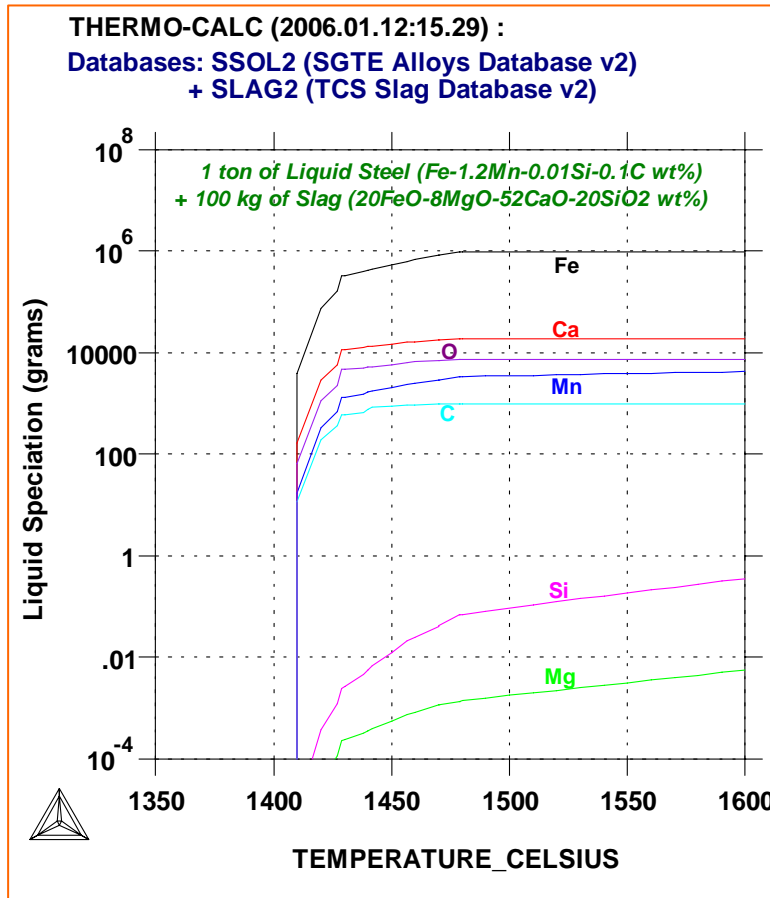
THERMO-CALC (2006.01.12:15.09) :

Databases: SSOL2 (SGTE Alloys Database v2)
+ SLAG2 (TCS Slag Database v2)

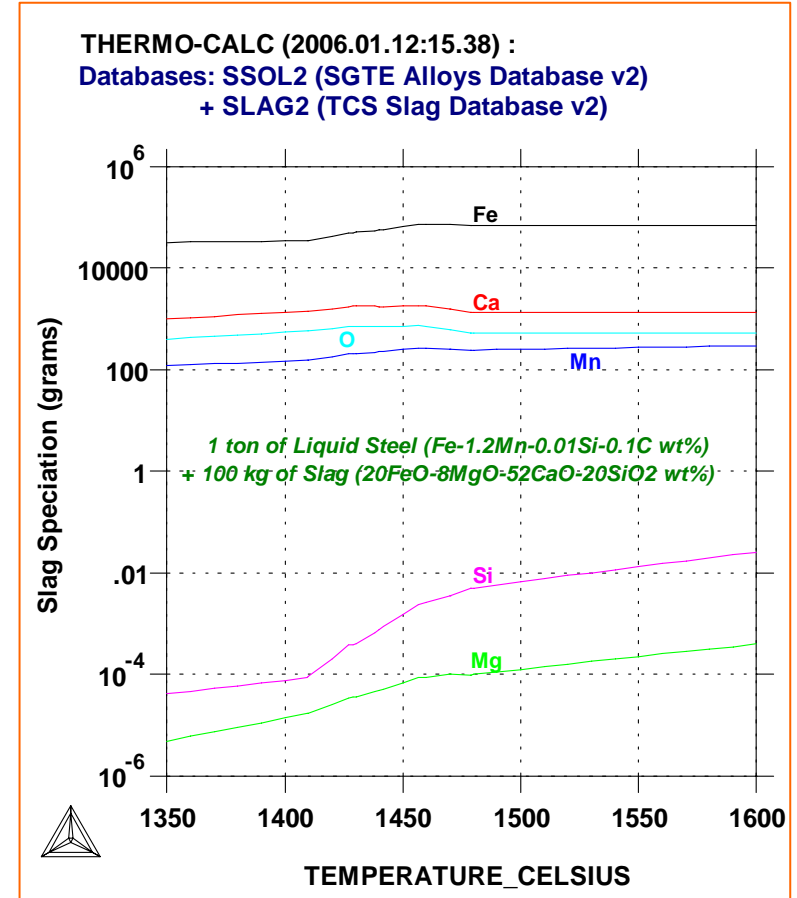


Equilibrated amounts of the liquid steel and slag phases in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO₂ wt%) over the temperature range from 1600 to 1350°C. Note: Various components moves among the two phases in different directions (at high temperatures). Other phases form at low temperature range.

Interaction between Liquid Steel and Slag



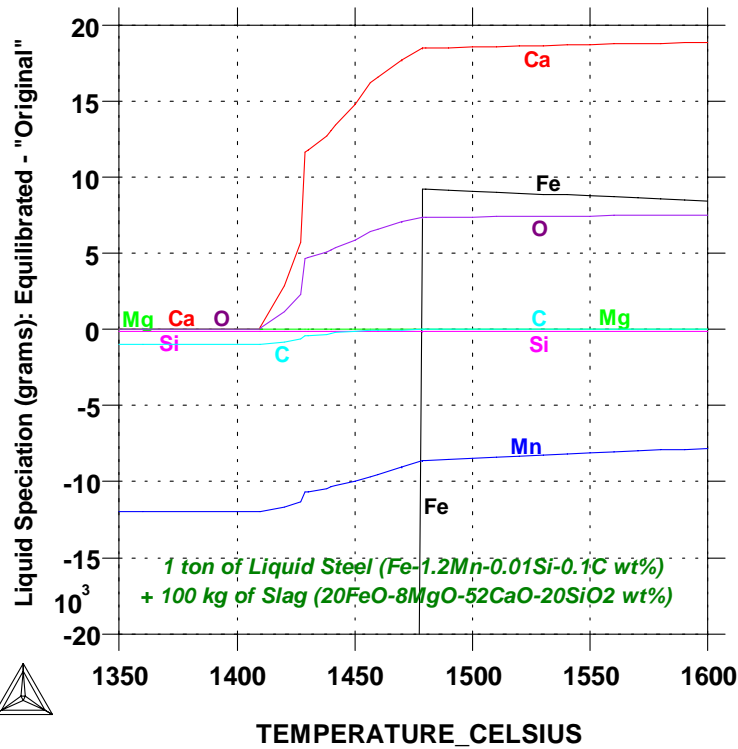
Composition (mass of components) of the equilibrated Liquid phase in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO₂ wt%) over the temperature range from 1600 to 1350°C.



Composition (mass of components) of the equilibrated Slag phase in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO₂ wt%) over the temperature range from 1600 to 1350°C.

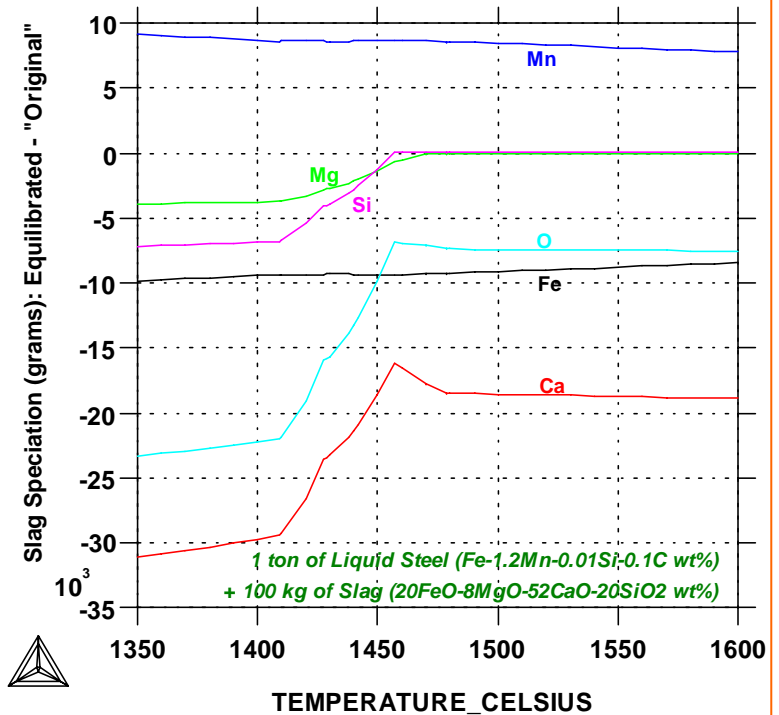
Interaction between Liquid Steel and Slag

THERMO-CALC (2006.01.12:16.05) :
 Databases: SSOL2 (SGTE Alloys Database v2)
 + SLAG2 (TCS Slag Database v2)



Variation of speciation (mass of components) of the equilibrated Liquid phase, compared with the “original” one, in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO₂ wt%) over the temperature range from 1600 to 1350°C.

THERMO-CALC (2006.01.12:16.21) :
 Databases: SSOL2 (SGTE Alloys Database v2)
 + SLAG2 (TCS Slag Database v2)



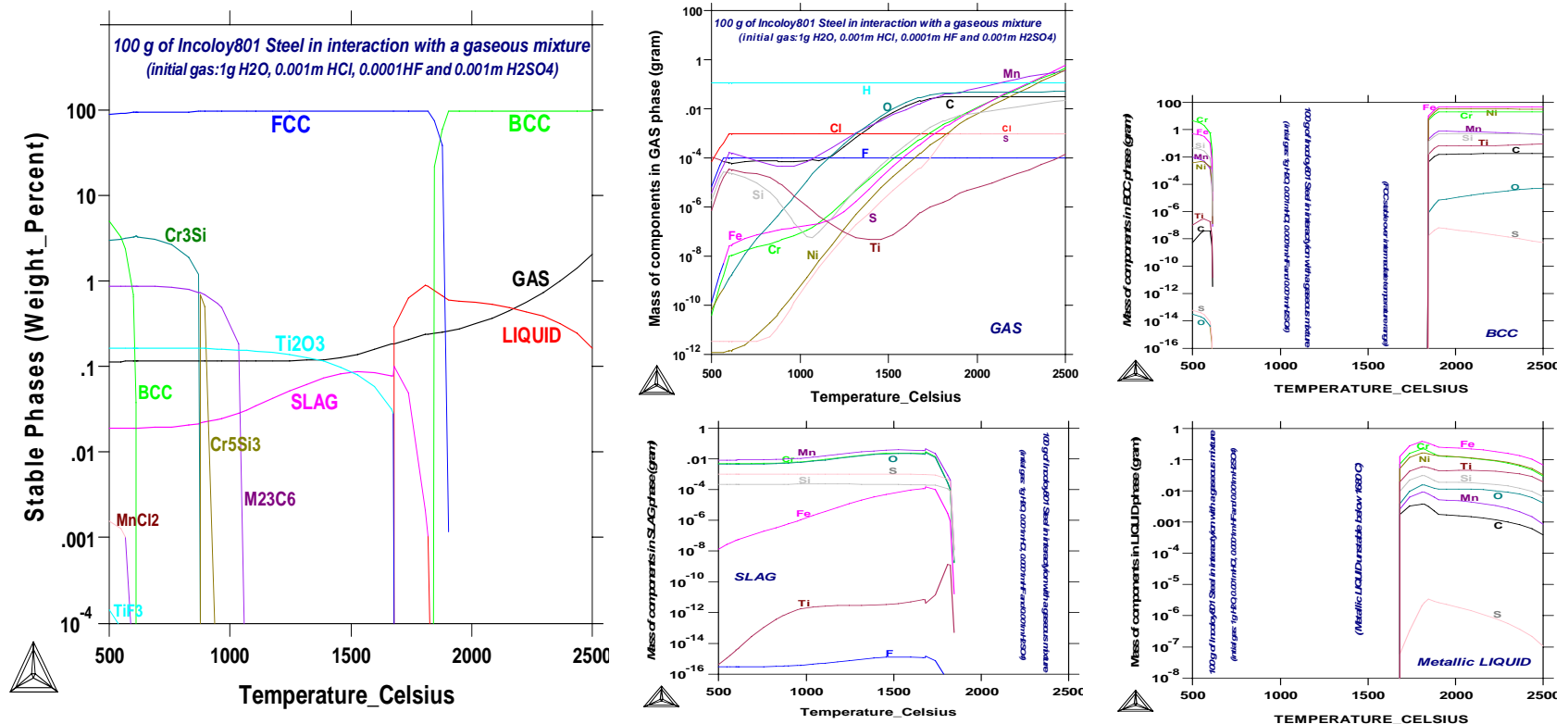
Variation of speciation (mass of components) of the equilibrated Slag phase, compared with the “original” one, in the interaction between 1 ton of liquid steel (Fe-1.2Mn-0.01Si-0.1C wt%) and 100 kg of slag (20FeO-8MgO-52CaO-20SiO₂ wt%) over the temperature range from 1600 to 1350°C.

- Metal-Slag-Gas Interactions
- **Metal-Gas Interactions (Redox Reactions, Coatings, CVD, ...)**
- Combustion/Sintering/Incineration/Remelting/Recycling
& Environmental Issues
- Dew Points
- Ellingham Diagrams
- *and more ...*

High-T Gaseous Corrosion

Example: High-Temperature Gaseous Corrosion of Alloys

Using the TCMP2 or SSUB3 database (and/or in a combination with other alloy databases), one can calculate various types of phase diagrams and property diagrams for heterogeneous interaction systems/processes involving gaseous mixtures.



Calculated property diagrams of the heterogeneous interaction between 100 g of Incoloy 801 steel (wrought Fe-based superalloy with a composition of Fe44.5-Ni32-Cr20.5-Ti1.1-Mn0.8-Si0.5-C0.05 wt%) and a gas mixture (of 1 g H₂O, 0.001 m HCl, 0.0001 m HF and 0.001 m H₂SO₄). The calculation shows that the gas mixture will dissolve the steel components (especially with increasing temperatures), meanwhile LIQUID phase or SLAG+Ti₂O₃ phases may form during the interaction over certain temperature ranges.

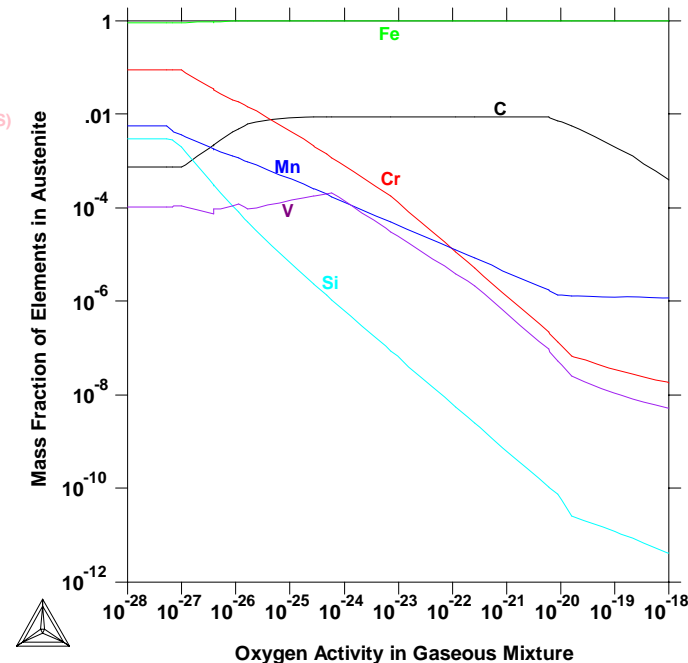
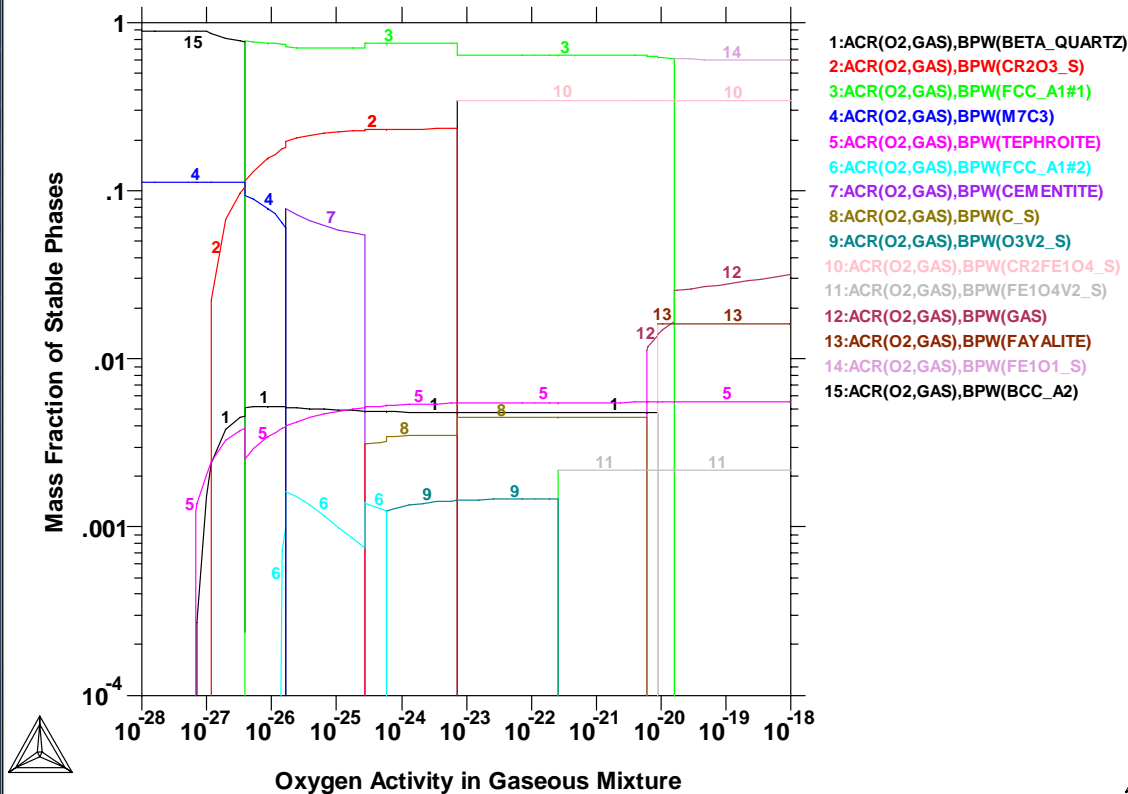
Surface Redox Reactions (I)

Example: Formation of Oxide Layer on Steel Surface: Protection against corrosion

THERMO-CALC (2008.05.22:17.49) : Formation of Oxide Layer on Steel Surface

DATABASE: TCFe6

$P=100000$, $T=1073$, $B=100$, $B(\text{Cr})=16.$, $B(\text{V})=1\text{E}-1$, $B(\text{C})=1.$, $B(\text{Mn})=3\text{E}-1$, $B(\text{Si})=3\text{E}-1$



Stable phases and element distribution of remaining austenite during the surface oxidation of the Fe-16Cr-0.3Mn-0.3Si-0.01V-1C (wt%) steel at 800°C, as a function of oxygen activity in the atmosphere.

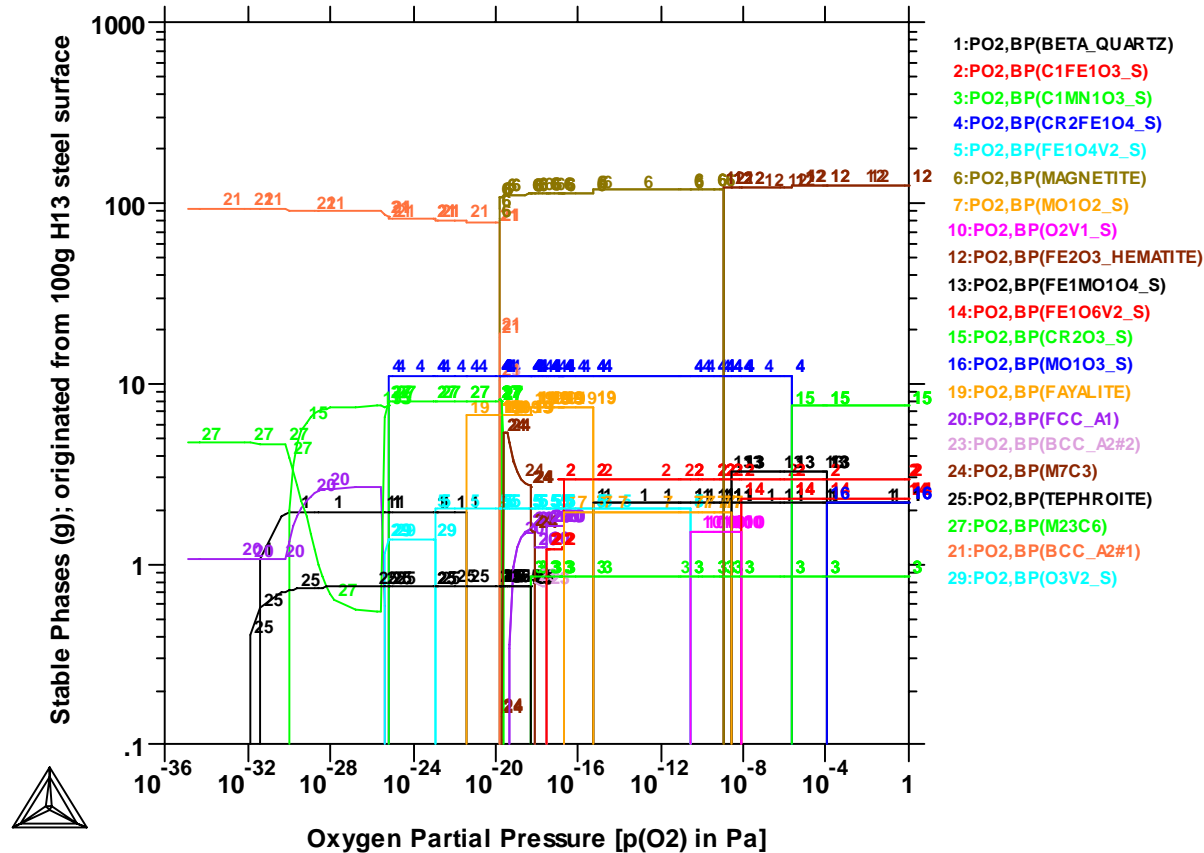
Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

THERMO-CALC (2008.02.29:16.47) :

DATABASE:SSOL4

P=1E5, T=873.15, B(Fe)=90.63, B(Cr)=5.14, B(Mn)=0.41, B(Si)=1.02, B(C)=0.4,
B(V)=0.93, B(Mo)=1.46, B(S)=1E-3, B(P)=9E-3;



Stable phases during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], varied with the oxygen partial pressure. The calculation is made for an interaction system at temperature of 600°C and a total pressure of 1 bar.

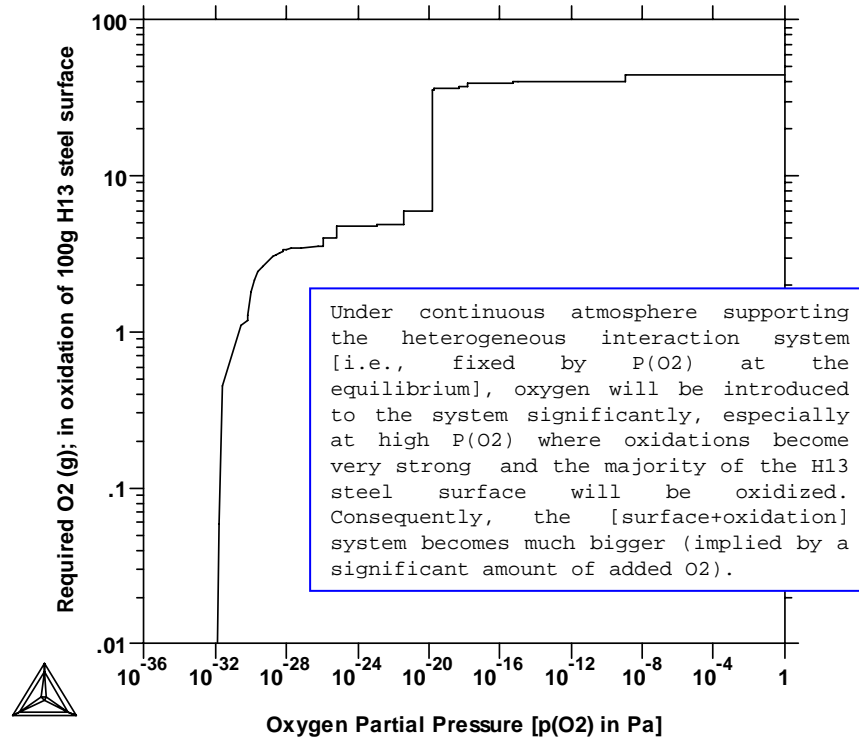
Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

THERMO-CALC (2008.02.29:16.16) :

DATABASE:SSOL4

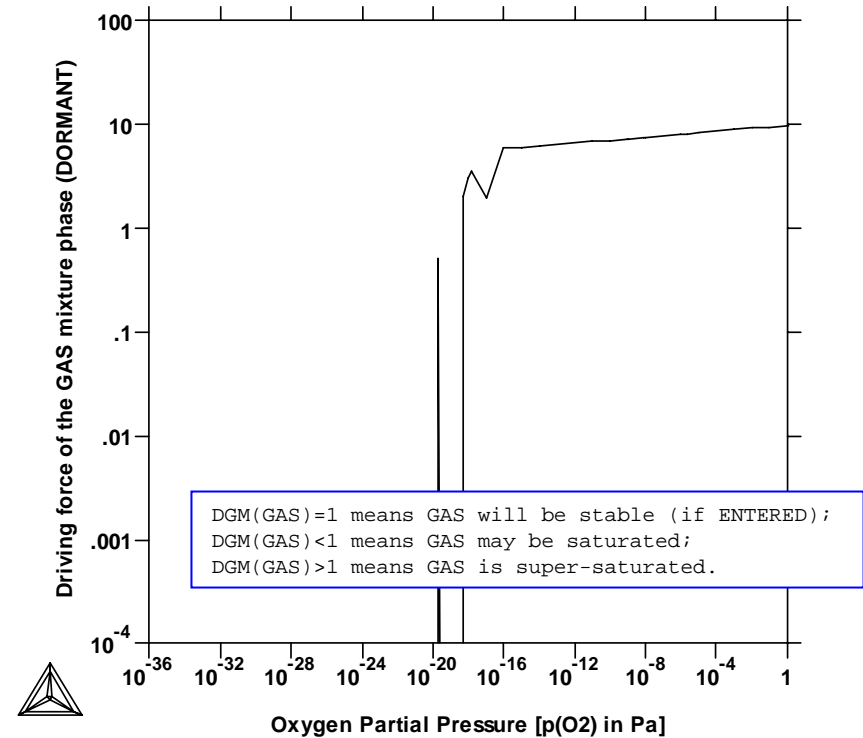
P=1E5, T=873.15, B(FE)=92.3, B(CR)=5, B(MN)=0.3, B(SI)=1, B(C)=0.4, B(V)=1;



THERMO-CALC (2008.02.29:16.16) :

DATABASE:SSOL4

P=1E5, T=873.15, B(FE)=92.3, B(CR)=5, B(MN)=0.3, B(SI)=1, B(C)=0.4, B(V)=1;



Required O₂ Input and Driving force of the dormant GAS phase during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], varied with the oxygen partial pressure. The calculation is made for an interaction system at temperature of 600°C and a total pressure of 1 bar.

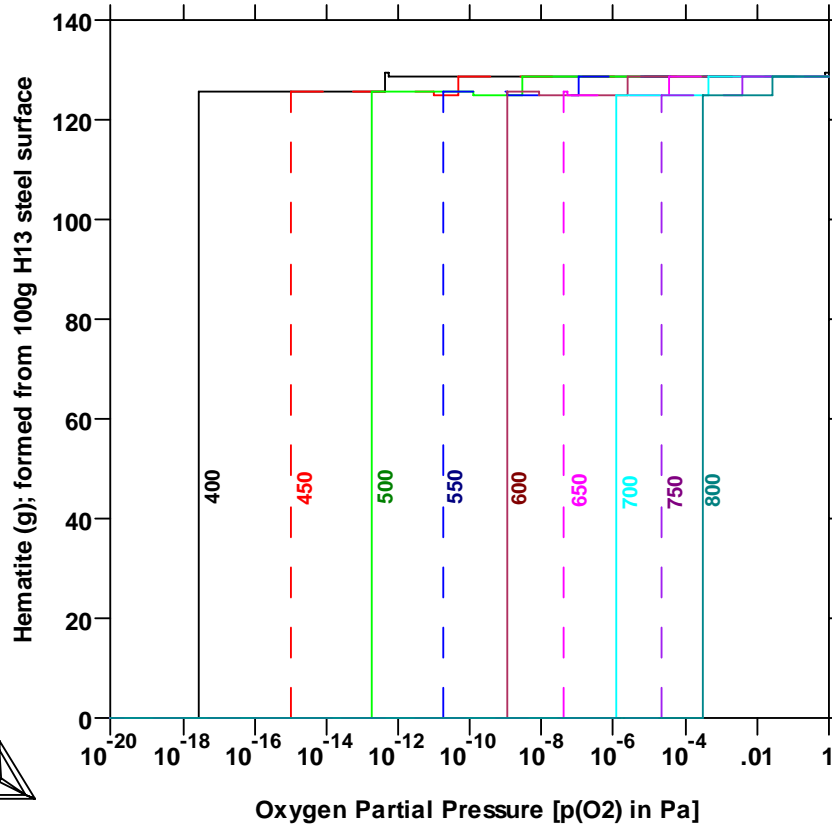
Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

THERMO-CALC (2008.05.22:09.32) :

Databases: SSOL4+SSUB4

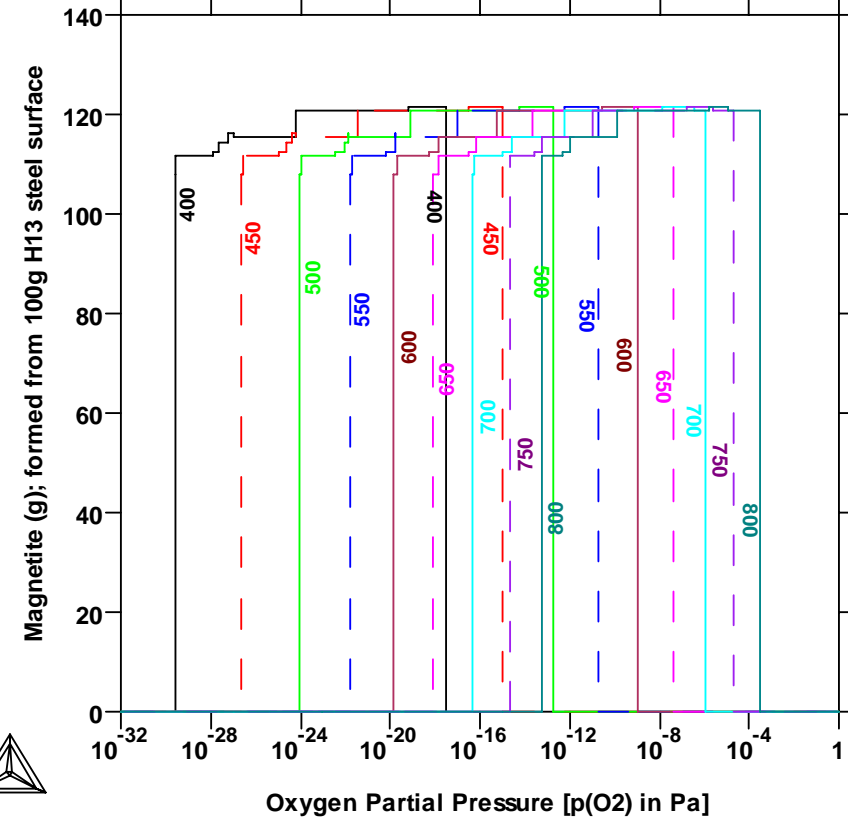
H13 Hot Work Steels: Phase Emergence with respect to Hematite



THERMO-CALC (2008.05.22:14.41) :

Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to Magnetite Phase



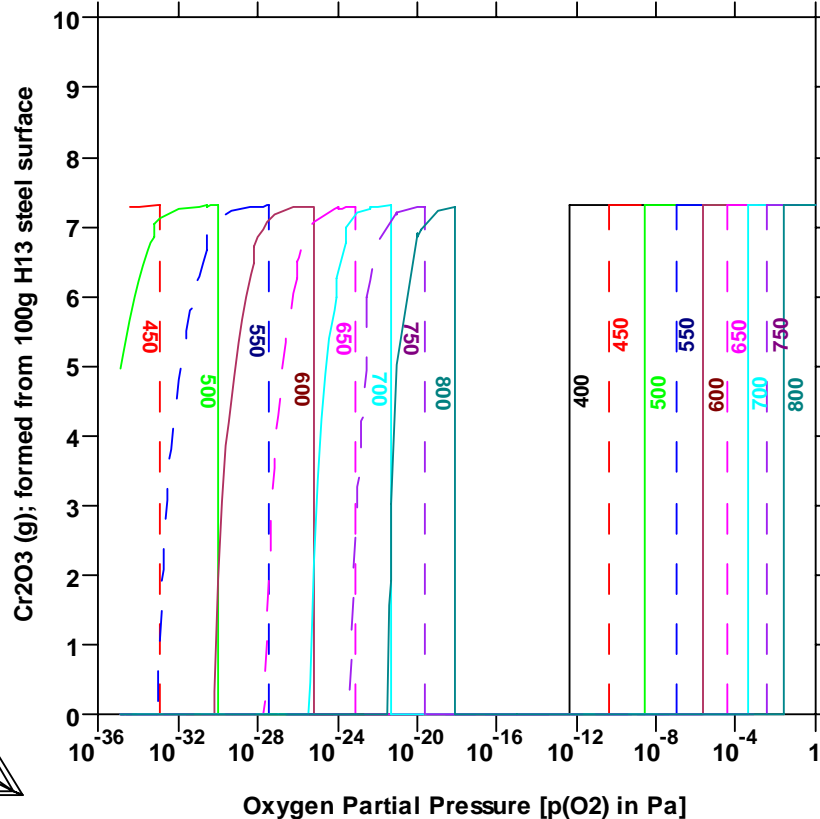
Emergence Conditions with respect to and Fe₂O₃ (Hematite) and Fe₃O₄ (Magnetite) during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], at 9 different temperatures (between 400 and 800°C, with an interval of 50°C) and 1 bar.

Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

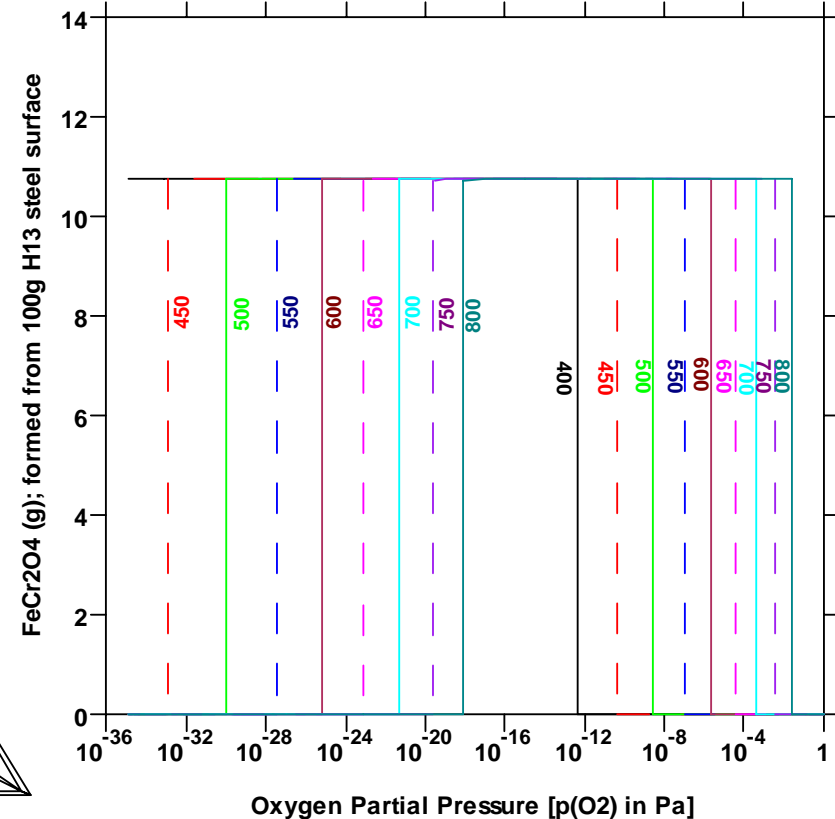
THERMO-CALC (2008.05.22:10.52) :
Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to Cr₂O₃ Phase



THERMO-CALC (2008.05.22:11.07) :
Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to FeCr₂O₄ Phase



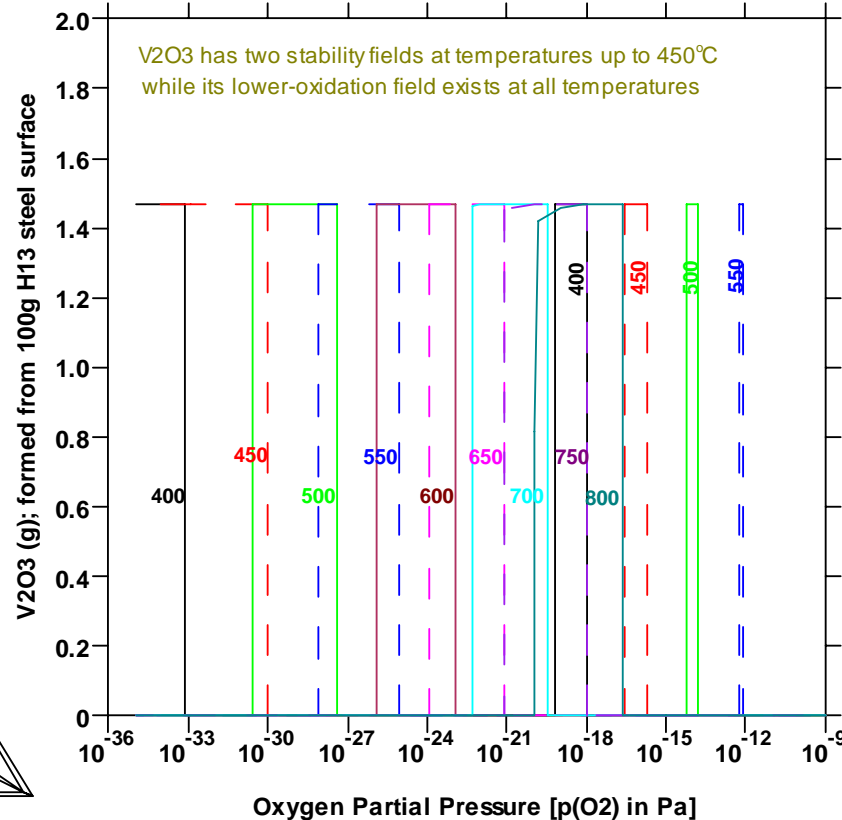
Emergence Conditions with respect to Cr₂O₃ and FeCr₂O₄ during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], at 9 different temperatures (between 400 and 800°C, with an interval of 50°C) and 1 bar.

Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

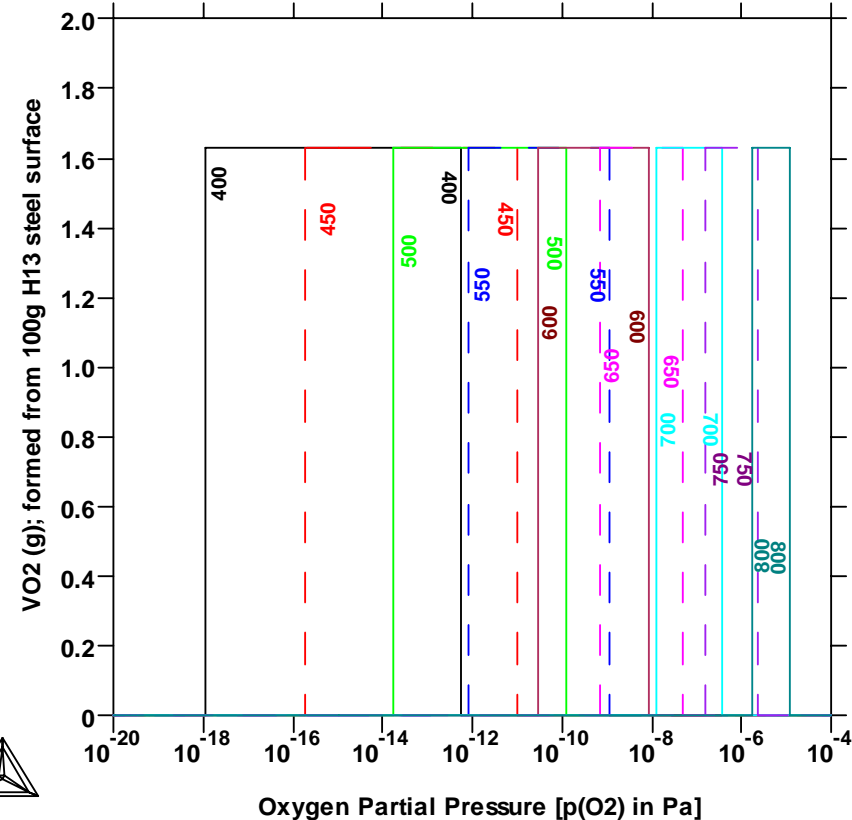
THERMO-CALC (2008.05.22:11.50) :
 Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to V₂O₃ Phase



THERMO-CALC (2008.05.22:14.15) :
 Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to VO₂ Phase



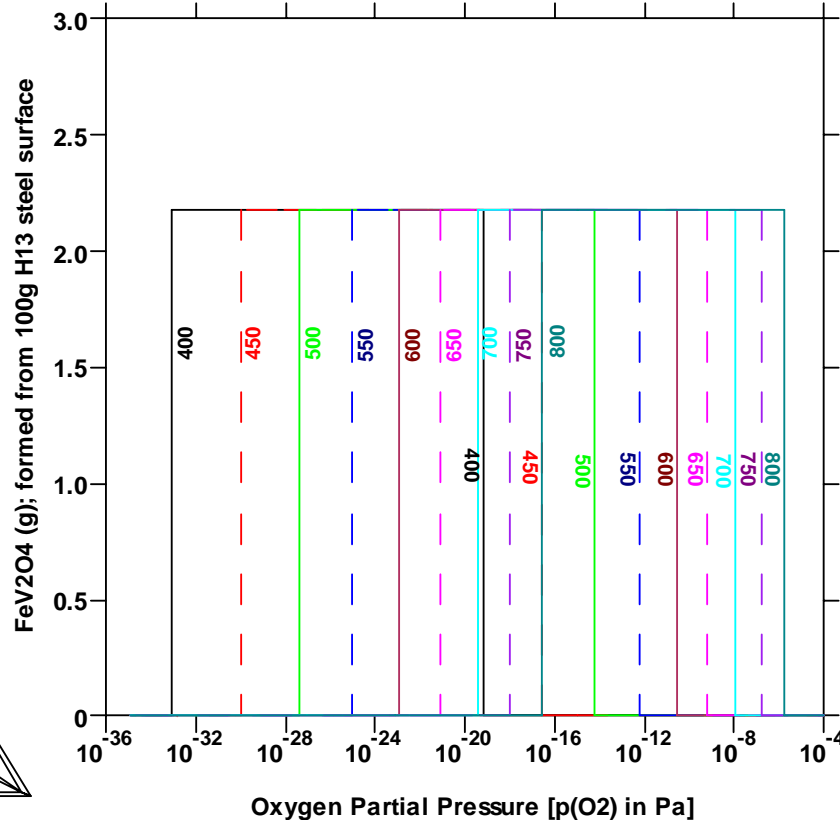
Emergence Conditions with respect to V₂O₃ and VO₂ during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], at 9 different temperatures (between 400 and 800°C, with an interval of 50°C) and 1 bar.

Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

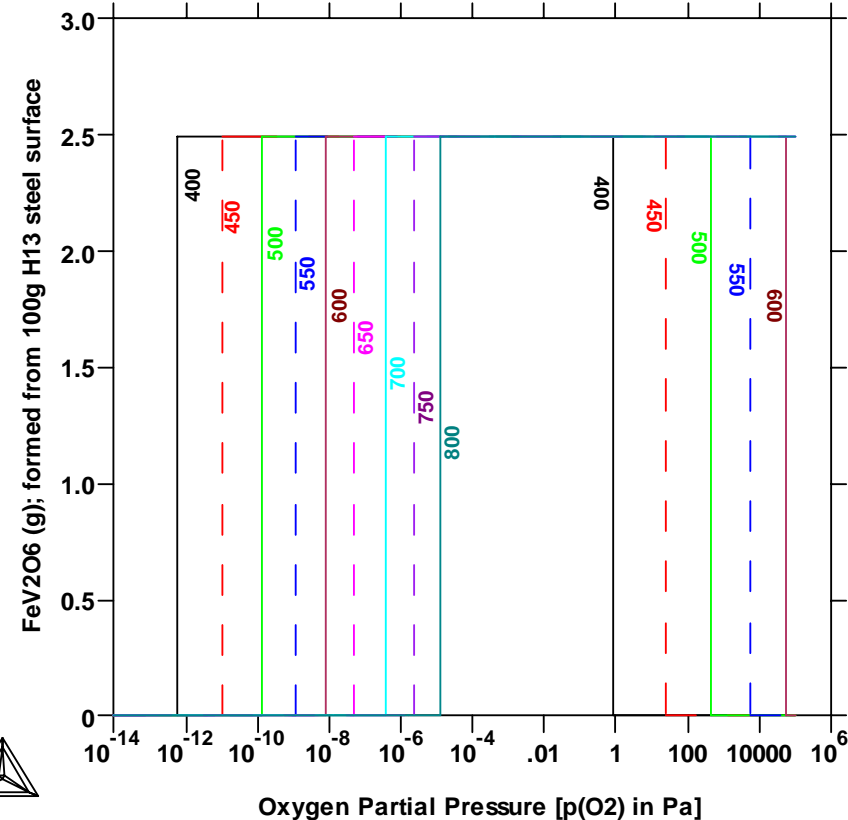
THERMO-CALC (2008.05.22:11.22) :
Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to FeV2O4 Phase



THERMO-CALC (2008.05.22:15.45) :
Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to FeV2O6 Phase



Emergence Conditions with respect to FeV₂O₄ and FeV₂O₆ during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], at 9 different temperatures (between 400 and 800°C, with an interval of 50°C) and 1 bar.

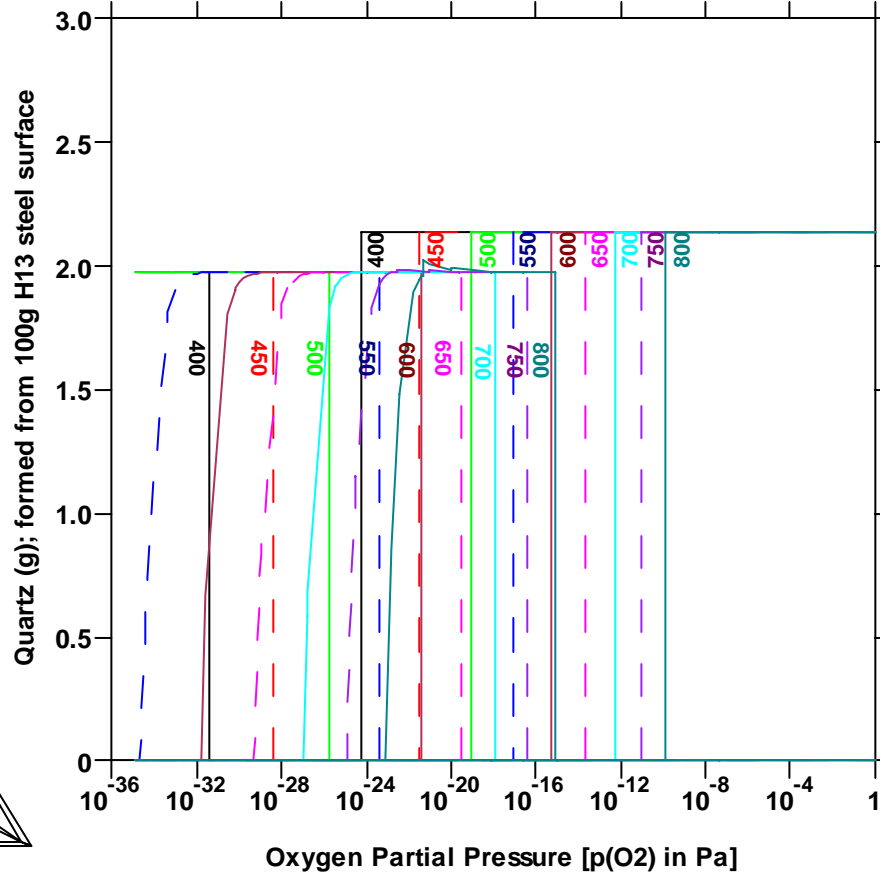
Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

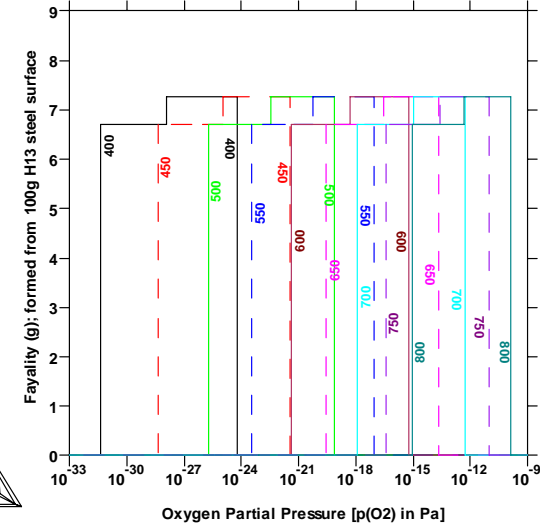
THERMO-CALC (2008.05.22:10.46) :

Databases: SSOL4+SSUB4

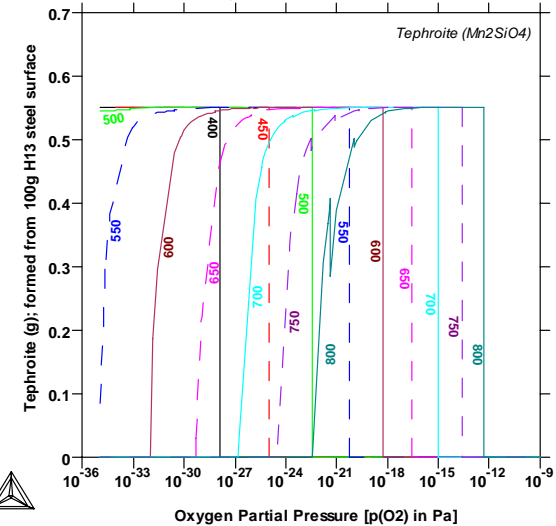
H13 Hot Work Steels: Emergence Condition with respect to α/β -Quartz Phase



H13 Hot Work Steels: Emergence Condition with respect to Fayalite Phase



H13 Hot Work Steels: Emergence Condition with respect to Tephroite Phase



Emergence Conditions with respect to SiO₂ (α/β -Quartz), FeSiO₄ (Fayalite) and MnSiO₄ (Tephroite) during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], at 9 different temperatures (between 400 and 800°C, with an interval of 50°C) and 1 bar.

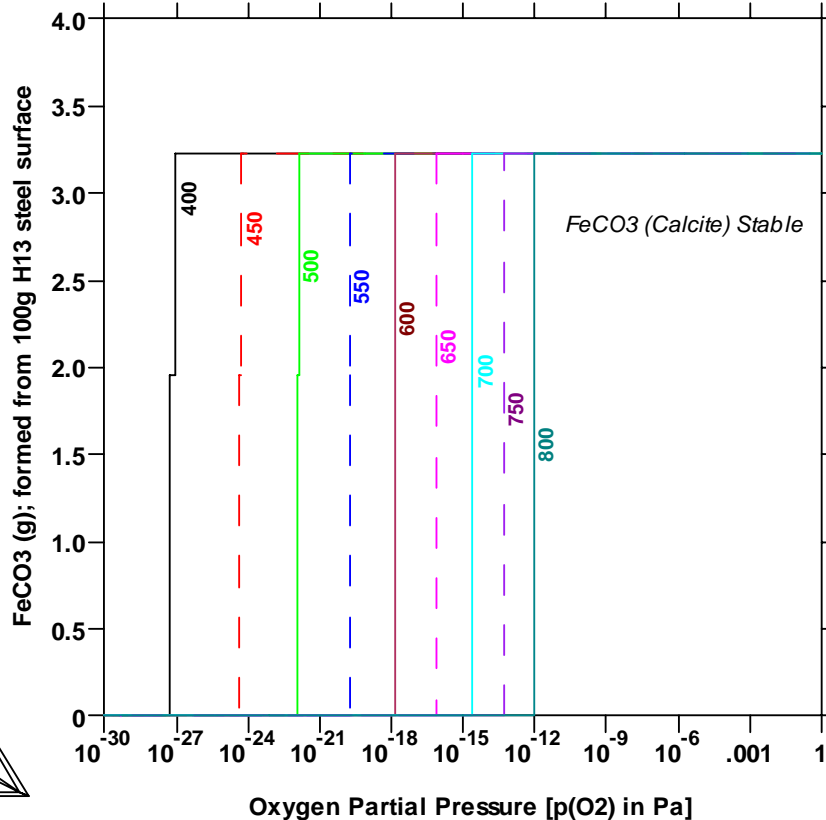
Surface Redox Reactions (II)

Example: Oxidation of H13 Hot Work Steel

THERMO-CALC (2008.05.22:15.18) :

Databases: SSOL4+SSUB4

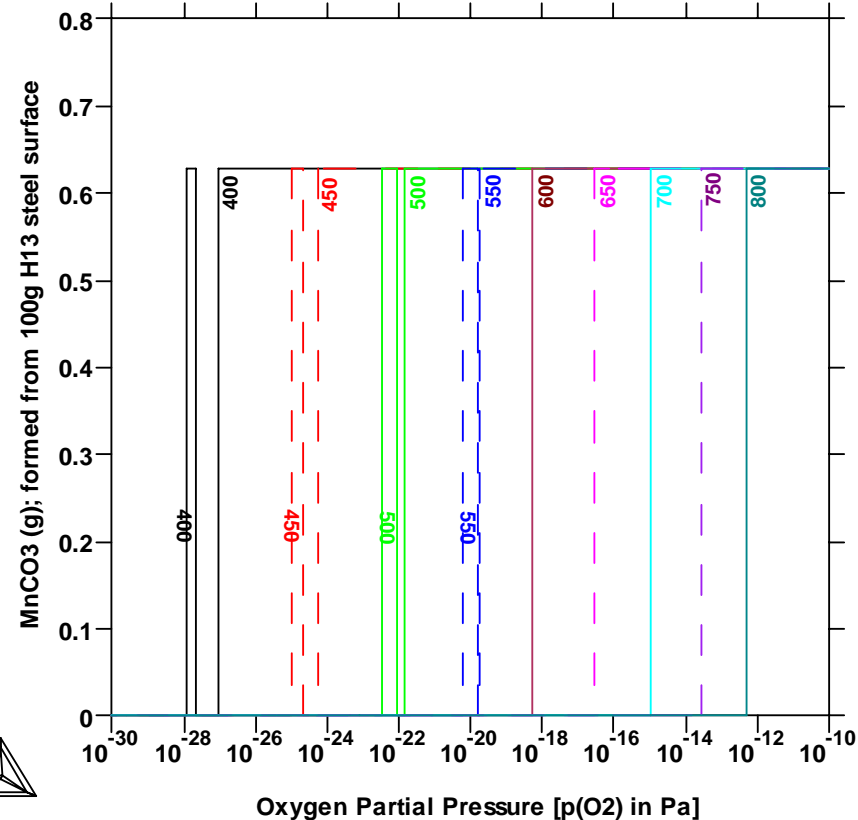
H13 Hot Work Steels: Emergence Condition with respect to FeCO₃ Phase



THERMO-CALC (2008.05.22:14.37) :

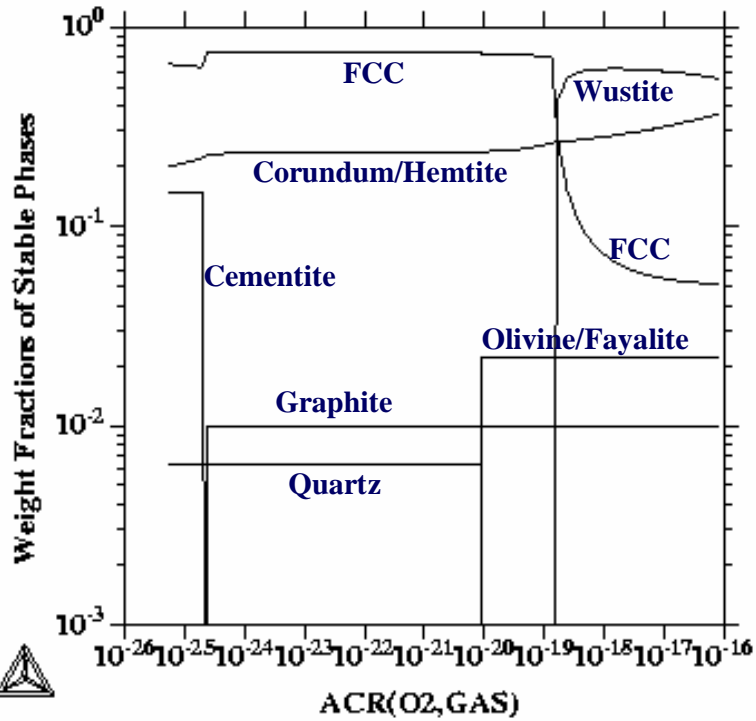
Databases: SSOL4+SSUB4

H13 Hot Work Steels: Emergence Condition with respect to MnCO₃ Phase

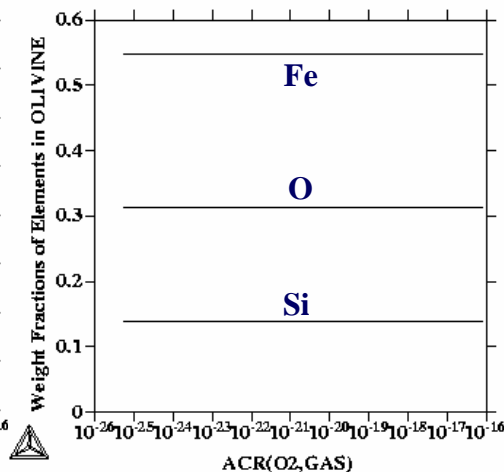
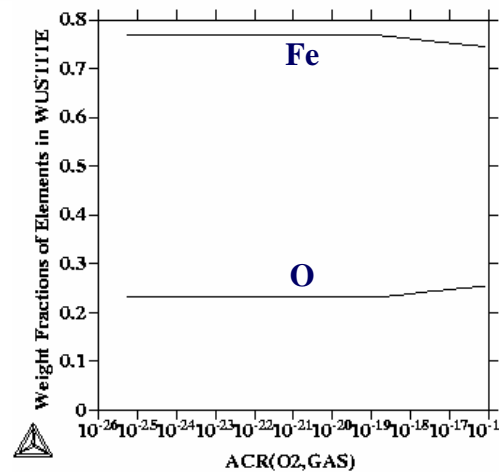
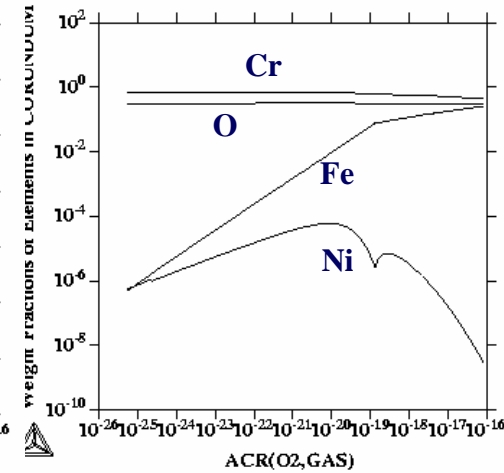
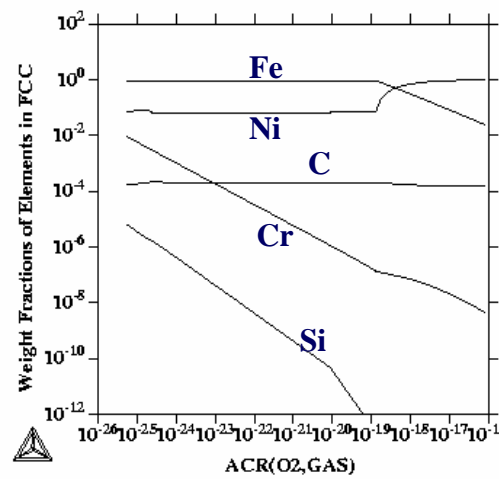


Emergence Conditions with respect to FeCO₃ (Calcite) and MnCO₃ during oxidation of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P-O], at 9 different temperatures (between 400 and 800°C, with an interval of 50°C) and 1 bar.

Surface Redox Reactions (III)



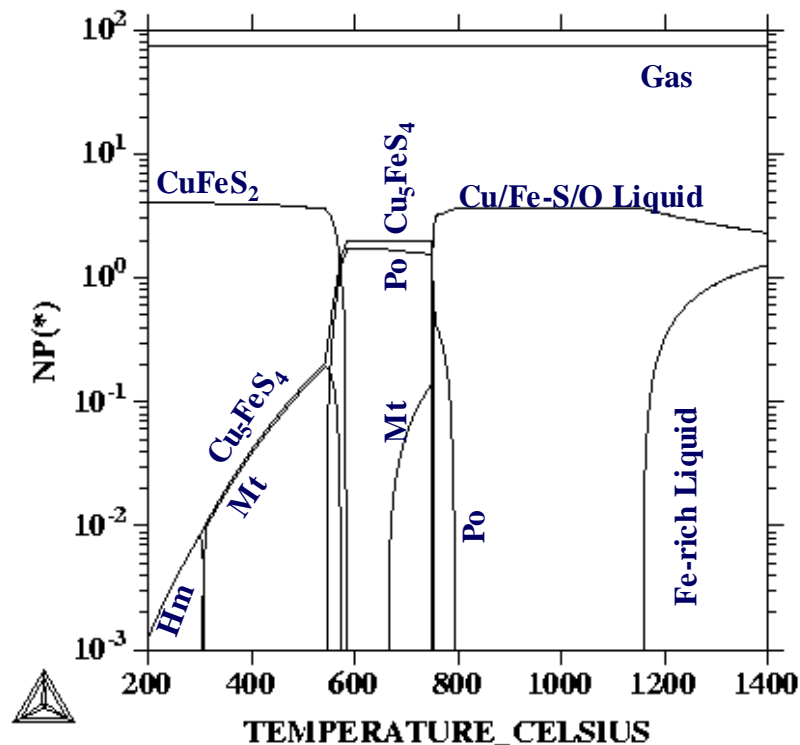
Gas Phase Oxidation of Steel



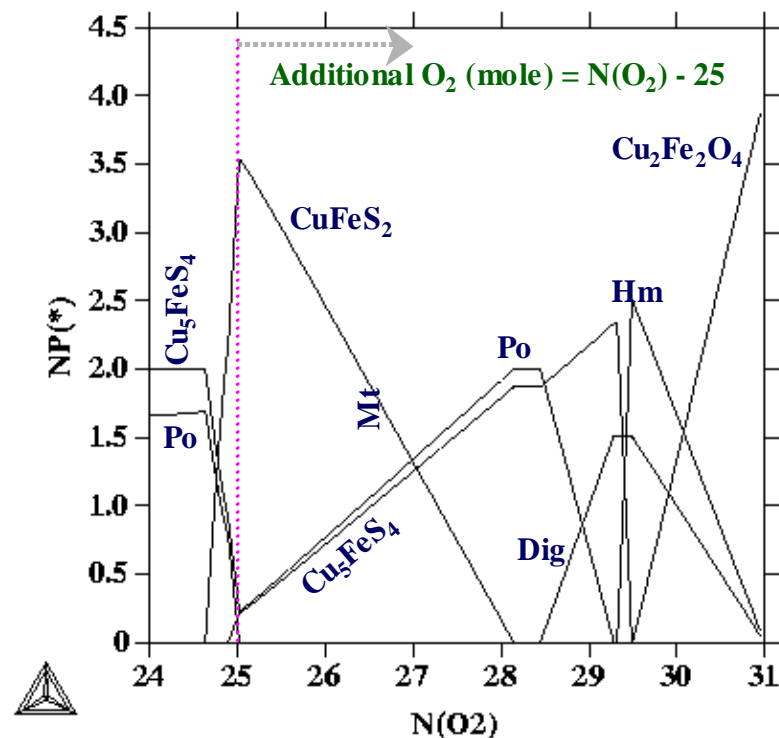
Surface Redox Reactions (IV)

Example: Oxidation of Sulfides (CuFeS₂)

Using the ION database, one can calculate various types of phase diagrams and property diagrams for oxidation processes of multiple-metal sulfides (e.g., CuFeS₂, FeS₂) or mixtures (e.g., CuFeS₂-FeS₂), to find optimal temperatures and initial bulk compositions (especially the additional oxygen input).



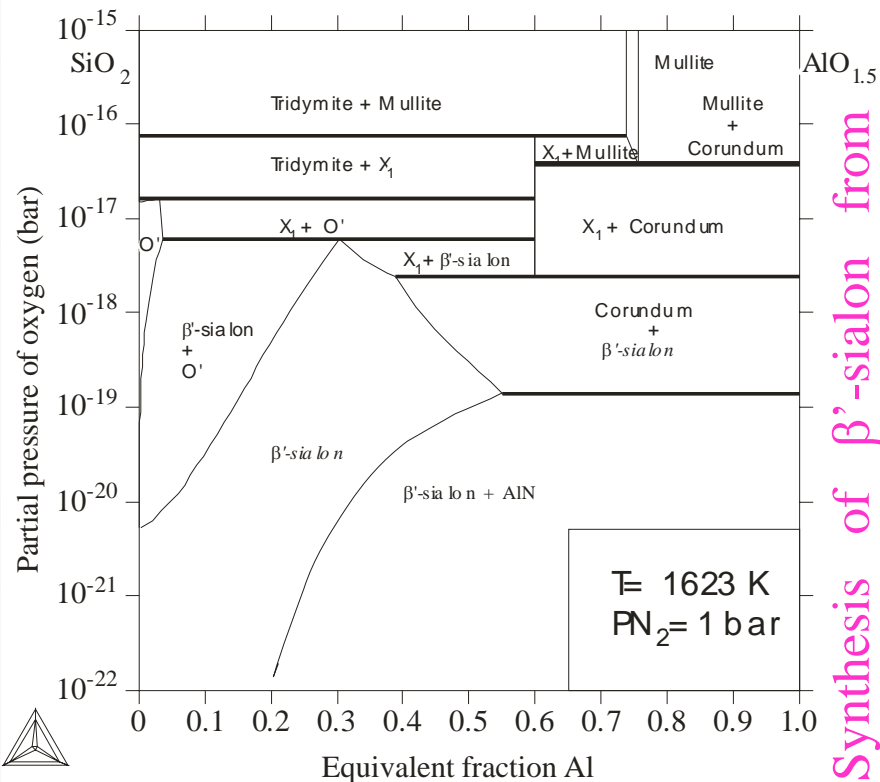
Stable phases during oxidation of CuFeS₂, as a function of the temperature condition. The calculation is made for an interaction system of 2 moles CuFeS₂ and 50 moles of vapour, at 1 bar and various temperatures (200 to 1400°C).



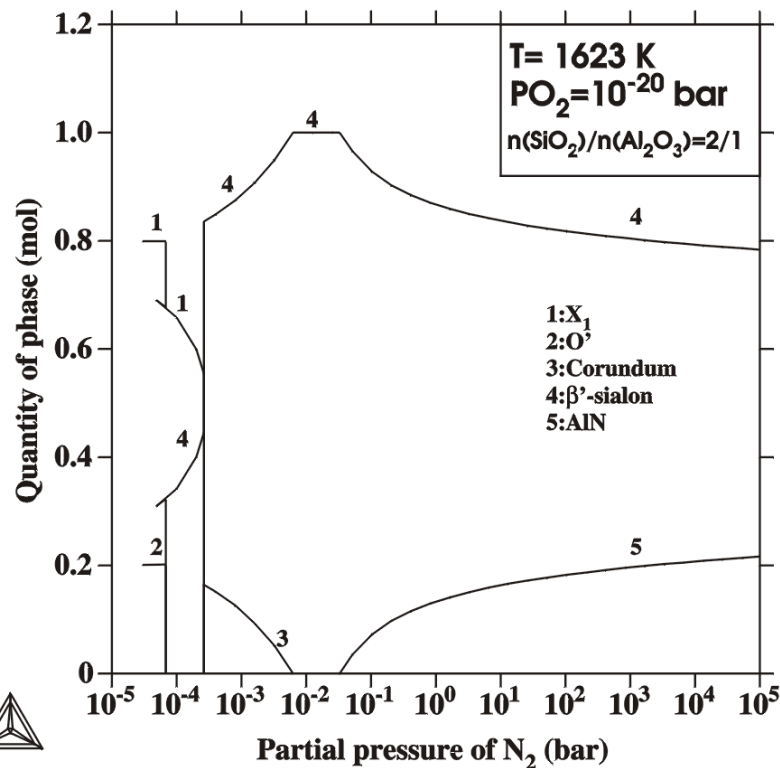
Stable phases during oxidation of CuFeS₂, varied with the additional oxygen amount. The calculation is made for an interaction system of 2 moles CuFeS₂ and 50 moles of vapour, at 550°C, 1 bar and various additional amounts of O₂.

Optimal Conditions for β' -Sialon

Simulations of optimal conditions for synthesis of β' -sialon from mixed SiO_2 and Al_2O_3 powder by reduction-nitridation. By making calculations in the Si-Al-O-N system, one can determine the optimal values of controlling temperature, partial pressures of oxygen and nitrogen, and Si:Al ratio in the precursor mixture.



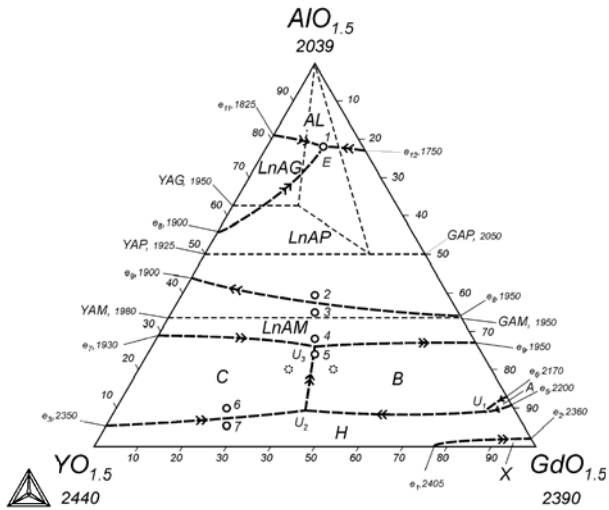
Synthesis of β' -sialon from mixed SiO_2 and Al_2O_3 powder by reduction-nitridation



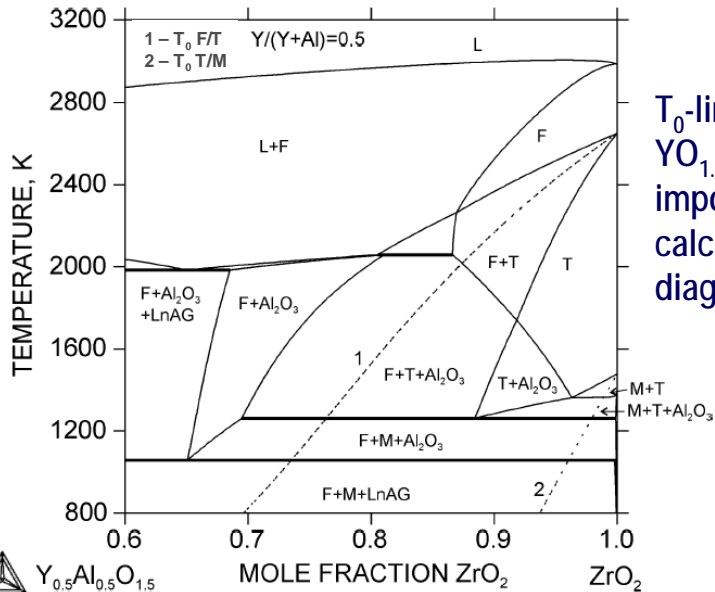
Property diagram of the Si-Al-O-N system at 1623 K and $P_{\text{N}_2}=1$ bar. Phase stabilities vary with oxygen partial pressure and equivalent fraction of Al in the system.

Property diagram of the Si-Al-O-N system at 1623 K and $P_{\text{O}_2}=10^{-20}$ bar. Phase stabilities vary with nitrogen partial pressure in the system.

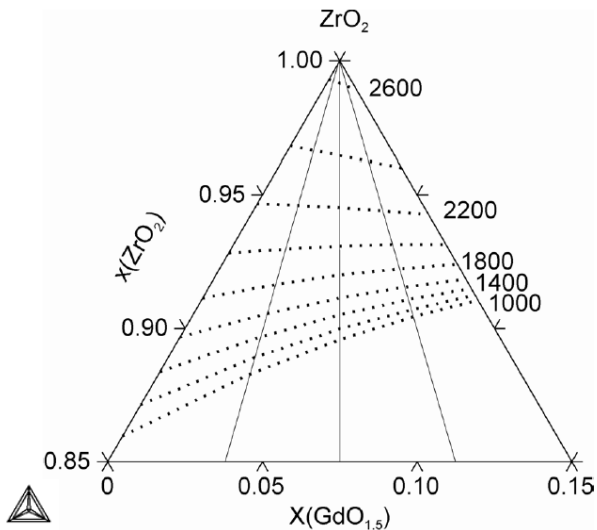
Thermal Barrier Coating



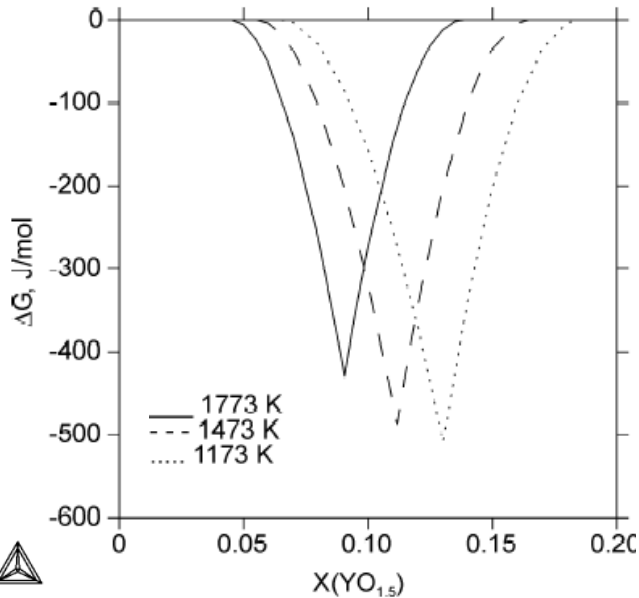
Liquidus surface projection of the $GdO_{1.5}$ - $YO_{1.5}$ - $AlO_{1.5}$ system.



T_0 -lines in the ZrO_2 - $YO_{1.5}$ - $AlO_{1.5}$ system, imposed on calculated phase diagram.



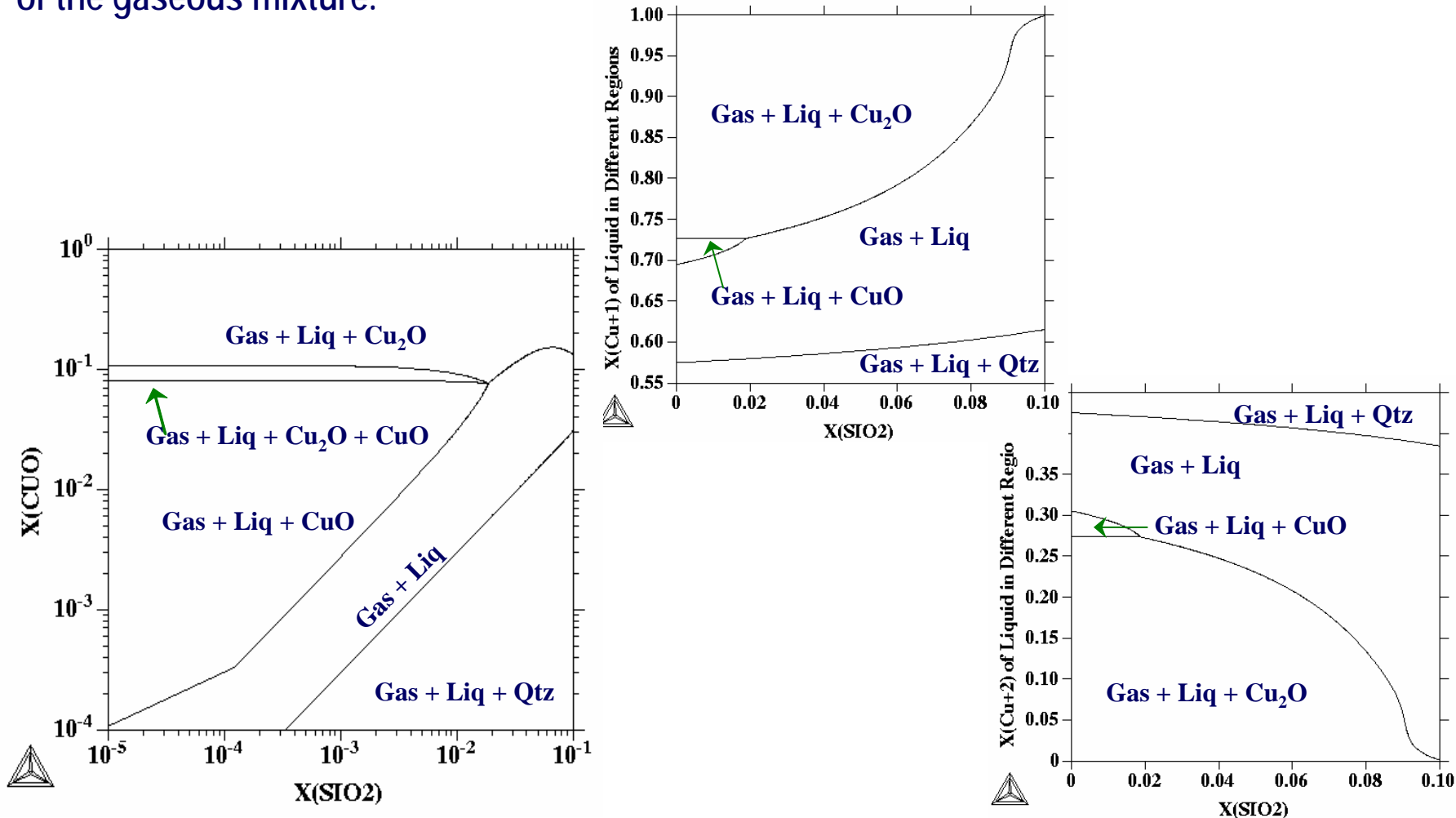
T_0 -lines projection of the ZrO_2 - $GdO_{1.5}$ - $YO_{1.5}$ system (for fluorite \leftrightarrow tetragonal M_2O_3A).



Driving forces for partitioning of F and T metastable phase to the F+T equilibrium assemblage in the ZrO_2 - $YO_{1.5}$ system. F stands for fluorite and T for tetragonal M_2O_3A .

Chemical Vapor Deposition (CVD)

Simulate the optimal conditions for CVD synthesis of various oxide/carbide/nitride/... films (such as Cu_2O or $\text{Cu}_2\text{O}/\text{CuO}$ film from mixed SiO_2 and CuO powder by reduction). By making calculations in the Si-Cu-C-O-N system, one can determine the optimal values of controlling temperature, partial pressures of oxygen and nitrogen, and initial composition of the gaseous mixture.



Effect of Nitrogen Pressure on Nitrogen Solubility in Molten Metal

High nitrogen steels are produced using processes with melting under pressurized nitrogen atmospheres.

- For high nitrogen solubility.

It's well known that nitrogen solubility in molten metal increases with pressure according to Sivert's law.

- To avoid formation of blow holes during solidification.

Calculate nitrogen content in a 18-8 stainless steel melt as function of nitrogen pressure at 1823 K.

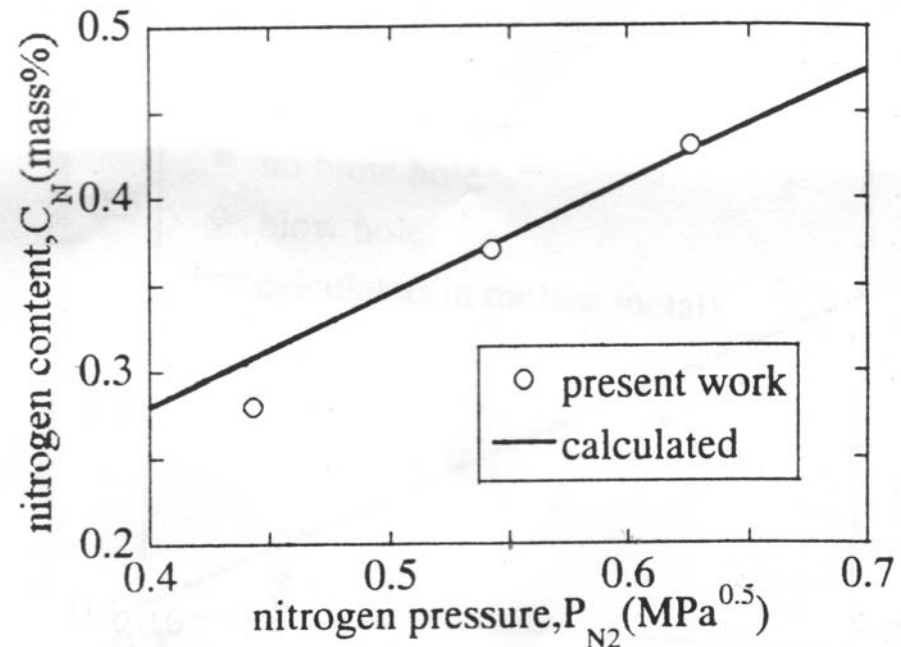


Fig.5 Effect of nitrogen pressure on the nitrogen contents at 1823K for 18Cr-8Ni.

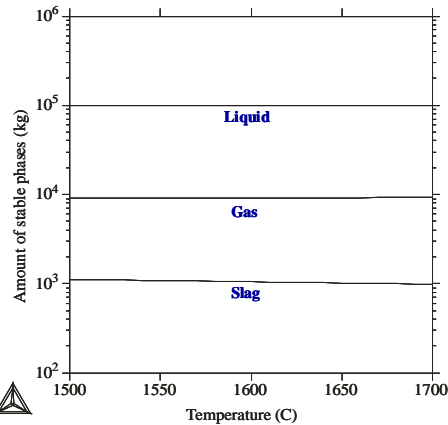
From Sugiyama et al.

- Metal-Slag-Gas Interactions
- Metal-Gas Interactions (Redox Reactions, Coatings, CVD, ...)
- **Combustion/Sintering/Incineration/Remelting/Recycling
& Environmental Issues**
- Dew Points
- Ellingham Diagrams
- *and more ...*

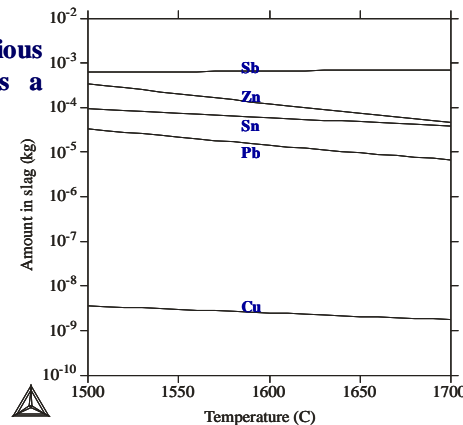
- Materials Reprocessing (re-melting, re-cycling, etc.)
- Sintering, Incineration and Combustion
- Waste Repository and Environmental Assessment

Re-melting and Re-cycling

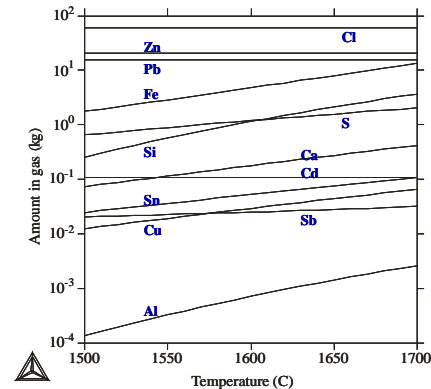
Special Case: Thermochemical calculations of element distribution between melt, slag and gas phases in relation to behaviour of minority elements in high temperature processes of waste incineration (also relevant to scrap remelting) in a bath of molten iron.



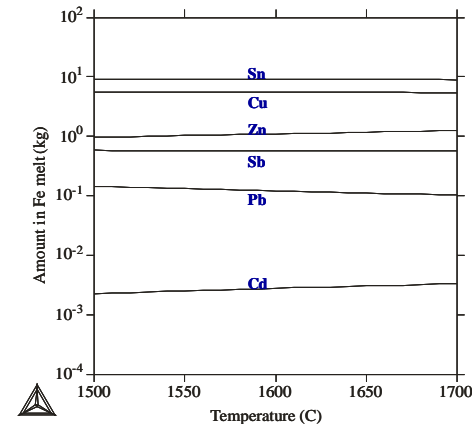
The equilibrium amounts of various stable phases in the system as a function of bath temperature.



The calculated amounts of various elements present in the slag phase, as a function of bath temperature.



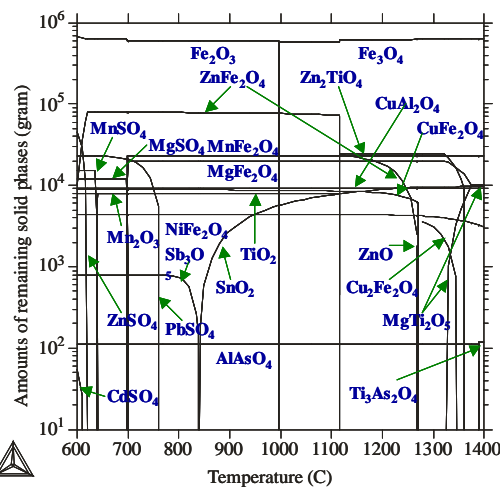
The calculated amounts of various elements present in the gas phase, as a function of bath temperature.



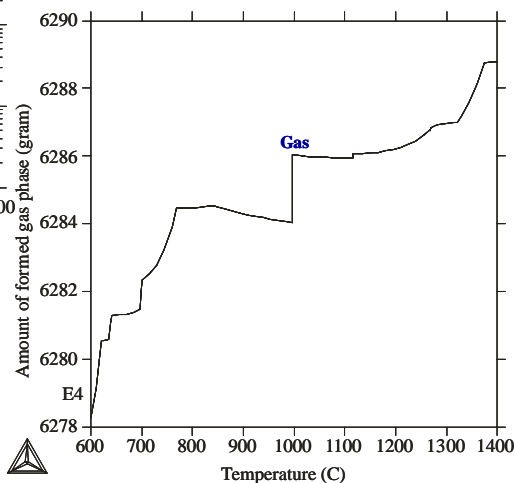
The calculated amounts of various elements present in the molten Fe phase, as a function of bath temperature.

Waste and Re-cycling

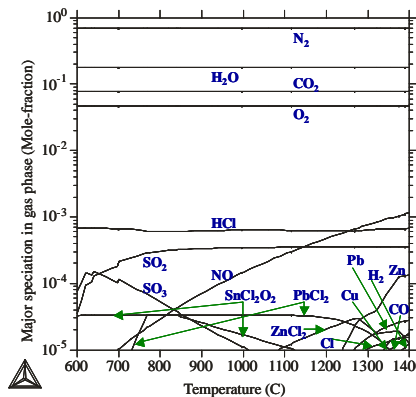
Simulation Step 1 - Calculate from 600 to 1400°C, in order to decide the optimal incineration temperature of a typical household waste (see the composition listed below), and to determine the composition of the gas phase produced by the waste incineration process.



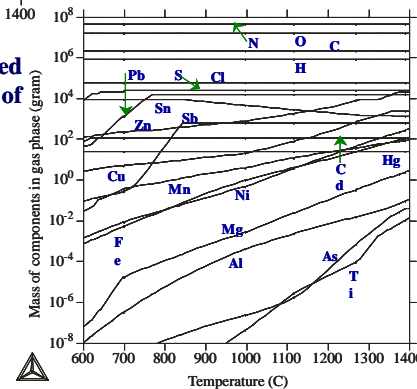
The amounts of various remaining solid phases in the system as a function of incineration temperature.



The amounts of the formed gas phase in the system as a function of incineration temperature.



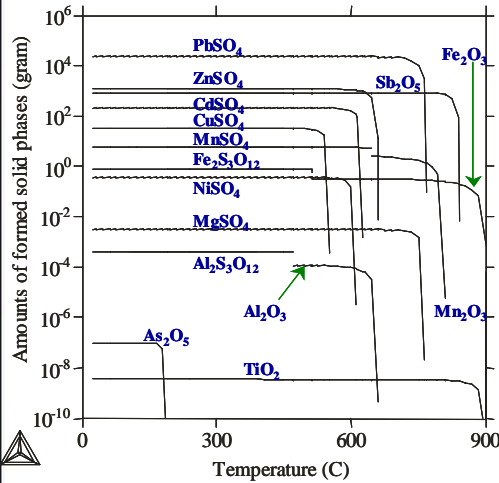
The major speciation in the formed gas phase, as a function of incineration temperature.



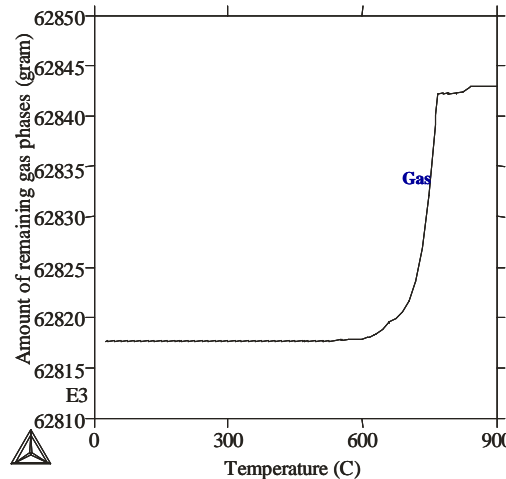
The amounts of various components (in gram) in the formed gas phase, as a function of incineration temperature.

Waste and Re-cycling

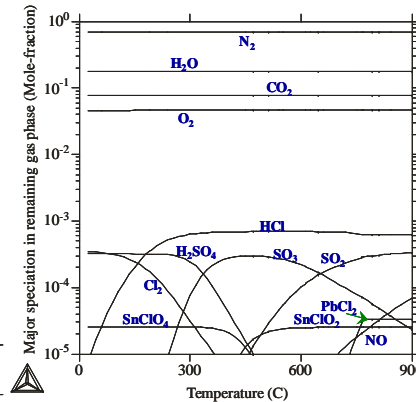
Simulation Step 2 - The second part of calculation is made on the condensed phases forming from the gas phase as it is cooled to room temperature.



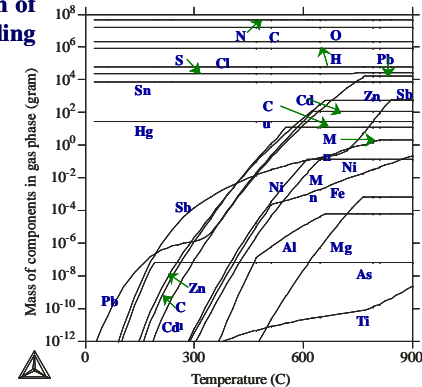
The amounts of various formed solid phases in the system as a function of temperature during the cooling process.



The amount of the remaining gas phase in the system as a function of temperature during the cooling process.



The major speciation in the remaining gas phase, as a function of temperature during the cooling process.



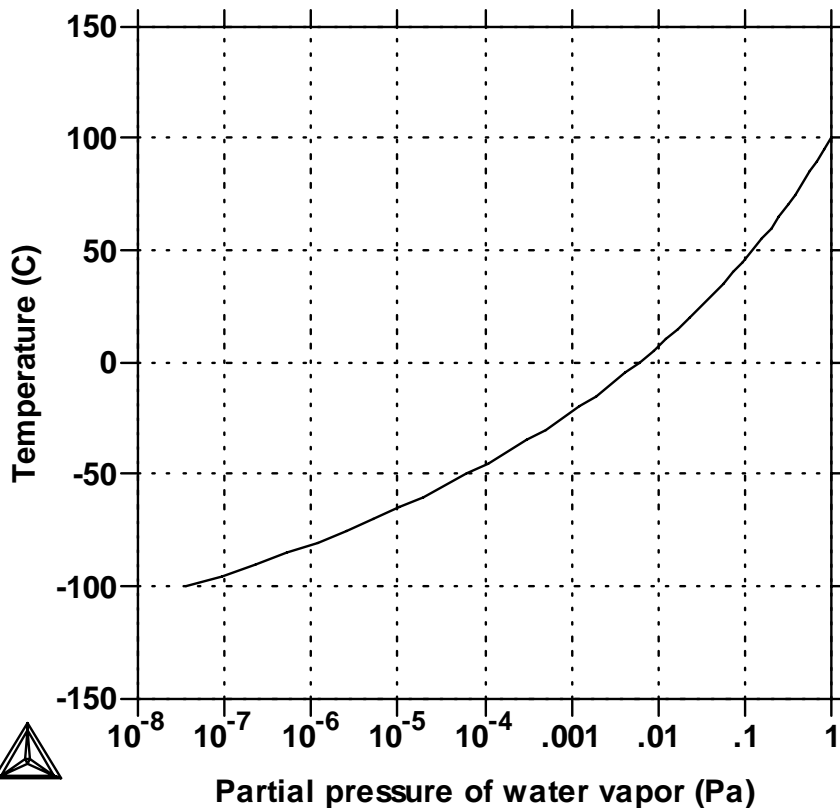
The amounts of various components (in gram) in the remaining gas phase, as a function of temperature during the cooling process.

- Metal-Slag-Gas Interactions
- Metal-Gas Interactions (Redox Reactions, Coatings, CVD, ...)
- Combustion/Sintering/Incineration/Remelting/Recycling
& Environmental Issues
- Dew Points
- Ellingham Diagrams
- *and more ...*

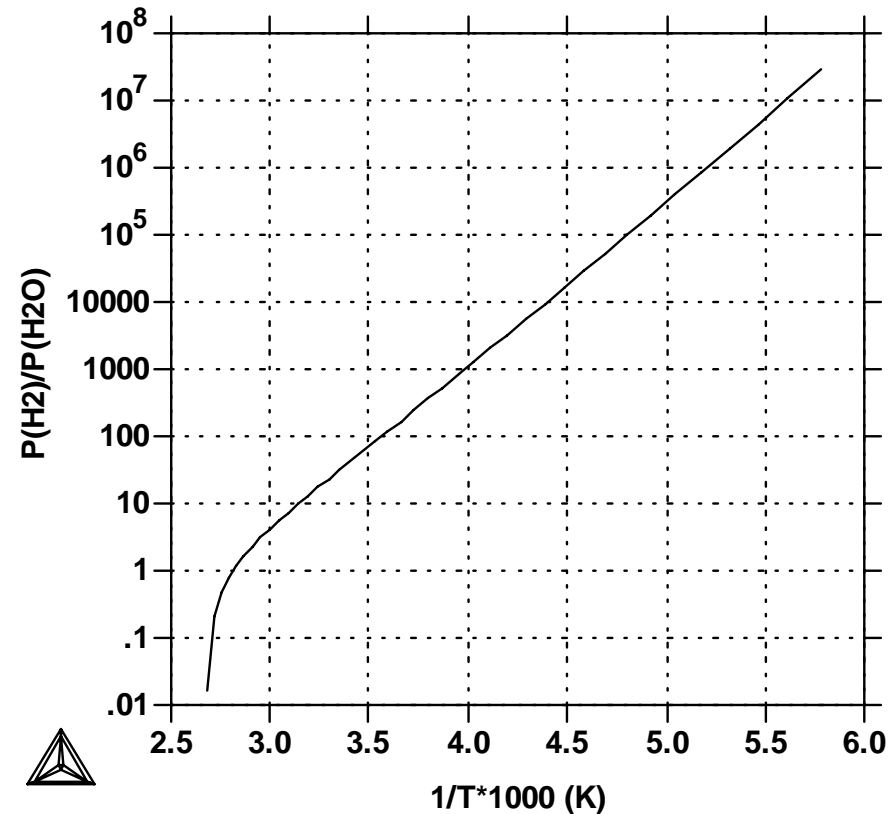
Dew Point Calculation

Total Pressure = 1 atm

THERMO-CALC (2008.05.26:22.55) :
DATABASE:SSUB4
N=1, P=1.01325E5, FIXED PHASES: H2O1_L=0;



THERMO-CALC (2008.05.26:22.55) :
DATABASE:SSUB4
N=1, P=1.01325E5, FIXED PHASES: H2O1_L=0;

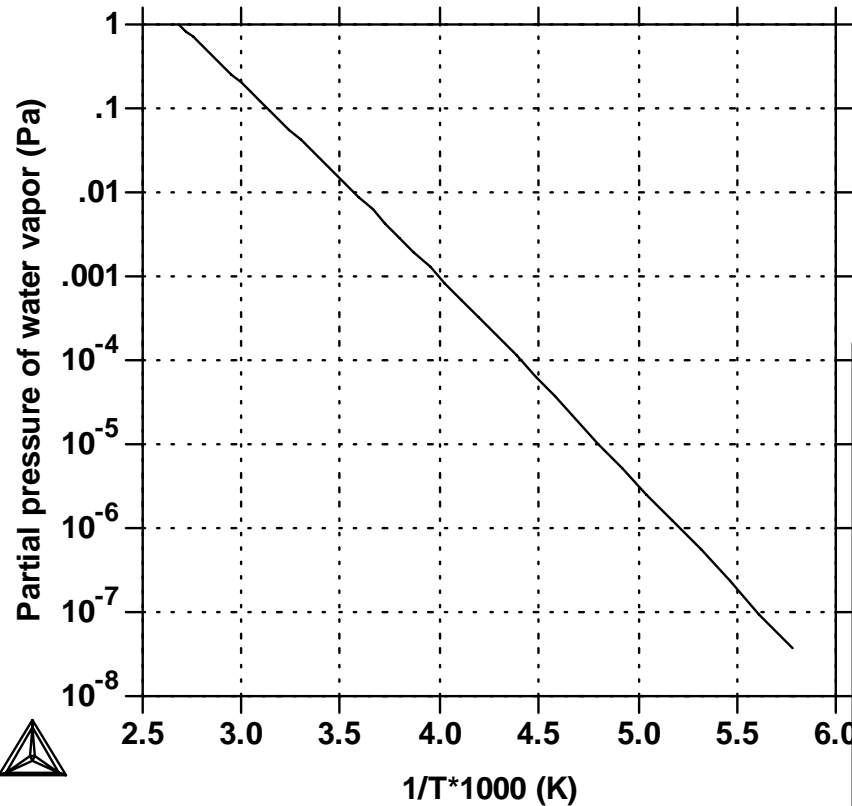


Different ways for presenting Dew Point (calculated by Thermo-Calc)

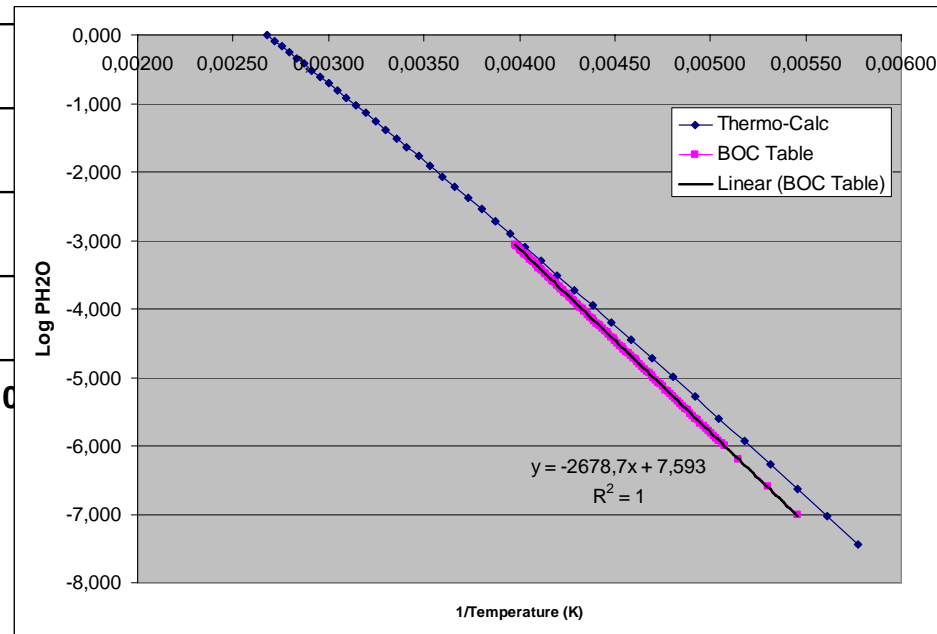
Dew Point Calculation

Total Pressure = 1 atm

THERMO-CALC (2008.05.26:22.55) :
 DATABASE:SSUB4
 N=1, P=1.01325E5, FIXED PHASES: H2O1_L=0;



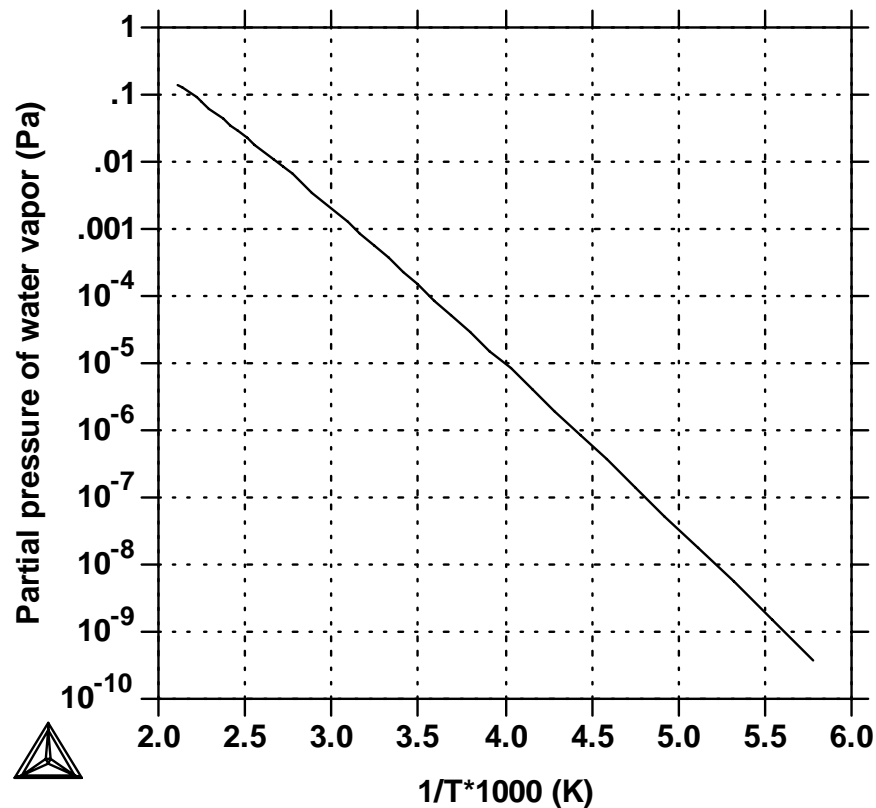
Dew Point: Calculation vs Empirical Eq



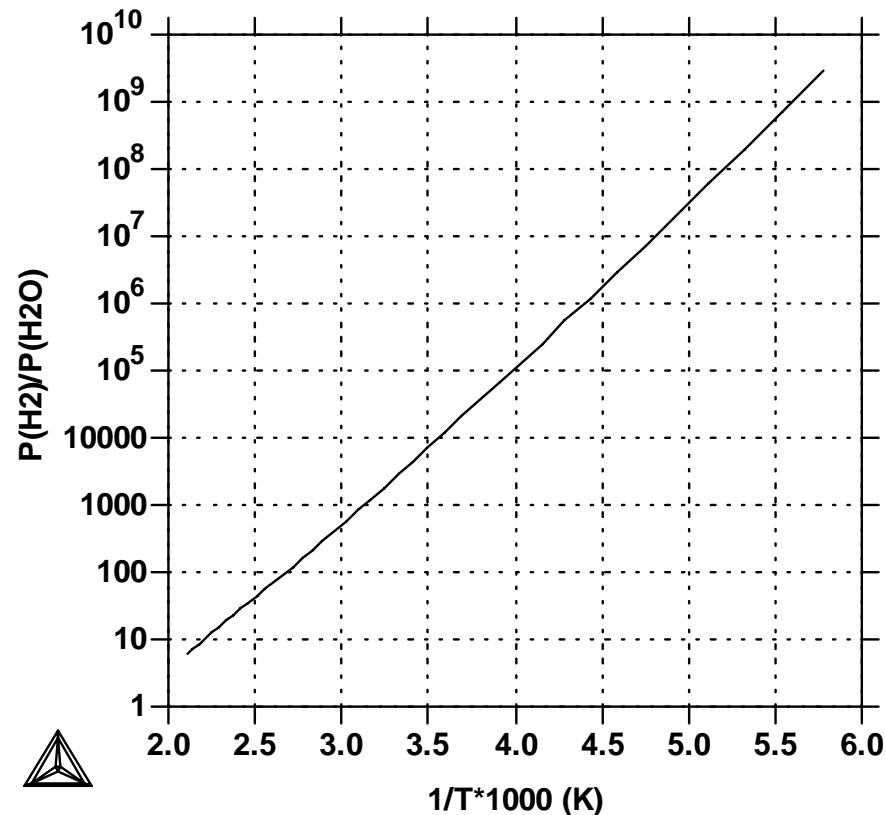
Dew Point Calculation

Total Pressure = 100 atm

THERMO-CALC (2008.05.26:23.22) :
DATABASE:SSUB4
N=1, P=1.01325E7, FIXED PHASES: H2O1_L=0;



THERMO-CALC (2008.05.26:23.22) :
DATABASE:SSUB4
N=1, P=1.01325E7, FIXED PHASES: H2O1_L=0;



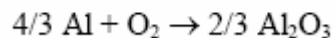
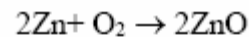
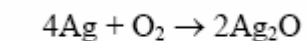
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& Environmental Issues
- Dew Points
- **Ellingham Diagrams**
- *and more ...*

Ellingham Diagrams: From Textbooks

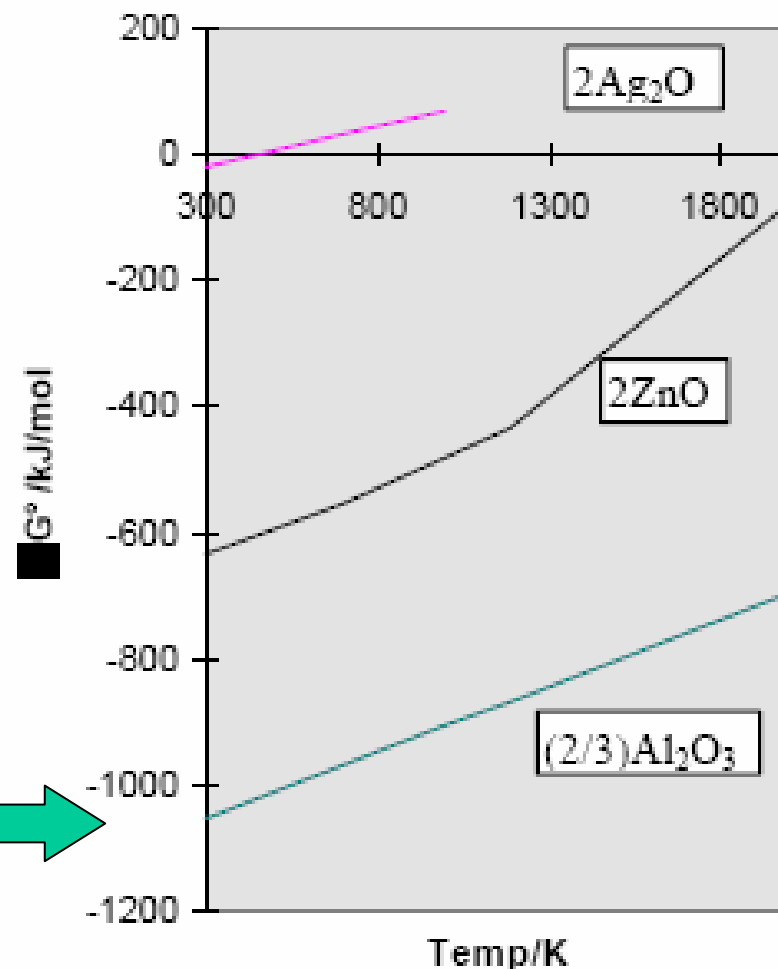
Ellingham Diagrams – Plots of ΔG° against T for analogous reactions but involving a fixed quantity of common component (e.g. O, S, C, ...)

TABLE 1 Thermodynamic Data at 298.15 K

Substance	State	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
Ag	s	0	0	42.7
Ag ₂ O	s	-30.5	-10.8	121.7
Al	s	0	0	28.3
Al	g	326	285.8	164.4
Al ₂ O ₃	s	-1673.6	-1580.2	51.0
C	s	0	0	5.7
CO	g	-110.5	-137.2	197.5
CO ₂	g	-393.5	-394.4	213.7
Ca	s	0	0	41.4
Ca	g	178.2	144.3	154.8
CaO	s	-635.1	-604.0	39.7
Cu	s	0	0	33.3
Cu	g	338.3	298.6	166.3
CuO	s	-155.8	-128.0	42.6
Fe	s	0	0	27.1
FeO	s	-272.0	-251.5	60.7
Hg	l	0	0	76.0
Hg	g	61.3	31.9	174.8
HgO	s	-90.8	-58.5	70.3
Pb	s	0	0	64.8
Pb	g	195.0	161.9	175.3
PbO	s	-219.3	-188.8	65.3
Zn	s	0	0	41.6
Zn	g	130.7	95.2	160.9
ZnO	s	-348.1	-318.1	43.5
O ₂	g	0	0	205.0

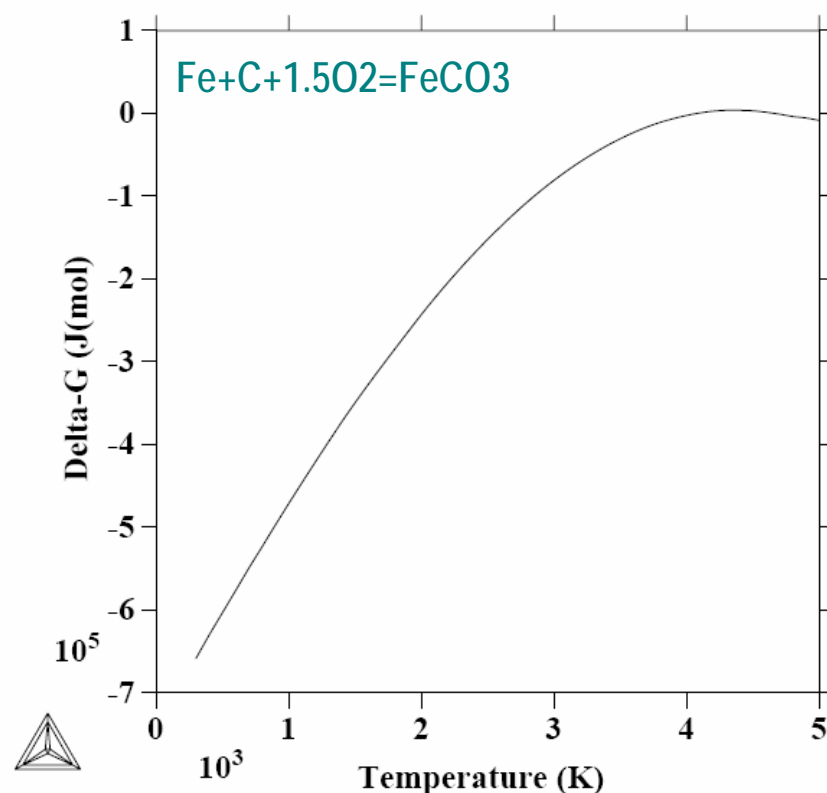
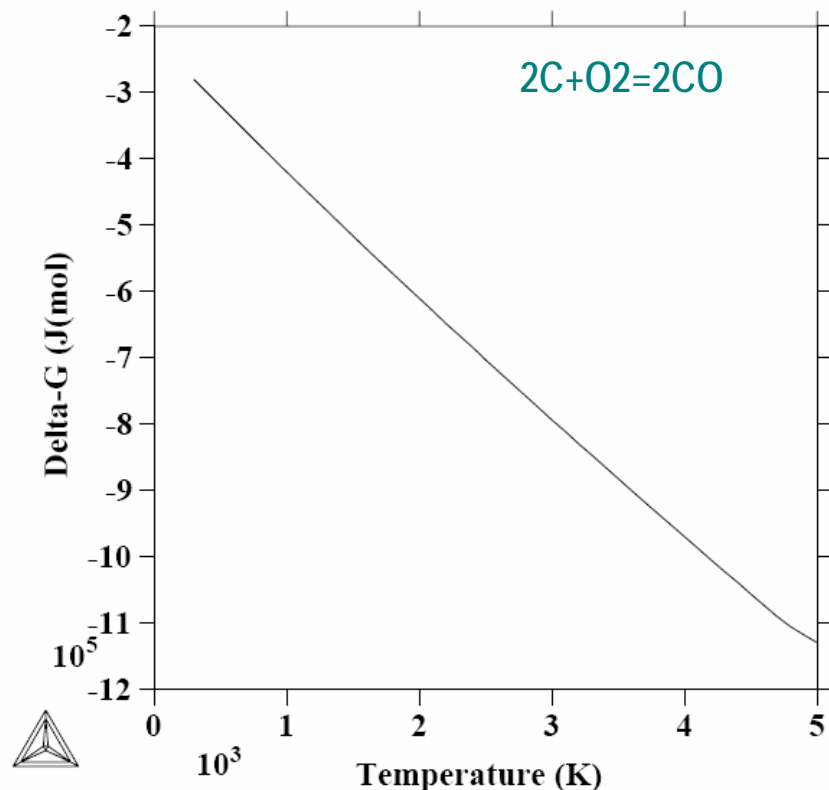


Ellingham Diagram



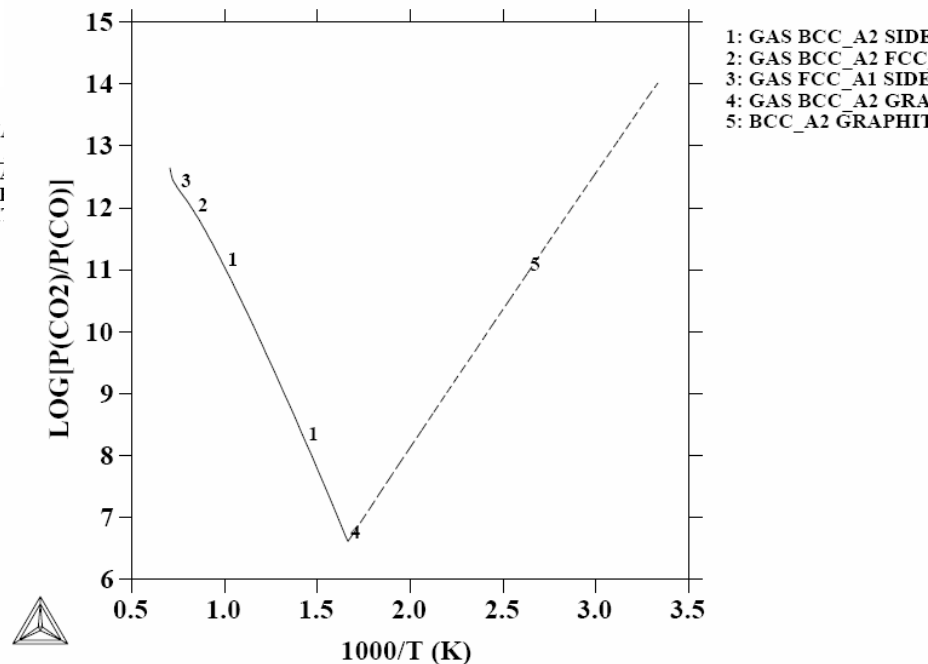
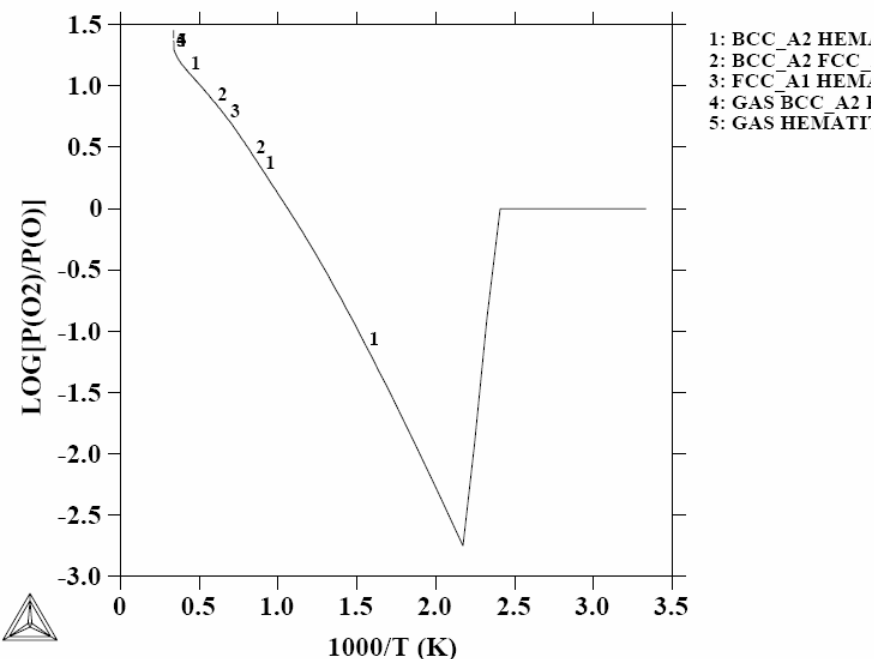
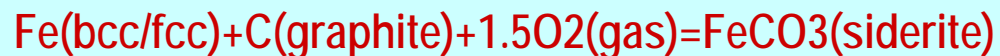
Ellingham Diagrams: Through Thermo-Calc

Extended Ellingham Diagrams – Plots of ΔG° (or other properties) against T for analogous reactions but involving a fixed quantity of common component (e.g. O, S, C, ...)



A series of such Thermo-Calc calculations using critically-assessed database(s) can easily and efficiently result in reliable Ellingham diagrams, for not only pure compounds (like above) but also in-solution components (like on next slide) involving in complex heterogeneous interactions.

Ellingham Diagrams: Through Thermo-Calc



Extended Ellingham Diagrams through Thermo-Calc – for in-solution components (in non-ideal solution phases), involving in complex heterogeneous interactions.

- ➡ Computational tools and methods can be used to rapidly accelerate design of new and innovative materials.
- ➡ Calculations can be made to better understand underlying mechanisms of processes and thus lead to process optimization and improved quality control and reproducibility.
- ➡ Such methods also lead to thinking outside the box, thus increasing innovation in a cost-effective manner.

***Thank you all
for your attentions!***