

SLAG4: TCS Fe-containing Slag Database

<i>Database name:</i>	TCS Fe-containing Slag Database	<i>Database acronym:</i>	SLAG
<i>Database owner:</i>	Thermo-Calc Software AB	<i>Database version:</i>	4.1

SLAG4 is suitable for thermodynamic activities, sulphide capacities and phase equilibrium calculations in multi-component metallurgical slag systems containing iron. It is used in applications for metallurgy, and alloy design and engineering.

Included Elements (30)

Ag Al Ar B C Ca Co Cr Cu F Fe H Mg Mn Mo N Na
Nb Ni O P Pb S Si Sn Ti U V W Zr

Included Phases

SLAG4 database contains a liquid slag phase, as well as an Fe-rich liquid phase (dilute solution), a simplified gaseous mixture phase, and many stoichiometric solids (e.g., oxides, silicates, sulfides, halites, etc.). Total amount of different phases is 115.

The liquid slag phase (containing oxide/silicate/sulfide/fluoride/phosphorates species), as well as various oxide, silicate, sulphide, fluoride and phosphorate solid phases, cover 13 elements (Al-Ca-Cr-Fe-Mg-Mn-Na-Si-Ti-O-S-F-P).

The Fe-Liquid solution phase includes 26 dilute components (Ag-Al-B-C-Ca-Co-Cr-Cu-H-Mg-Mn-Mo-N-Nb-Ni-O-P-Pb-S-Si-Sn-Ti-U-V-W-Zr). The recommended composition limit of any minority component, in the 27-component diluted Fe-rich liquid, is only 0.1wt%. In some cases e.g. stainless steel, data could be used at much higher concentrations in the Fe-rich liquid phase, but the user must carefully check each of such cases.

The gas phase is simplified as an ideal mixture of (Ar,CO,CO₂,H₂,H₂O,N₂,Na,O₂,P₂,P₄,S₂). Many solid phases are included in the entire 30-element framework.

For steels and various alloys, as well as other substance or solution phases, which are in interactions with the liquid slag phase or the Fe-rich liquid phase, thermodynamic data can be appended from other available databases, such as TCFE, TCNI, SSUB, SSOL, TCMP, TCES, TTAI/Mg/Ni/Ti, SALT, TCAQ, AQS, GCE, NUMT, NUOX, etc.

Assessed Systems

Thermodynamic data for the liquid slag phase and oxide/silicate solid phases within the Al₂O₃-CaO-CrO-Cr₂O₃-FeO-Fe₂O₃-MgO-MnO-Na₂O-SiO₂ system were critically assessed by IRSID, using the Kapoor-Frohberg-Gaye Quasichemical Cell Model, i.e., the Kapoor-Frohberg Slag Model with the extensions introduced by Gaye and Welfringer [1984] for complex multicomponent slag solution systems. Data for the additional components S and F (as sulphide and fluoride species in the Al-Ca-Cr-Fe-Mg-Mn-Na-Si-O-S-F system) in the slag phase and solid phases critically assessed by Gaye et al. [1992] were included in the database. Thereafter titanium-containing slag and more fluoride constituents were assessed. Phosphorus was added back in the liquid slag phase in this version based on the re-assessment on phosphorus distribution between slags and liquid iron. No solid solution phases are considered in this particular database.

Data for a dilute solution of many elements in the Fe-rich liquid phase are critically assessed and converted to regular solution parameters according to Hillert [1986], with modified dilute solution parameters (plus a quadratic term) in liquid iron from Sigworth and Elliot [1974], so that it becomes a consistent thermodynamic model and also generally improves the agreements of calculated results with available experimental data.

Limits

Critical calculations must always be verified by equilibrium experimental data. It is the user's responsibility to verify the calculations but Thermo-Calc Software is interested to know about any significant deviations in order to improve any future release. This database is not suitable for binary or ternary phase diagram calculations where the chemical compositions and temperature ranges are beyond the usual steel-making conditions.

Thermodynamic Modelling

The Liquid Slag Phase

The slag phase description was mainly based on the evaluation by H. Gaye, J. Lehmann and co-workers of IRSID (now called ArcelorMittal Global R&D Maizières Process) in France using the Kapoor-Frohberg-Gaye Quasichemical Cell Model [1984 and 1992, Gaye], Ti and P was (re-)included based on the assessment work. The model was implemented in Thermo-Calc through the G-E-S command "AMEND_PHASE_DESCRIPTION SLAG STAT 04208000". It's NOT a substitutional solution model. The cations should be in the correct order of decreasing chemical valence (and acidity), i.e. in the order of P^{+5} , Si^{+4} , Ti^{+4} , $(PO)^{+3}$, Cr^{+3} , Al^{+3} , Fe^{+3} , Cr^{+2} , Fe^{+2} , Mn^{+2} , Mg^{+2} , Ca^{+2} , Na^{+1} . The excess G is not expressed by Redlich-Kistor polynomial. The composition-dependent term in the formation energy W_{ij} for an asymmetric cell was transited into the interaction parameter in Thermo-Calc TDB file. Parameter value for the formation energy is given per formula constituent; while parameter values for interaction energy is given per cell. The slag phase covers 13 elements (Al-Ca-Cr-Fe-Mg-Mn-Na-Si-Ti-O-P-S-F).

Table 1. The complete (cell) constitution list

A0_01_C00C02_25_P2O5	A0_01_C00C04_12_SiO2	A0_01_C00C06_23_P2O2O3	A0_01_C00C07_23_CR2O3
A0_01_C00C08_23_AL2O3	A0_01_C00C10_23_FE2O3	A0_01_C00C14_11_CRO	A0_01_C00C16_11_FEO
A0_01_C00C22_11_MNO	A0_01_C00C24_11_MGO	A0_01_C00C27_11_CAO	A0_01_C00C30_21_NA2O
A0_01_C00C05_12_TiO2	A0_02_C00C04_12_SiS2	A0_02_C00C07_23_CR2S3	A0_02_C00C08_23_AL2S3
A0_02_C00C10_23_FE2S3	A0_02_C00C14_11_CRS	A0_02_C00C16_11_FES	A0_02_C00C22_11_MNS
A0_02_C00C24_11_MGS	A0_02_C00C27_11_CAS	A0_03_C00C04_12_SiF4	A0_03_C00C08_23_AL2F6
A0_03_C00C10_23_FE2F6	A0_03_C00C16_11_FEF2	A0_03_C00C22_11_MNF2	A0_03_C00C24_11_MGF2
A0_03_C00C27_11_CAF2	A0_01_C02C04_PSI	A0_01_C02C05_PTI	A0_01_C02C06_PP
A0_01_C02C08_PAL	A0_01_C02C10_PFE	A0_01_C02C16_PFE	A0_01_C02C22_PMN
A0_01_C02C24_PMG	A0_01_C02C27_PCA	A0_01_C02C30_PNA	A0_01_C04C06_SIP
A0_01_C04C07_SICR	A0_01_C04C08_SIAL	A0_01_C04C10_SIFE	A0_01_C04C14_SICR
A0_01_C04C16_SIFE	A0_01_C04C22_SIMN	A0_01_C04C24_SIMG	A0_01_C04C27_SICA
A0_01_C04C30_SINA	A0_01_C05C06_TIP	A0_01_C06C08_PAL	A0_01_C06C10_PFE
A0_01_C06C16_PFE	A0_01_C06C22_PMN	A0_01_C06C24_PMG	A0_01_C06C27_PCA
A0_01_C06C30_PNA	A0_01_C07C08_CRAL	A0_01_C07C10_CRFE	A0_01_C07C14_CRCR
A0_01_C07C16_CRFE	A0_01_C07C22_CRMN	A0_01_C07C24_CRMG	A0_01_C07C27_CRCA
A0_01_C08C10_ALFE	A0_01_C08C14_ALCR	A0_01_C08C16_ALFE	A0_01_C08C22_ALMN
A0_01_C08C24_ALMG	A0_01_C08C27_ALCA	A0_01_C10C14_FECR	A0_01_C10C16_FEFE
A0_01_C10C22_FEMN	A0_01_C10C24_FEMG	A0_01_C10C27_FECA	A0_01_C14C16_CRFE
A0_01_C14C22_CRMN	A0_01_C14C24_CRMG	A0_01_C14C27_CRCA	A0_01_C16C22_FEMN
A0_01_C16C24_FEMG	A0_01_C16C27_FECA	A0_01_C22C24_MNMG	A0_01_C22C27_MNCA
A0_01_C24C27_MGCA	A0_01_C04C05_SITI	A0_01_C05C08_TIAL	A0_01_C05C10_TIFE

A0_01_C05C16_TIFE	A0_01_C05C22_TIMN	A0_01_C05C24_TIMG	A0_01_C05C27_TICA
A0_02_C04C07_SICR	A0_02_C04C08_SIAL	A0_02_C04C10_SIFE	A0_02_C04C14_SICR
A0_02_C04C16_SIFE	A0_02_C04C22_SIMN	A0_02_C04C24_SIMG	A0_02_C04C27_SICA
A0_02_C07C08_CRAL	A0_02_C07C10_CRFE	A0_02_C07C14_CRCR	A0_02_C07C16_CRFE
A0_02_C07C24_CRMG	A0_02_C07C27_CRCA	A0_02_C08C10_ALFE	A0_02_C08C14_ALCR
A0_02_C08C16_ALFE	A0_02_C08C22_ALMN	A0_02_C08C24_ALMG	A0_02_C08C27_ALCA
A0_02_C10C14_FECR	A0_02_C10C16_FEFE	A0_02_C10C22_FEMN	A0_02_C10C24_FEMG
A0_02_C10C27_FECA	A0_02_C14C16_CRFE	A0_02_C14C24_CRMG	A0_02_C14C27_CRCA
A0_02_C16C22_FEMN	A0_02_C16C24_FEMG	A0_02_C16C27_FECA	A0_02_C22C24_MNMG
A0_02_C22C27_MNCA	A0_02_C24C27_MGCA	A0_03_C04C27_SICA	A0_03_C08C27_ALCA
A0_03_C10C27_FECA	A0_03_C16C27_FECA	A0_03_C22C27_MNCA	A0_03_C24C27_MGCA
A0_01_C05C30_TINA	A0_01_C07C30_CRNA	A0_01_C08C30_ALNA	A0_01_C10C30_FENA
A0_01_C14C30_CRNA	A0_01_C16C30_FENA	A0_01_C22C30_MNNA	A0_01_C24C30_MGNA
A0_01_C27C30_CANA	A0_03_C00C30_21_NA2F2	A0_03_C00C14_11_CRF2	A0_03_C00C07_23_CR2F6
A0_03_C00C05_12_TIF4			

The notation for constituent is in the form of A0_kk_CiiCjj_uv_Text, where kk is the anion index number, ii is the cation1 index number, jj is the cation2 index number, u and v are stoichiometries of cation and anion (when ii=00), text is the normal string. For example,

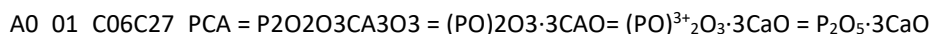
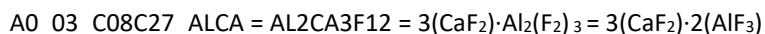
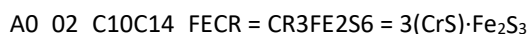
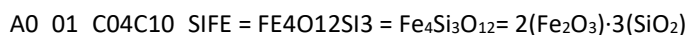
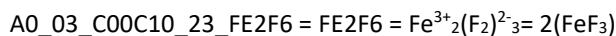
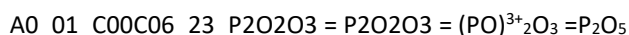


Table 2. Index for anions (kk)

1	2	3
O ²⁻	S ²⁻	(F ₂) ²⁻

Table 3. Index for cations (ii or jj)

1	2	3	4	5	6	7	8	9	10
	P ⁵⁺		Si ⁴⁺	Ti ⁴⁺	(PO) ³⁺	Cr ³⁺	Al ³⁺		Fe ³⁺
11	12	13	14	15	16	17	18	19	20
			Cr ²⁺		Fe ²⁺				
21	22	23	24	25	26	27	28	29	30
	Mn ²⁺		Mg ²⁺			Ca ²⁺			Na ¹⁺

The Dilute Liquid Iron Phase

The FE_LIQUID phase was evaluated based on Sigworth-Elliott dilute model [1974], where the epsilon parameters had been transited into the regular solution parameter according to Hillert [1986]. It was intended for the application in low-alloy steels. It seems work well in stainless steel as well in combination with the slag phase. However, FE_LIQUID is not compatible with some solid metallic phases such as ferrite and austenite.

Application Examples

Slag Phase Stability Region and Thermodynamic Activities of Component Oxides

Since this database includes a well-assessed liquid slag phase and many stoichiometric solid (oxides, silicates, sulphides etc.) phases, it can be used to study the phase equilibrium especially the solubility region of the liquid slag phase, and the chemical activities of component oxides. Figure 1 shows the activities of FeO in the system CaO-FeO-SiO₂ in equilibrium with iron at 1550 °C. Figure 1a represents the present calculation, where the digits inside bracket stands for the activity value, the black curves indicates the homogeneity region of the slag phase and the colour curves illustrate the equilibria between the liquid slag and solid phases. Figure 1b is the corresponding experimental information by Timucin and Morris [1970].

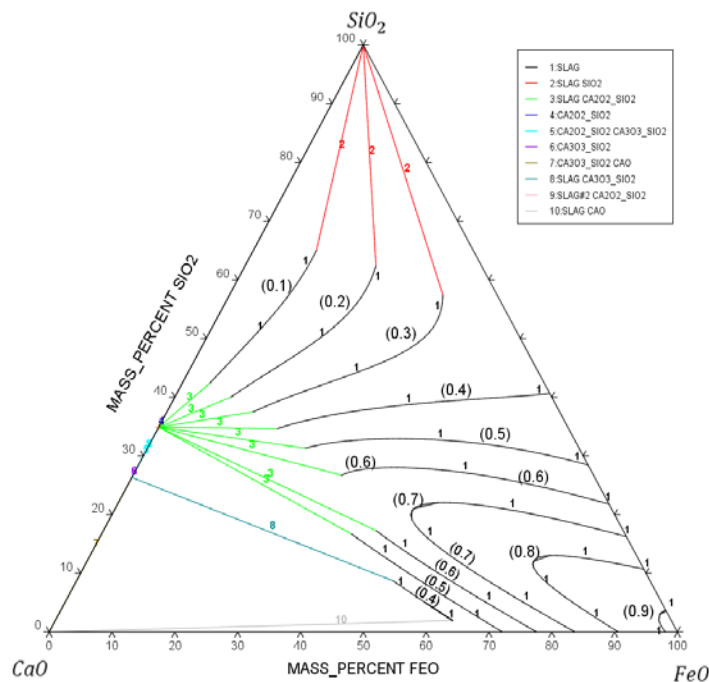


Figure 1a. Iso-activities of FeO in the CaO-FeO-SiO₂ system. 1a). Calculations according to SLAG4.

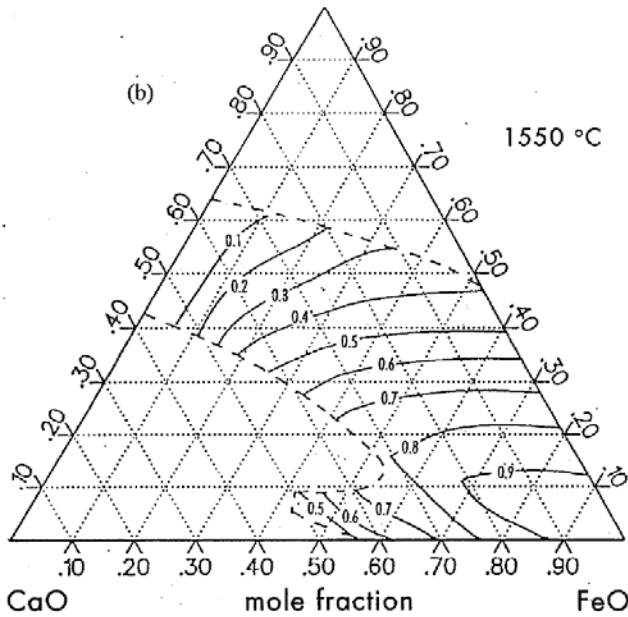


Figure 1b. Experiments of Timucin and Morris [1970].

Calculation tips: Go to POLY-3 and define the components as CaO, FeO, SiO₂, Fe. Suspend the gas and FE_LIQUID phases. Set ACR(Fe, Fe_Liquid)=1 assuming the slag phase in equilibrium with liquid iron. Set slag as the reference for FeO. Give the value to ACR(FeO) as a condition. The command STEP will calculate the isocontour curve at given ACR(FeO) value. Use the command ADD_INITIAL_EQUILIBRIUM to obtain a complete figure for various activities.

Sulphide Capacity of Metallurgical Slags

Based on IRSID slag phase description Gaye [1992] calculated the sulphide capacities and compared with hundreds of experimental data in the Al₂O₃-CaO-FeO-Fe₂O₃-MgO-MnO-SiO₂ system, see Figure 2.

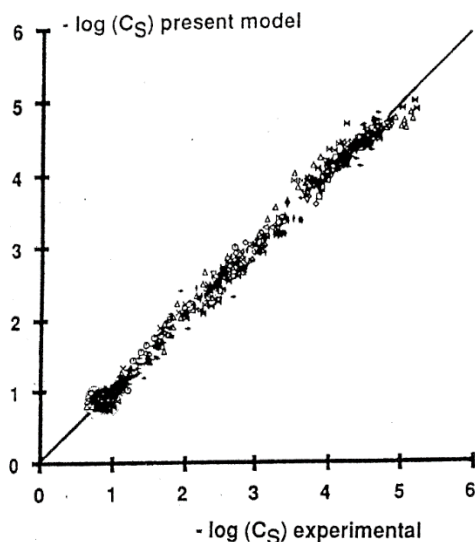


Figure 2. Comparison of experimental and calculated sulphide capacity [1992, Gaye].

Calculation tips: Go to POLY-3 and suspend all phases except the gas and the liquid slag. The sulphide capacity (CS) can be estimated by the function $CS=100*w(\text{slag},S)*SQRT(ac(O2,\text{gas})/ac(S2,\text{gas}))$.

Phosphorus Distribution Between the Steelmaking Slags and FE_LIQUID

The SLAG database can be used to estimate the phosphorus solubility in liquid iron which is in equilibrium with steelmaking slag. *Figure 3* compares the phosphorus solubility estimated based on SLAG and the corresponding experimental data in the Ca-Fe-Mg-O-P-Si system.

Calculation tips: Go to POLY-3 and define the components as SiO₂, CaO, MgO, Fe, P and O. Suspend all phases except the liquid slag phase and some refractory solid phases such as CaO and MgO. Set ACR(Fe, Fe_Liquid)=1 assuming the slag phase in equilibrium with liquid iron. Using the experimental equilibrium slag composition, i.e. w(SiO₂), w(CaO), w(MgO) and w(P), for the overall composition of the system. Set gas as the reference state for P. Calculate the P activity ACR(P) or its logarithm LNACR(P). Adopt the Gibbs energy change for the reaction $0.5 \cdot P_2$ (gas) = [P] (1 wt% P in FE_LIQUID) as DGP2L=-122200-19.25*T (Chen, Zhang and Lehmann, 2013). The P activity with 1 wt% P as the standard state can be derived as PSTEEL = EXP(LNACRPL), where LNACRPL = LNACR(P) - DGP2L/(8.314*T). The value of the function PSTEEL is directly comparable to the experimental wt% of P in liquid steel since in most cases the solubility is far below 1%.

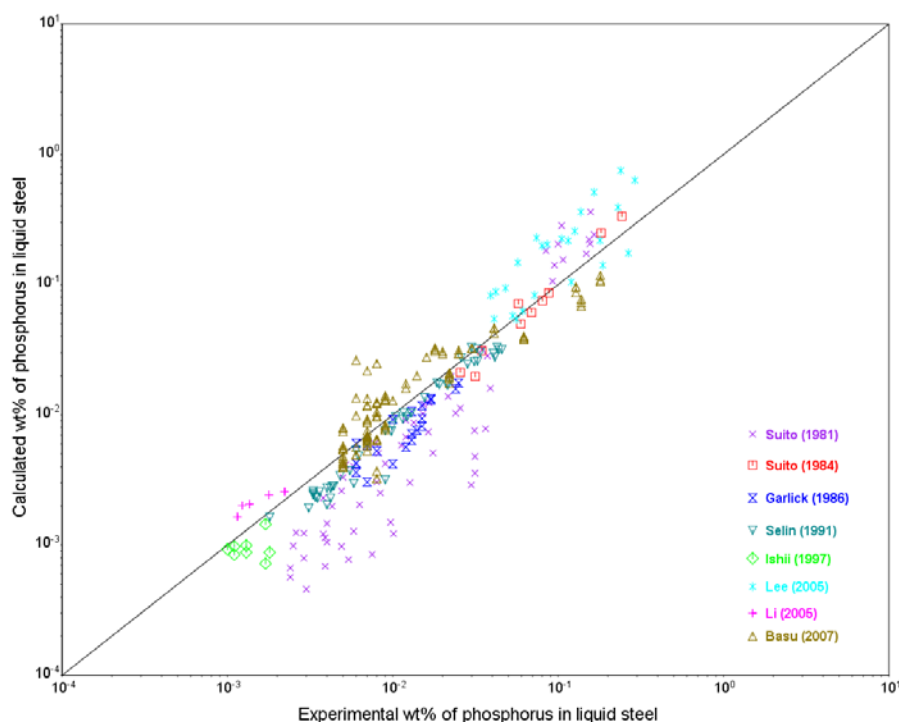


Figure 3. Comparison of experimental and calculated phosphorus solubility in liquid iron in equilibrium with slag in the Ca-Fe-Mg-O-P-Si system.

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