The Data Clearing House
in the

Li-battery project

Klaus Hack & Michael Schick, GTT-Technologies, Herzogenrath

The WeNDeLIB project

Materials with New Design for Improved Lithium Ion Batteries

Priority Program 1473 of the German Research Foundation

Program Commission:

Hans Jürgen Seifert	KIT Karlsruhe (Chair)
Rainer Schmid-Fetzer	TU Clausthal (Co-Chair)
Martin Winter	Uni Münster (Co-Chair)

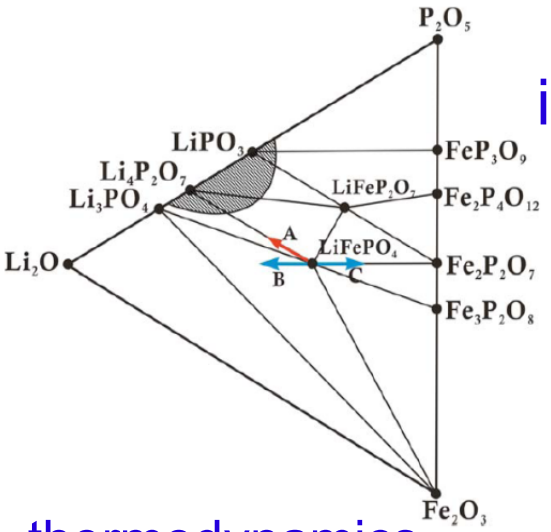
International Member:

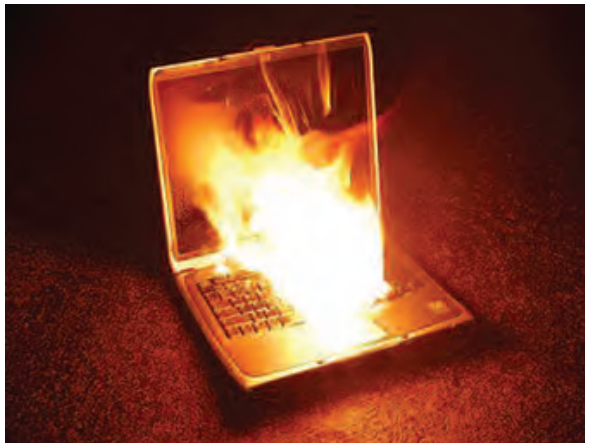
Alexandra Navrotsky	University of California, Davis

The WeNDeLIB project

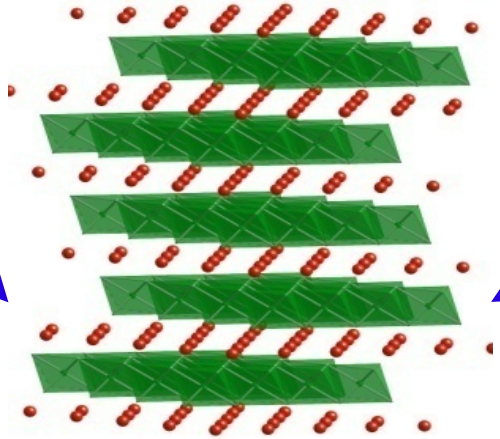
scientific aim:

interdisciplinary work





thermodynamics
constitution
kinetics



electrochemical performance, safety of batteries and cells

crystal structures, crystal chemistry, microstructure, reactivity

Source of images: H. Seifert, KIT Karlsruhe

Major Tasks of *Clearing House*

GTT-Contribution:

- **Provision of information on „thermochemistry“:**
  data for various chemical subsystems of WeNDeLIB
  → use of the online cooperation tool (LIBworks)

- **Translation of thermochemical base-data:**
  data available for chemical systems (databases)
  → translation into various formats:
  FactSage, ChemSage, Pandat, ThermoCalc

- **Check of thermochemical third party data:**
  → check for consistency and correctness

Provided Information on “Thermochemistry”

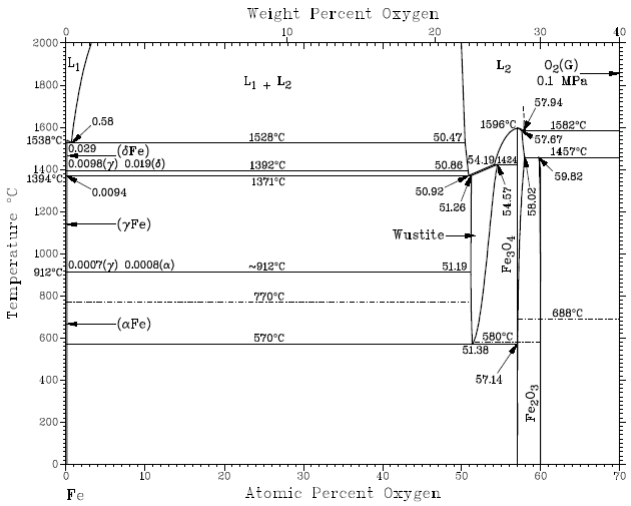
-System lists

-Base data (from standard sources)

-Phase diagrams

-Reports on data assessments
- Phase lists
- Phase diagrams
- Literature references

-Thermodynamic databases




```
$ From database: User data 2011. 7.27
 ELEMENT /-   ELECTRON_GAS              0.0000E+00  0.0000E+00  0.0000E+00!
 ELEMENT VA   VACUUM                    0.0000E+00  0.0000E+00  0.0000E+00!
 ELEMENT CU   FCC_A1                    6.3546E+01  5.0041E+03  3.3150E+01!
 ELEMENT FE   BCC_A2                    5.5847E+01  4.4890E+03  2.7280E+01!
 ELEMENT O    1/2_MOLE_O2(G)            1.5999E+01  4.3410E+03  1.0252E+02!
 SPECIES CU+1                          CU1/+1!
 SPECIES CU+2                          CU1/+2!
 SPECIES CU2O                          CU2O1!
 SPECIES CUO                           CU1O1!
 FUNCTION GFE3O4 2.98150E+02 -161731+144.873*T-24.9879*T*LN(T)
                             -.0011952256*T**2+206520*T**(-1);  3.00000E+03  N !
 FUNCTION BFE3O4 2.98150E+02 +46826-27.266*T;  3.00000E+03  N !
 FUNCTION GCUFE2O4 2.98150E+02 +139.6201*T-139.6201*T*LN(T)-.0588898*T**2
      +1171520*T**(-1)-967968-146.758*T-54721.2+843.794*T+20000;
          6.75000E+02  Y
      +227.191*T-227.191*T*LN(T)-897390-295.737*T-153353.925+1480.08409*T
      +20000;  7.95000E+02  Y
      +166.021*T-166.021*T*LN(T)-.0205015*T**2-870127-332.912*T-144944.156
      +1141.34242*T+20000;  9.53000E+02  Y
      +166.021*T-166.021*T*LN(T)-.0205015*T**2-870127-332.912*T-144944.156
      +1141.34242*T;  1.35800E+03  Y
      +225.936*T-225.936*T*LN(T)-738753-454.502*T-306821.088+1629.84996*T;
          3.00000E+03  N !
```

Provided Information on "Thermochemistry"

Base files on LIBworks (online):

General CompoundData.xls		→ numeric compd. data
GeneralCompoundData.doc		→ comments on compd. data
Sy-St-Em_Constituents_SpeciesList.txt		→ list of species + const. in a system
Sy-St-Em_Author_assess.pdf		→ complete thermodyn. assessments
Sy-St-Em_ThermoCalc.tdb	(TC)	→ databases
Sy-St-Em_ChemSage.dat	(ChemSage)	
NaMeBASE.CDB	(FactSage)	
NaMeSOLN.SDB	(FactSage)	
Sy-St-Em_SGTE_Lit.txt		→ lists of literature references

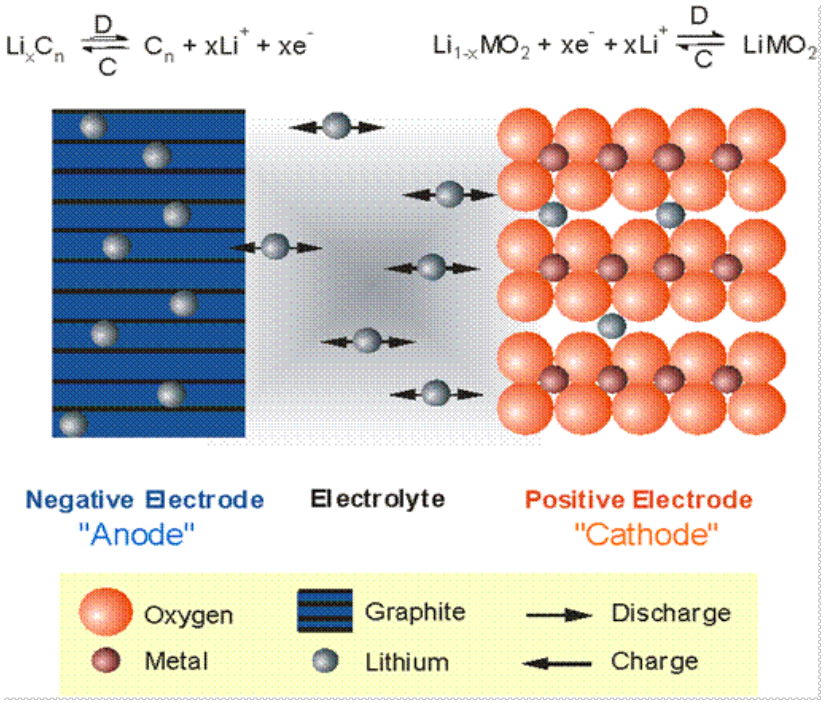
Relevant Systems for WeNDeLIB

Cathode materials:

Li-Mn-Co-Ni-O (+Mg(?), Al)
Li-Fe-P-O (+Al)
Si-C-N-O

Anode materials:

Co-Li-Sn
Cu-Li-Sn
Li-Ni-Sn
Li-Si-C
Li-Sn-C



Conversion electrodes

Li-Cu-Fe-O

Source of image: H. Seifert, KIT Karlsruhe

System Lists

The Cathode II System : Li-Fe-P-O (+Al)

Binary Subsystems (6/10)

Li-Fe, Li-P, Li-O, (Li-Al)
Fe-P, Fe-O, (Fe-Al)
P-O, (P-Al)
(O-Al)

Ternary Subsystems (4/10)

Li-Fe-P, Li-Fe-O, (Li-Fe-Al)
Li-P-O, (Li-P-Al)
(Li-O-Al)
Fe-P-O, (Fe-P-Al)
(Fe-O-Al)
(P-O-Al)

Quaternary Subsystems (1/5)

Li-Fe-P-O, (Li-Fe-P-Al)
(Li-Fe-O-Al)
(Li-P-O-Al)
(Fe-P-O-Al)

Quinary Subsystems (1)

(Li-Fe-P-O-Al)

Check of completeness with combinatorial mathematics

$N_{53} = 5! / (3!\ 2!) = 10$

$N_{52} = 5! / (2!\ 3!) = 10$

Sources of Base Data (Pure Substances)

Search in Standard Databases:
Li-containing compounds in the system Al-C-Fe-Li-N-O-P-Si:
(relevant for anode and cathode materials, Co,Cu,Mn,Ni and Sn missing yet)

- SGTE → 144 entries

- FACT → 109 entries
  → SGTE is used

Sources of Base Data (Pure Substances)

SGTE list of compounds in Al-C-Fe-Li-N-O-P-Si system

Unary:

Al(SLG), Al_2(G), C(SLG), C_2(G), C_3(G), C_4(G), C_5(G), C_{60}(SG), Fe(SLG), Fe_2(G), Li(SLG),Li_2(G), N(G), N_2(G), N_3(G), O(G), O_2(G), O_3(G), P(SLG), P_2(G), P_3(G), P_4(G), Si(SLG), Si_2(G), Si_3(G)

Binary:

AlC(G), AlC_2(G), Al_2C_2(G), Al_4C_3(S), AlLi(S), AlN(SG), Al_2O(G), AlO(G), Al_2O_2(G), Al_2O_3(SLG), AlO_2(G), AlP(SG), AlP_2(SG), … , Si_2P_2(G)

Ternary:

Al_2CO(G), Al_4CO_4(S), $AlPO_4$(S), Al_2SiO_5(S), $Al_2Si_2O_7$(S), $Al_6Si_2O_{13}$(S), CNO(G), $FeAl_2O_4$(S), $FeCO_3$(S), $Fe(CO)_5$(LG), $FePO_4$(SL), $FeSiO_3$(S), Fe_2SiO_4(SL), $LiAlO_2$(SL), $Li_2Al_2O_4$(S), …, Si_2N_2O(S)

Quaternary: $Li_2Al_2Si_2O_8$(S), $Li_2Al_2Si_4O_{12}$(S)

Base Data for Elements and Compounds

example: Fe (bcc and fcc phase)

- enthalpies and entropies of formation
- enthalpies, entropies and temperatures of transition
- magnetic properties
- polynomials for $c_p(T)$ and $G(T)$

347	Compound	Fe									
348	Phase	BCC_A2	$\Delta H^{trans}_{FCC\_A1 \rightarrow BCC\_A2} / J \cdot mol^{-1}$	825.8	magn. Properties						
349	$\Delta H^{f}_{298} / J \cdot mol^{-1}$	9149.45 + H magnetic	$\Delta S^{trans}_{FCC\_A1 \rightarrow BCC\_A2} / J \cdot mol^{-1} \cdot K^{-1}$	0.459	T_c (Curie) /K	1043					
350	$S_{298} / J \cdot K^{-1} mol^{-1}$	38.863499 + S magnetic	$T^{trans}_{FCC\_A1 \rightarrow BCC\_A2} / K$	1667.47	magn. moment β	2.22					
351					p-factor	0.4					
352					structure factor	1.0					
353	Function	T^0	T^1	$T \ln T$	T^2	T^3	T^{-1}	T^{-2}	T^{-9}	T^{-10}	T-Range/K
354	$c_p(T)$	23.5143	8.79504E-03		3.53562E-07			-154718			298.15-1811
355		46								-2.066427E+33	1811-6000
356		45.999966									6000-6001
357			$+c_p$ magnetic								
358											
359	$G(T)$	1225.69998474632	124.1339996578	-23.5143	-4.39752E-03	-5.8927E-08	77359				298.15-1811
360		-25383.5790910647	299.312551966292	-46					2.29603E+31		1811-6000
361		-25383.3523077817	299.312218765298	-45.999966							6000-6001
362			+G magnetic								
390	Compound	Fe									
391	Phase	FCC_A1	$\Delta H^{trans}_{BCC\_A2 \rightarrow FCC\_A1} / J \cdot mol^{-1}$	1012.9	magn. Properties						
392	$\Delta H^{f}_{298} / J \cdot mol^{-1}$	7973.03 + H magnetic	$\Delta S^{trans}_{BCC\_A2 \rightarrow FCC\_A1} / J \cdot mol^{-1} \cdot K^{-1}$	0.855	T_c (Neel) /K	67					
393	$S_{298} / J \cdot K^{-1} mol^{-1}$	35.902103 + S magnetic	$T^{trans}_{BCC\_A2 \rightarrow FCC\_A1} / K$	1184.81	magn. moment β	0.7					
394					p-factor	0.28					
395					structure factor	3.0					
396	Function	T^0	T^1	$T \ln T$	T^2	T^3	T^{-1}	T^{-2}	T^{-9}	T^{-10}	T-Range/K
397	$c_p(T)$	23.5143	8.79504E-03		3.53562E-07			-154718			298.15-1811
398		46								-2.066427E+33	1811-6000
399		45.999966									6000-6001
400			$+c_p$ magnetic								
401											
402	$G(T)$	1225.69998474632	124.1339996578	-23.5143	-4.39752E-03	-5.8927E-08	77359				298.15-1811
403		-25383.5790910647	299.312551966292	-46					2.29603E+31		1811-6000
404		-25383.3523077817	299.312218765298	-45.999966							6000-6001
405			+G magnetic								

Reports on Data Assessments

Thermodynamic assessment from WeNDeLIB (Cu-Fe-O)

Alexandra V. Khvan, Olga B. Fabrichnaya, Galina Savinykh, Robert Adam, Hans J. Seifert, JPEDAV **32(6)** (2011) 498

system components:

1: Cu	2: Fe	3: O
4: e(HALITE)	5: e(SPINEL)	

mixture phases:

1: GAS	2: IONIC_LIQ	3: BCC_A2
4: FCC_A1	5: HALITE	6: SPINEL

stoichiometric condensed phases:

1: CORUNDUM	2: Cu2O	3: CuO
4: DIAMOND_A4	5: F5_1	6: HCP_A3
7: SP2		

Reports on Data Assessments

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GAS	Model IDMX:	<O2>
IONIC_LIQ	Model SUBI:	<Cu+1, Cu+2, Fe+2>p <O-2, Va, FeO3/2>q
BCC_A2	Model SUBL:	<Cu, Fe>1.000 <O, Va>3.000
FCC_A1	Model SUBL:	<Cu, Fe>1.000 <O, Va>1.000
F5_1	Model STCO:	< Cu+1>1.000 <Fe+3>1.000 <O-2>2.000
HALITE	Model SUBL:	<Fe+2, Fe+3, Va>1.000 <O-2>1.000
SPINEL	Model SUBL:	<Cu+1, Cu+2, Fe+2, Fe+3>1.000 <Cu+2, Fe+2, Fe+3>2.000 <O-2>4.000
SP2	Model STCO:	<Cu+2>1.000 <Fe+3>2.000 <O-2>4.000

Translation of Thermochemic Base Data

Translation of Thermocalc data (TDB-file) into database for FactSage is a two step process:

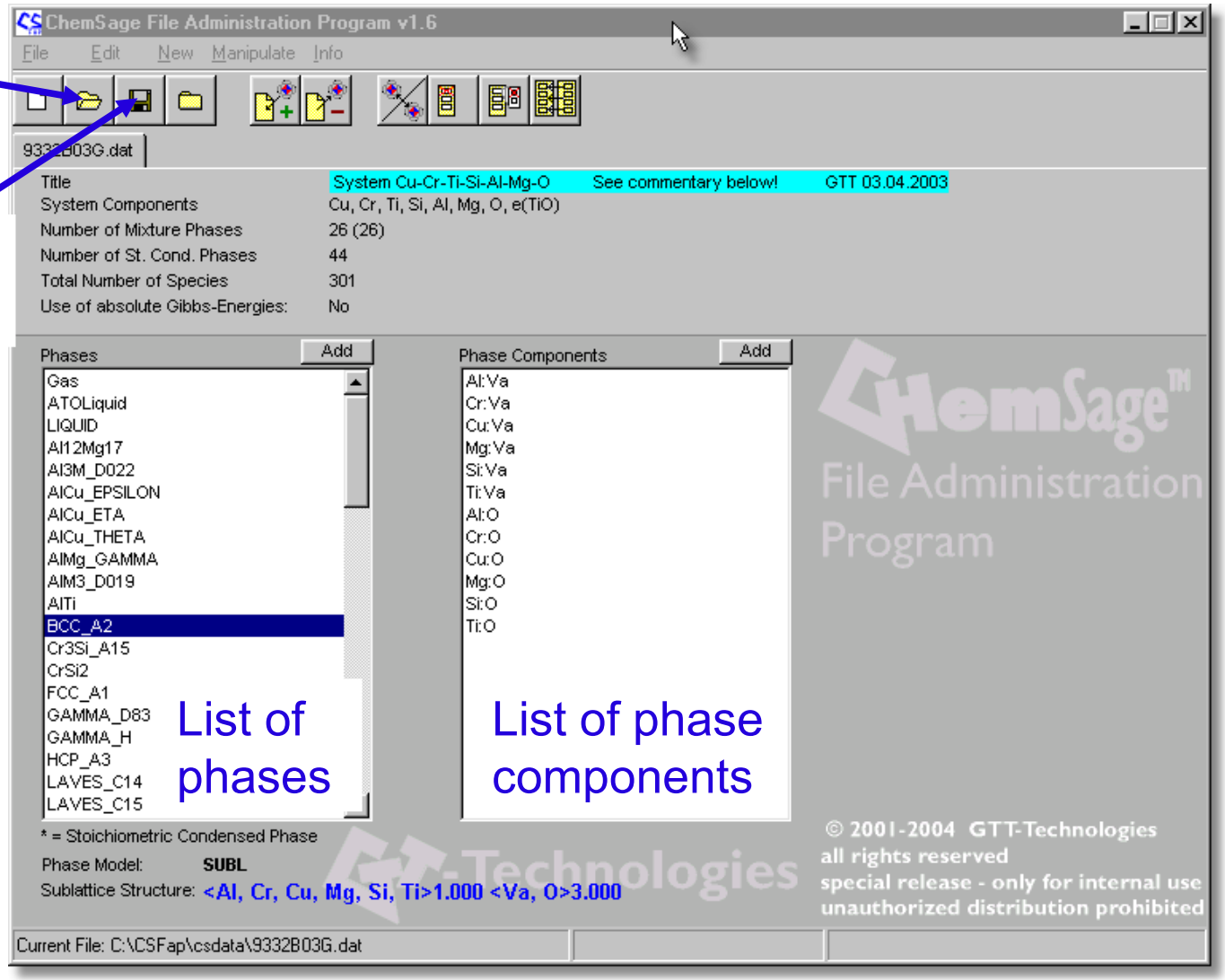
1) TDB → ChemSage using CSFAP

2) ChemSage → FactSage using Equilib feature

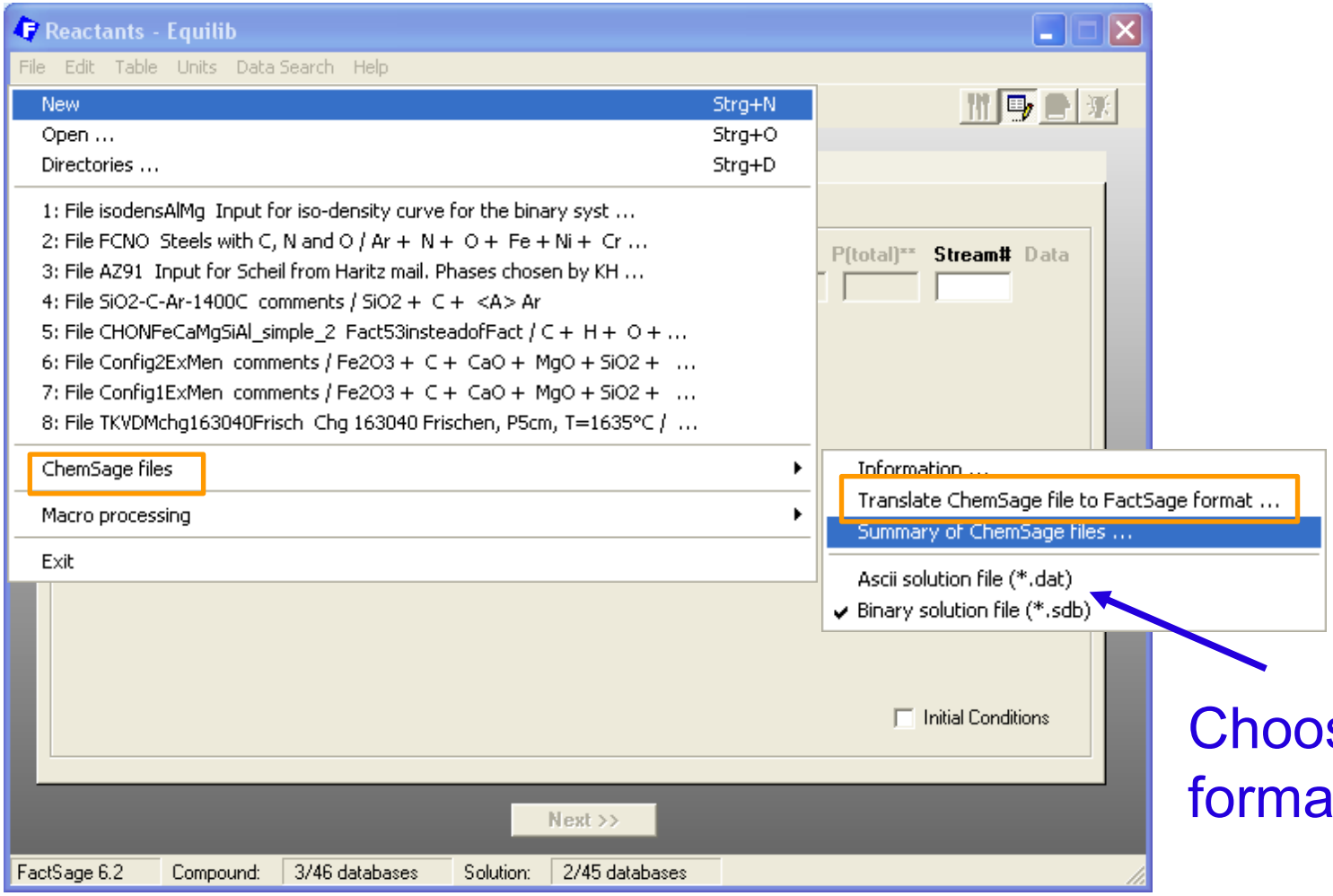
Translation of Thermochemical Base Data

Load database file (tdb)

Choose output format + save



Translation of Thermochemic Base Data



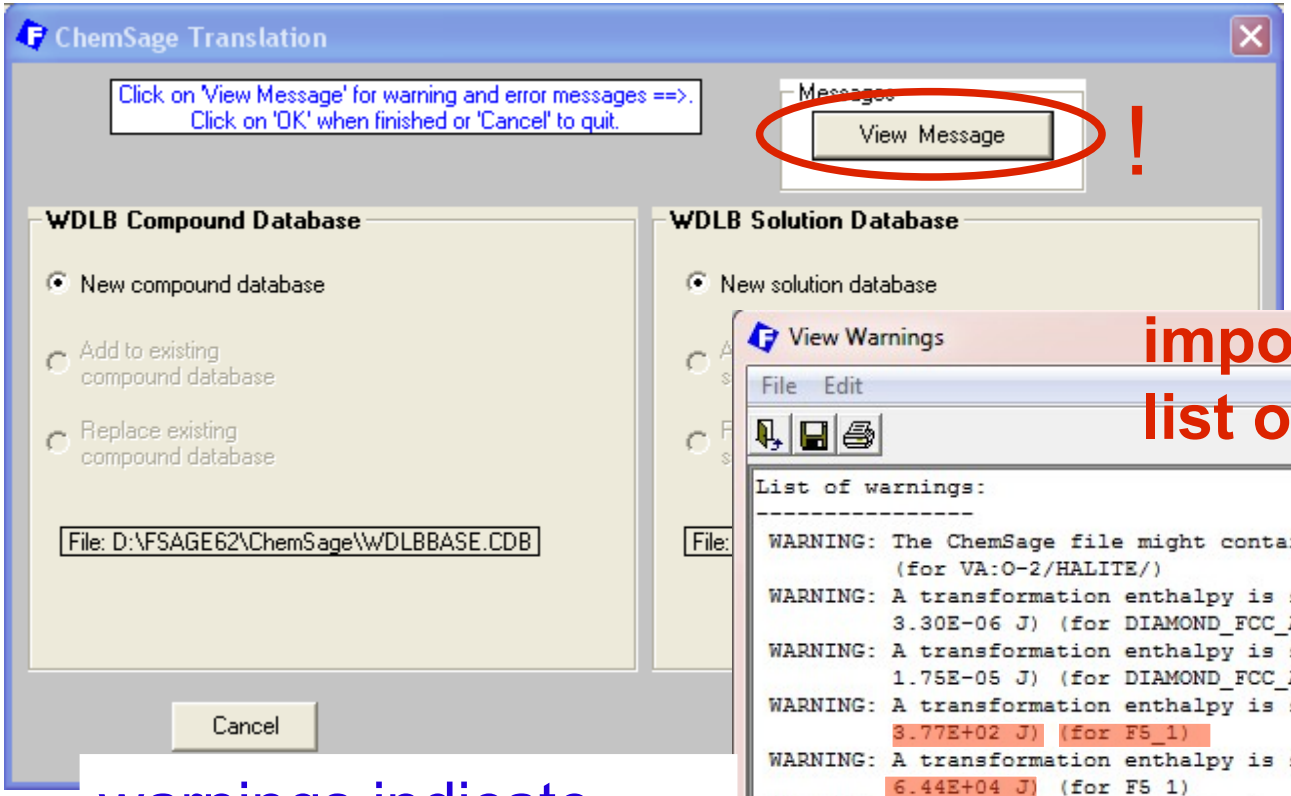
Choose output format

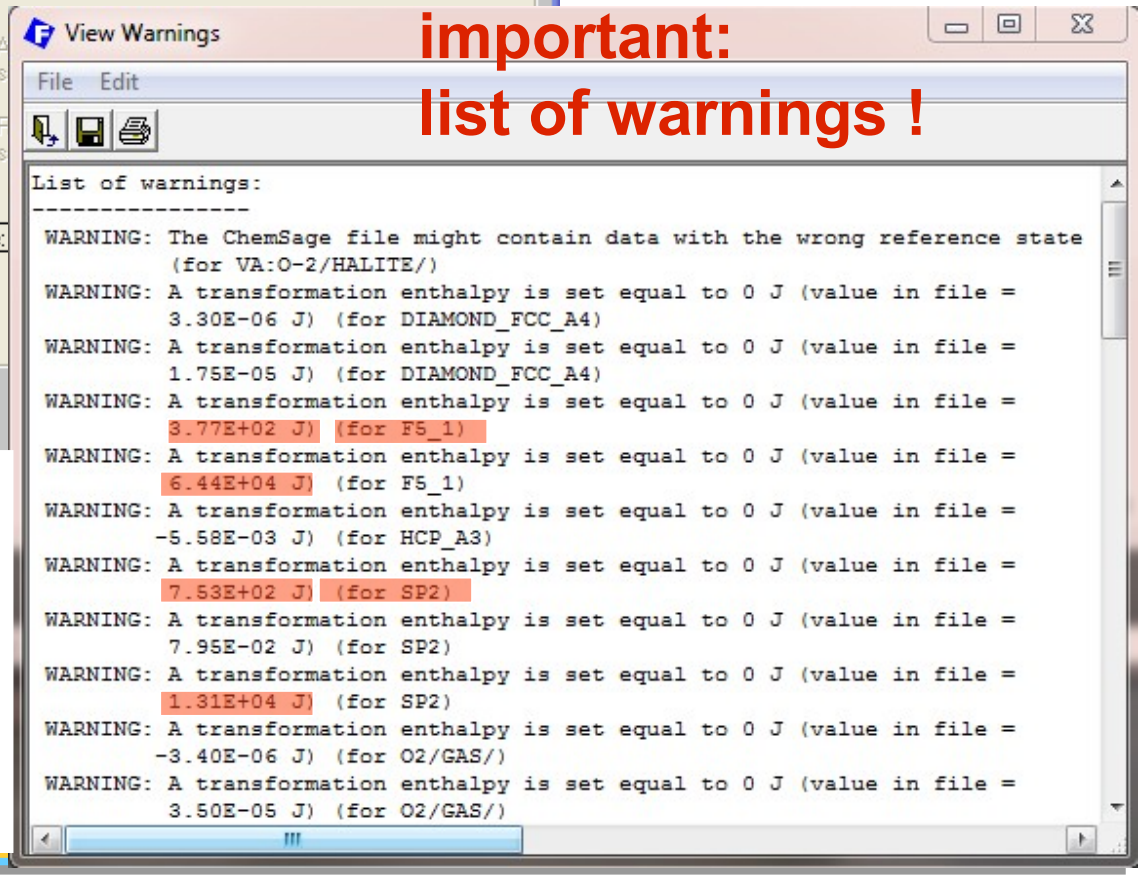
Translation of Thermochemic Base Data

ChemSage format (dat)

```
Cu-Fe-O system
   5   6    1   9   4   4   3  12    7
 Cu                          Fe                          O
 e(HALITE)                   e(SPINEL)
 63.546                      55.847                      15.999
 0.0005                      0.0005
...
 SPINEL
 SUBL
 (Cu+1)1(Cu+2)2(O-2)4
  13  5    3.0   0.0   4.0   0.0   3.0
  675.0  -5.821523177E+05  393.3686773  -69.0297 -0.1599362416 0.0  6.2328E+05
  795.0  -6.663164927E+05 2118.0146473 -331.7424  0.0167331584 0.0 -2.89128E+06
  953.0  -5.592981857E+05  806.7546373 -148.2324 -0.0447713416 0.0 -2.89128E+06
  1358.0 -6.192981857E+05  806.7546373 -148.2324 -0.0447713416 0.0 -2.89128E+06
  3000.0 -7.108069817E+05 2087.2522573 -327.9774  0.0167331584 0.0 -2.89128E+06
  ...
  3
   1.0000  2.0000  4.0000
  4      3      1
  Cu+1                        Cu+2                        Fe+2
  Fe+3
  Cu+2                        Fe+2                        Fe+3
  O-2
```

Check of Thermochemic Base Data





important:
list of warnings !

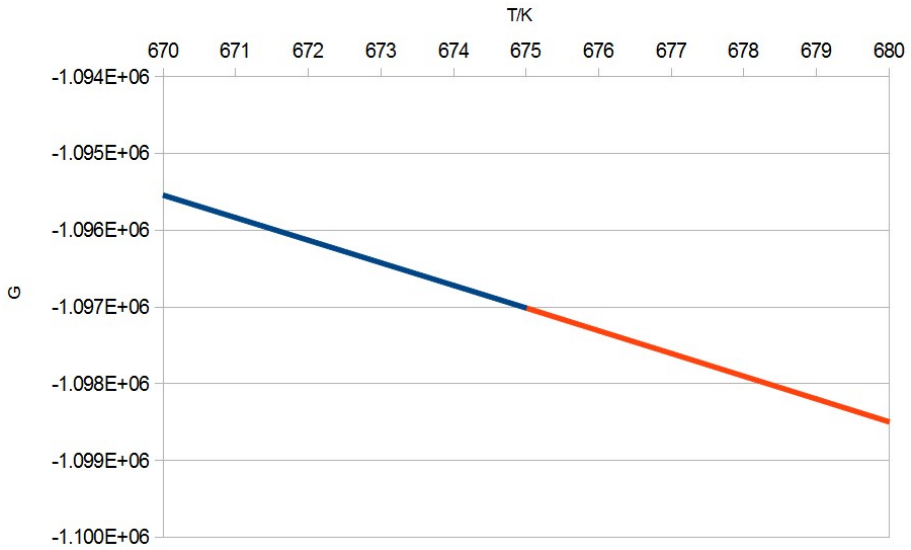
warnings indicate kinks in Gibbs-energy functions

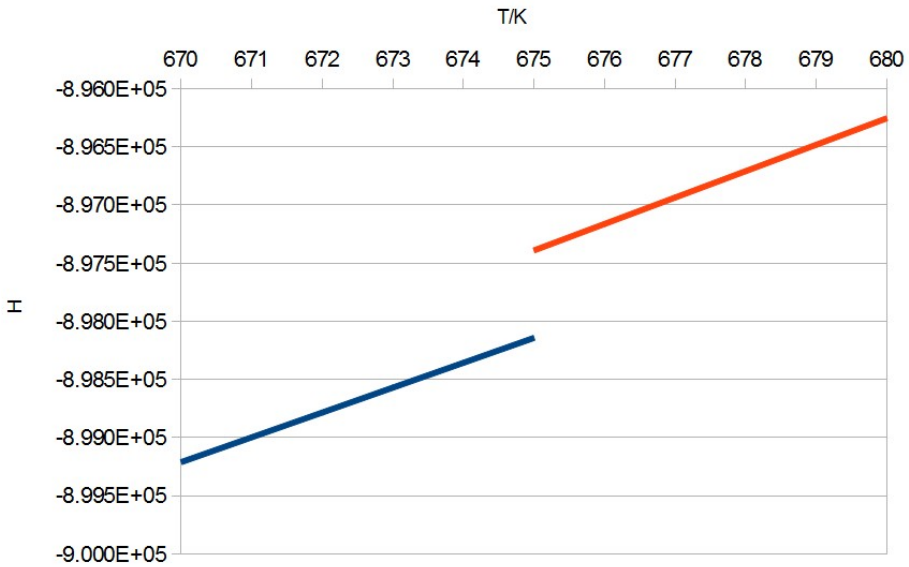
→ jumps in enthalpy functions

Check of Thermochemic Base Data

system Cu-Fe-O, phase SP2:
examination of function GSP2CUFE

Intervals: 298.15 – 675 K, 675 – 795 K,
795 – 1358 K, 1358 – 3000 K





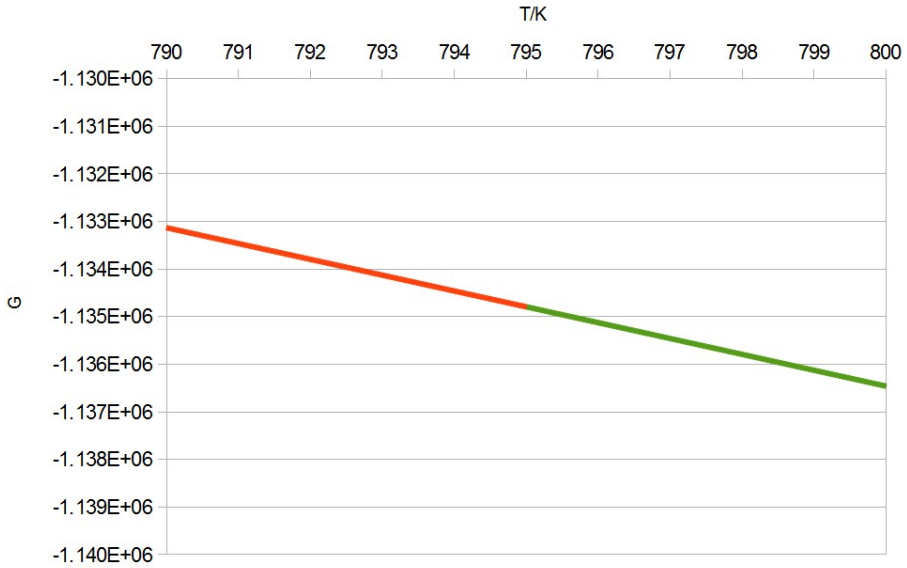
Gibbs-energy *G*
difference: 0.30 J

enthalpy *H*
difference: **752.8 J**

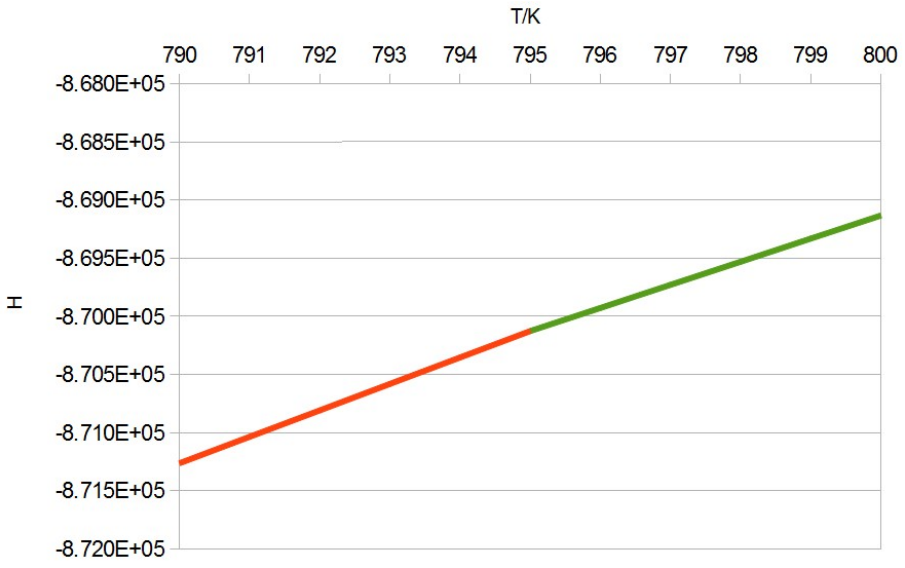
Check of Thermochemic Base Data

system Cu-Fe-O, phase SP2:
examination of function GSP2CUFE

Intervals: 298.15 – 675 K, 675 – 795 K,
795 – 1358 K, 1358 – 3000 K



Gibbs-energy *G*
difference: 0.18 J

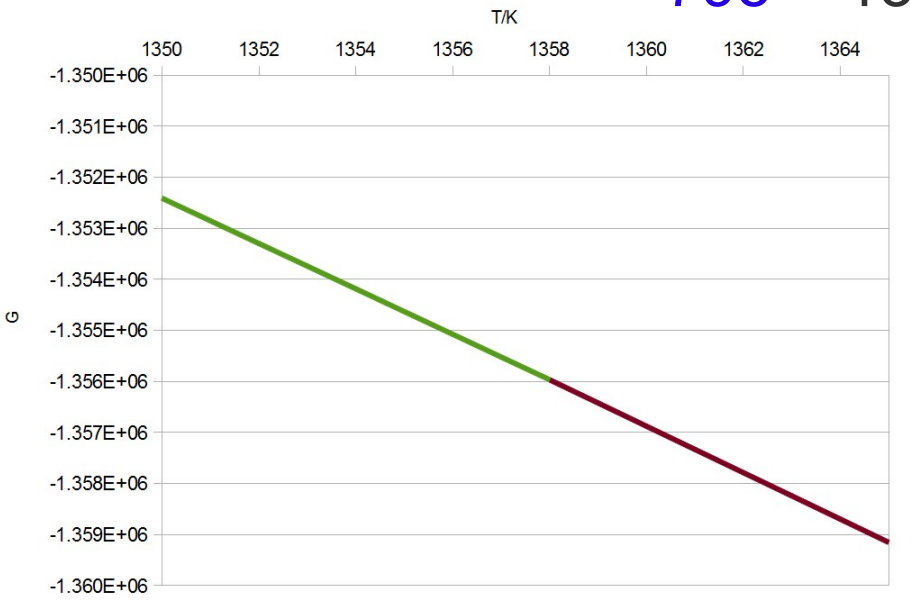


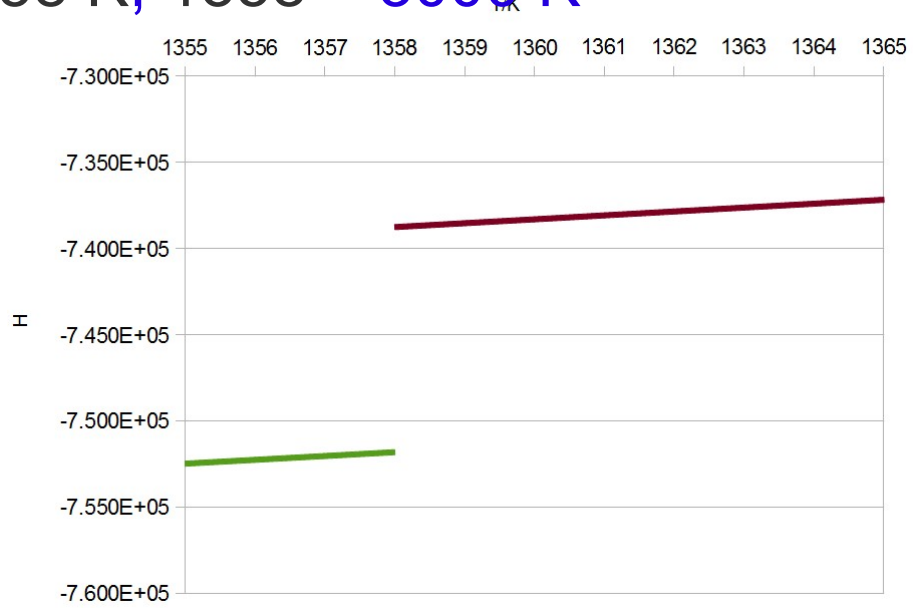
enthalpy *H*
difference: $7.95*10^{-2}$ J

Check of Thermochemic Base Data

system Cu-Fe-O, phase SP2:
examination of function GSP2CUFE

Intervals: 298.15 – 675 K, 675 – 795 K,
795 – 1358 K, 1358 – 3000 K





Gibbs-energy *G*
difference: 1.37 J

enthalpy *H*
difference: **$1.305*10^4$ J !**

Check of Thermochemic Base Data

Jumps in *G*, *H* (and *S*) functions of single phase

→ thermodynamically not permitted (intrinsic phase transitions)

Such databases are not recommended for calculation !

Conclusion

Clearing House

- **central information hub**:
  provision of thermochemical information on systems for **WeNDeLIB**
- **translation service**:
  translation of databases for thermodynamic systems
- **checkpoint:**
  check of thermodynamic data used in the project

Thank you for your attention !