

Exporting emc2 Data to PARROT Module (Thermo-Calc) for CALPHAD Optimization: An Example for the hcp Phase in Al-Ti System

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Background: To export the output of emc2 to PARROT module (in Thermo-Calc) for CALPHAD optimization, the user has to perform three following tasks. First, to select the desired mixing property (enthalpy or free energy of mixing). Also, the user has to decide whether to include the effect of short range order (sro) on the mixing property. Second, to convert the unit of thermodynamic quantities, such as heat of mixing and free energy of mixing, from eV/atom (in emc2) to J/mol (for Thermo-Calc). Third, to introduce a linear correction term for the end points. In the following example, the hcp phase in Al-Ti system, we demonstrate how this is done.

1. The input file for the hcp structure (or lat.in) for maps run

```
2.93 2.93 4.71 90 90 120
1 0 0
0 1 0
0 0 1
0 0 0 Al,Ti
0.66666666 0.33333333 0.5 Al,Ti
```

Note: Here, Al and Ti is defined as the first and second element. Therefore, all compositions defined below are mole fraction of Ti. On the other hand, if the elements were defined in the sequence Ti,Al, then the compositions defined below would have been mole fraction of Al.

2. The output file for the hcp phase fit.out after maps run

```
x(Ti)      E_VASP      E_CE      ΔE
0.000000  0.000000  -0.023145  0.023145  1.000000  0
1.000000  0.000000  0.016285  -0.016285  1.000000  1
0.500000  -0.275442  -0.259697  -0.015745  1.000000  2
-----
-----
-----
```

Note: After cluster expansion (CE), we find that the fitted formation energies (E_{CE}) of pure components (Al and Ti) are not zero, even though ideally they should be zero when we consider the mixing properties. Therefore, it is necessary to introduce a linear correction term to account for this fitting artefact.

3. Unit conversion and a linear correction term

Suppose, after cluster expansion of the hcp phase we have performed a monte carlo simulation at 1000 K using emc2 and the output file is mc_AlTi_HCP_1000.out, then

Case I: Thermodynamic properties with sro

I.a: To create a table of x(Ti) and free energy of mixing in J/mol: w.r.t. HCP-Al and HCP-Ti

```
awk '{print ((1+$4)/2), ($5+$2*$4)}' mc_AlTi_HCP_1000.out > tc_AlTi_HCP_1000.out
awk '{print ($1), (($2-(1-$1)*(-0.023145)-($1*(0.016285)))*96325)}'
tc_AlTi_HCP_1000.out > tcfe_AlTi_HCP_1000.out
```

where -0.023145 is fitted energy for Al and 0.016285 is the fitted energy for Ti (i.e., $-\Delta E$ of Al and Ti in **fit.out**), and $((\$2-(1-\$1)*(-0.023145)-(\$1*(0.016285))))$ is referred to as the linear correction term. In the tcfe_AlTi_HCP_1000.out file, column#1 is x(Ti) and column#2 is free energy of mixing in J/mol.

I.b: To create a table of x(Ti) and enthalpy of mixing in J/mol: w.r.t. HCP-Al and HCP-Ti

```
awk '{print ((1+$4)/2), ($3+$2*$4)}' mc_AlTi_HCP_1000.out > tch_AlTi_HCP_1000.out
awk '{print ($1), (($2-(1-$1)*(-0.023145)-($1*(0.016285)))*96325)}'
tch_AlTi_HCP_1000.out > tchmr_AlTi_HCP_1000.out
```

where -0.023145 is fitted energy for Al and 0.016285 is the fitted energy for Ti (i.e., $-\delta E$ of Al and Ti in **fit.out**), and $((\$2-(1-\$1)*(-0.023145)-(\$1*(0.016285))))$ is referred to as the linear correction term. In the `tchmr_AlTi_HCP_1000.out` file, column#1 is x(Ti) and column#2 is enthalpy of mixing in J/mol.

Case II: Thermodynamic properties w/o sro (i.e. random solid solutions)

II.a: To create a table of x(Ti) and free energy of mixing (of completely random solid solution i.e., no SRO contribution using high-temperature expansion) in J/mol: w.r.t. HCP-Al and HCP-Ti

```
awk '{print ((1+$15)/2), ($16+$2*$15)}' mc_AlTi_HCP_1000.out > tch_AlTi_HCP.out
awk '{print ($1), (($2-(1-$1)*(-0.023145)-($1*(0.016285)))*96325)}' tch_AlTi_HCP.out
> htefe_AlTi_HCP.out
```

where -0.023145 is fitted energy for Al and 0.016285 is the fitted energy for Ti (i.e., $-\delta E$ of Al and Ti in **fit.out**), and $((\$2-(1-\$1)*(-0.023145)-(\$1*(0.016285))))$ is referred to as the linear correction term. In the `htefe_AlTi_HCP.out` file, column#1 is x(Ti) and column#2 is free energy of mixing in J/mol.

II.b: To create a table of x(Ti) and enthalpy of mixing (of completely random solid solution i.e., no SRO contribution using high-temperature expansion) in J/mol: w.r.t. HCP-Al and HCP-Ti

```
awk '{print ((1+$15)/2), ($14+$2*$15)}' mc_AlTi_HCP_1000.out > hte_AlTi_HCP.out
awk '{print ($1), (($2-(1-$1)*(-0.023145)-($1*(0.016285)))*96325)}' hte_AlTi_HCP.out
> htehmr_AlTi_HCP.out
```

where -0.023145 is fitted energy for Al and 0.016285 is the fitted energy for Ti (i.e., $-\delta E$ of Al and Ti in **fit.out**), and $((\$2-(1-\$1)*(-0.023145)-(\$1*(0.016285))))$ is referred to as the linear correction term. In the `htehmr_AlTi_HCP.out` file, column#1 is x(Ti) and column#2 is enthalpy of mixing in J/mol.

4. Creating data table for the PARROT module (in Thermo-Calc)

After executing two awk commands listed above (i.e, as in I.a or I.b or II.a or II.b) , it is very straightforward to export corresponding thermodynamic quantities to the PARROT module of Thermo-Calc. For example, the values listed below are taken from the file `htehmr_AlTi_HCP.out` (i.e, Case II.b) at an interval of about 4 at.% Ti.

§*****

§ Example of exporting **emc2** data to create Thermo-Calc input file for PARROT optimization

§ Values of composition and enthalpy of mixing are taken from the output file “htehmr_AlTi_HCP.out”

§ i.e., Case II.b

TABLE-HEAD 10

CREATE_NEW @@,1

CHANGE_STATUS PHASE HCP=FIX, 1

SET-REF-STATUS AL HCP,,,,,

SET-REF-STATUS TI HCP,,,,,

SET-CONDITION T=1000, P=1E5, X(TI)=@1

EXPERIMENT HMR(HCP)=@2:5%

S-S-V Y(HCP,TI)=@1

TABLE_VALUE

§ here are the values of heat of mixing of the hcp phase (w.r.t. hcp-Al and hcp-Ti): no sro, or random SS

0.0 0.0

0.040283 -4117.43

0.079834 -7821.19

0.120362 -11269.7

.....

0.559814 -26237.4

0.601318 -25525.2

.....

.....

0.880615 -11200.6
0.920166 -7832.75
0.960693 -4035.05
1.0 0.0

TABLE_END

\$*****

Notes:

- Line#1,2: standard Thermo-Calc chores.
- Line#3: defines the phase (BCC or FCC or HCP, as the case may be).
- Line#4,5: define the reference states of pure elements (irrespective of the ground states of pure elements, in the case of **emc2** output the reference states are same as the structure of the phase in line#3).
- Line#6: defines the conditions for equilibrium calculations in TC (i.e., temperature, pressure and composition). For the enthalpy of mixing of a random alloy, the choice of T is not important. For example, in the above example, one could set T=500 as well without affecting the model parameters. However, this is not true when SRO is taken into account when T should be set as the temperature of MC simulation during **emc2** run.
- Line#7: HMR defines the value of enthalpy of mixing (in column#2) and the associated uncertainty (in +/- % of the value). The value of CV score of cluster expansion determines the level of uncertainty, and, of course, the level of uncertainty varies from one case to another.
- Line#8: start value composition for TC (not so important!).

The values of free energy listed below are from the file `htefe_AlTi_HCP.out` (i.e, Case II.a) at an interval of about 4 at.% Ti.

\$*****

\$ Example of exporting **emc2** data to create Thermo-Calc input file for PARROT optimization

\$ Values of composition and free energy of mixing are taken from the output file "htefe_AlTi_HCP.out", i.e., Case II.a

\$ CAUTION: in the MC simulation at 1000 K we did not consider the free energy contribution

\$ due to vibrational entropy! So, the temperature scale is inaccurate! This is just an example of exporting data!

TABLE-HEAD 100

CREATE_NEW @@,1

CHANGE_STATUS PHASE HCP=FIX, 1

SET-REF-STATUS AL HCP,,,,,

SET-REF-STATUS TI HCP,,,,,

SET-CONDITION T=1000, P=1E5, X(TI)=@1

EXPERIMENT GMR(HCP)=@2:5%

S-S-V Y(HCP,TI)=@1

TABLE_VALUE

\$ here are the values of free energy of mixing of the hcp phase (w.r.t. hcp-Al and hcp-Ti): no sro, or random SS

0.0 0.0
0.040283 -7620.11
0.079834 -13598
0.120362 -18901.8
.....
.....
0.559814 -40471.8
0.601318 -39479.6
.....
.....
0.880615 -18782.4
0.920166 -13598
0.960205 -7540.07
1.0 0.0

TABLE_END

\$*****

Notes:

- Line#6: defines the conditions for equilibrium calculations in TC (i.e., temperature, pressure and composition). For the free energy of mixing property, the choice of T is important even for a random alloy. In the MC simulation, we did not consider the contributions due to vibrational entropy. Therefore, the temperature scale is inaccurate. The user has to exercise caution while exporting such free energy data to PARROT module!
- Line#7: GMR defines the value of free energy of mixing (in column#2) and the associated uncertainty (in +/- % of the value). The value of CV score of cluster expansion determines the level of uncertainty, and, of course, the level of uncertainty varies from one case to another.