Use the **PARROT** module in Thermo-Calc software to **CALPHAD** evaluation (using As-Sn system as an example)

1. Overview

The ultimate goal of the assessment is a thermodynamic database, also known as a **TDB** file, which includes Gibbs energy descriptions for all phases in the system. The steps are as follows:

(1) Search and evaluate literature data to identify all phases and reactions in the system.

(2) For each phase, define a Gibbs energy model based on its crystal or chemical structure. Each Gibbs energy function contains a number of coefficients that are fitted to the experimental data by least square method, and the results of the calculation are saved to the SETUP file.

(3) Gather all relevant experimental data into the **POP** file.

(4) Fit the coefficients of the Gibbs energy function to the experimental data in the evaluation step. The relevant file in this step is the PAR file.
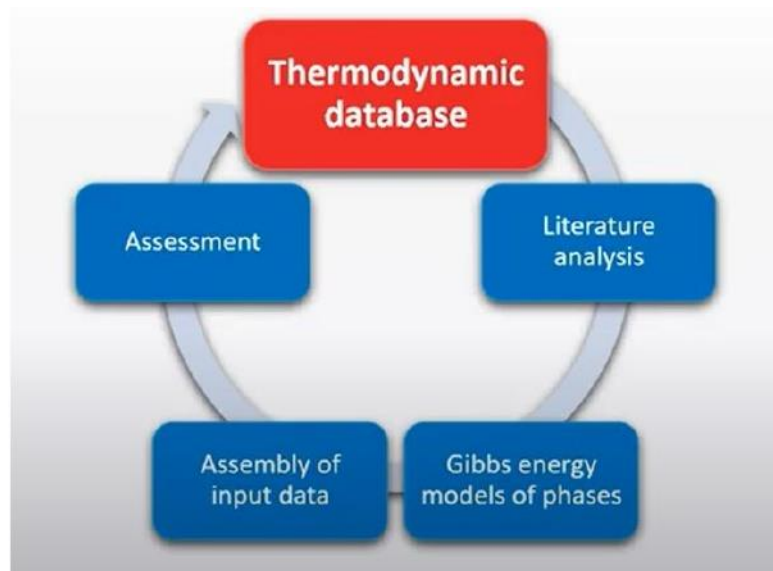

FIG.1 Schematic diagram of the **CALPHAD** evaluation process

2. Literature analysis

The experimental data used include phase diagram data (see Figure 2), such as melting point, invariant reaction, phase composition and stable region.

For example, in the As-Sn system there are two intermetallic phases, namely As_3Sn_4 and AsSn, one of which is the formation of a uniform melting compound (stableDefinite compound), and the other is formed by peritectic reaction. Two eutectic reactions and one peritectic reaction.
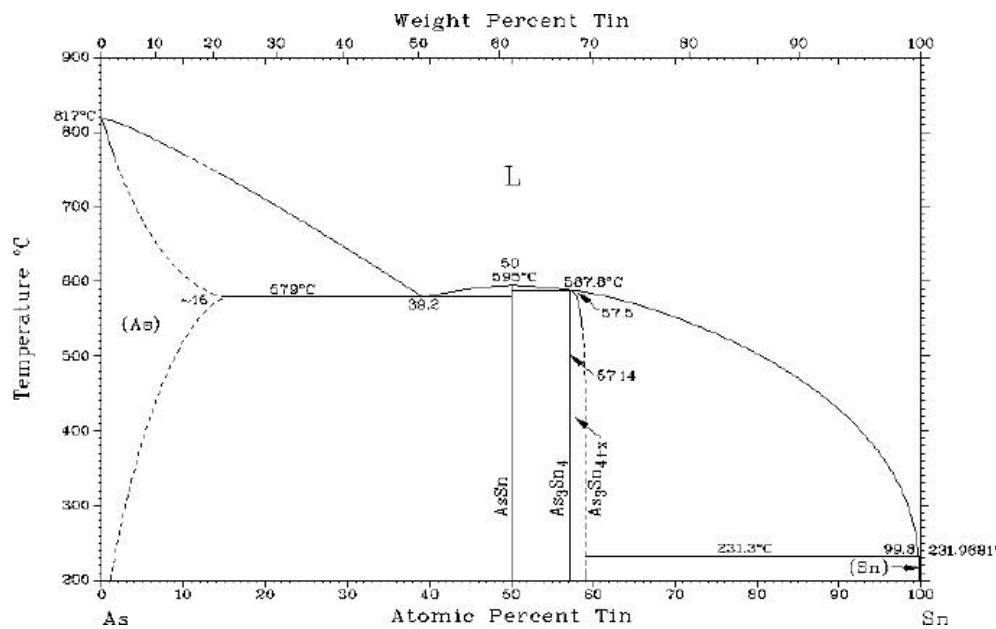

FIG.2 Phase diagram of As-Sn binary system

In addition to this, the crystal structure of each phase is needed to define its Gibbs energy model, as well as thermochemical information such as enthalpy of formation, heat capacity, etc., in order to give a consistent description of the phase diagram and thermochemistry of the system. For example, in the As-Sn system, the relationship between temperature and heat capacity of the AsSn phase is shown in Table 1.

TAB.1 Temperature and heat capacity relationship of AsSn phase

Temperature, K	For AsSn		
	Heat capacity, J/K·mol of AsSn	Enthalpy relative to 0 K, J/mol of AsSn	Entropy, J/K·mol of AsSn
55	26.61	540	14.39
70	32.89	992	21.59
80	36.11	1 335	26.19
100	40.58	2 105	34.81
120	43.30	2 946	42.38
140	45.31	3 833	49.29
160	46.69	4 753	55.40
180	47.70	5 699	61.00
200	48.49	6 661	65.98
220	49.20	7 640	70.71
240	49.79	8 632	75.02
260	50.21	9 632	78.99
280	50.79	10 640	82.80
298.15	51.21	11 560	85.98

3. Model and **SETUP** files


```
ent-phase LIQUID  ,  1
     AS,SN ;  N N

  ent-param G(LIQUID,AS;0)      298.15 +GLIQAS;   1200 N
  ent-param G(LIQUID,SN;0)      298.15 +GLIQSN;   3000 N
  ent-param L(LIQUID,AS,SN;0)   298.15 +V1+V2*T;  3000 N
  ent-param L(LIQUID,AS,SN;1)   298.15 +V3+V4*T;  3000 N
  ent-param L(LIQUID,AS,SN;2)   298.15 +V5+V6*T;  3000 N




ent-phase ASSN , 2 1 1
     AS; AS,SN; N N

  ent-sym fun CPASSN  298.15 +V20*T*LN(T)+V21*T**2+V22*T**(-1)+V23*T**3;,,,,,

  ent-param G(ASSN,AS:SN;0)      298.15 +V18+V19*T+CPASSN ;,,,,
  ent-param G(ASSN,AS:AS;0)      298.15 2*GFCCAS;,,,
  ent-param L(ASSN,AS:AS,SN;0)   298.15  +V9+V10*T; 3000 N
  ent-param L(ASSN,AS:AS,SN;1)   298.15 +V11+V12*T; 3000 N
```

$$G_m^{liq} = x_{As}\,{}^oG_{As}^{liq} + x_{Sn}\,{}^oG_{Sn}^{liq}$$
$$+RT(x_{As}\ln x_{As} + x_{Sn}\ln x_{Sn})$$
$$+x_{As}x_{Sn}(V_1 + V_2 \times T)$$
$$+x_{As}x_{Sn}(V_3 + V_4 \times T)(x_{As} - x_{Sn})$$
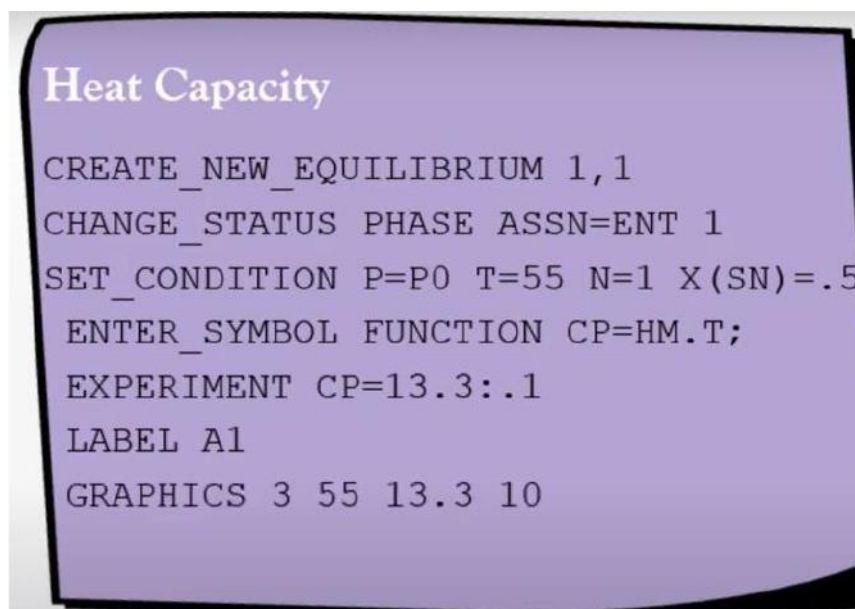$$+x_{As}x_{Sn}(V_5 + V_6 \times T)(x_{As} - x_{Sn})^2$$

FIG.3 Liquid and AsSn phase sublattice model and Gibbs energy expression

Once we know the crystal structure of a phase, we can specify a Gibbs energy model for that phase. For example two examples are shown, namely the liquid phase model and the intermetallic AsSn phase model. The liquid phase is a solution phase and is modelled with only one sublattice. This means that the As and Sn components are mixed on a single sublattice. The way the phases are described in the setup file is shown on the left, and the corresponding terms in the Redlich-Kister polynomial are shown in the box on the right. The coefficients to be adjusted are V1 through V6. Note that all of these coefficients may not be needed. Usually start with V1 and V2, then add more directly to get a good fit with excess energy. The second example is an AsSn phase model with two sublattice. The first is occupied only by As atoms, but on the second, As and Sn can be mixed. As you can see earlier, there is heat capacity data for this stage. Therefore, the coefficients V20 to V23 match the heat capacity data. V18 and V19 are related to the enthalpy of formation of AsSn and its melting point. Add V9 through V12 to reproduce the solubility of As on the second sublattice. As mentioned earlier, the SETUPE file includes the Gibbs energy descriptions for all phases, which themselves contain the coefficients to be adjusted.

4 Evaluate the data in the **POP** file

After creating the **SETUP** file, we need to create another file containing the experimental data, which is called the **POP** file. Here, four examples of entering different experimental data are shown.
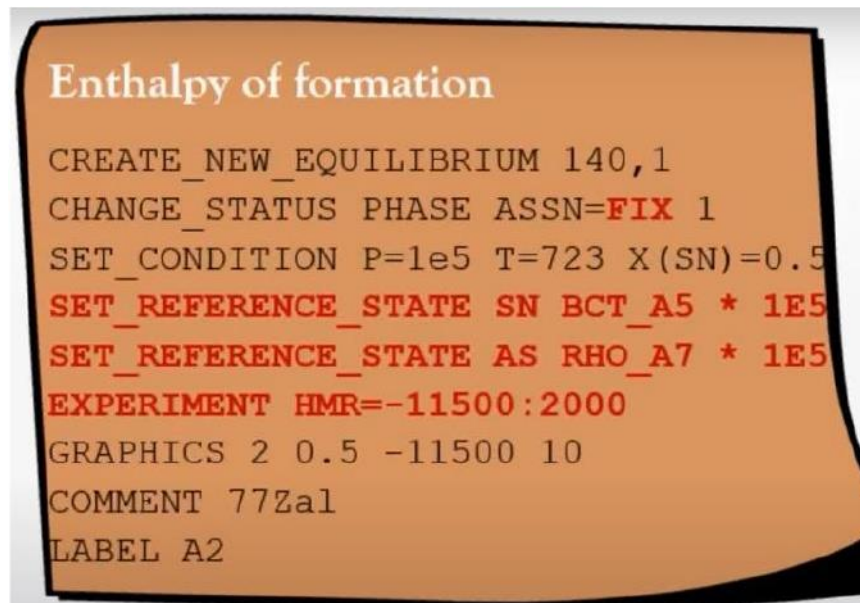
The first example is how to enter heat capacity data. The first line in each **LABEL** is the command to create a new balance. Then we set the state of the associated phase, here is the input **AsSn**. Next, enter the condition according to the corresponding experiment.

The first time we use it in a **POP** file, we need to define a way to calculate it by an input function. Note that many thermodynamic functions, such as enthalpy, are already defined in the software. However, the heat capacity is a derivative, and the first time we use it in a **POP** file, we need to define it as a function of an existing variable. Once the **CP** function is defined, we can enter the heat capacity measured under the given experimental conditions. We can add a **LABEL** to each **LABEL** so that later we can call the balance in the **label** through the label. After compiling the **POP** file in **PARROT**, you can also use the command **GRAPHICS** to create an **EXP** file that contains all the experimental data points. In addition, you can add comments to each balanced **LABEL**.

FIG.4 Enter heat capacity
data into the **POP** file

The next **LABEL** shows how to enter the formation enthalpy. There is more than one way to enter the enthalpy of formation, but the method I show here is the fixed correlation phase. If you use this method, you need to give one less condition. (An alternative method is to set the phase state to **ENTERED** instead of adding the mole condition. We also need to set the reference state of the pure element to the reference state that was enabled in the experiment.) The relevant experimental data here is the enthalpy of formation.
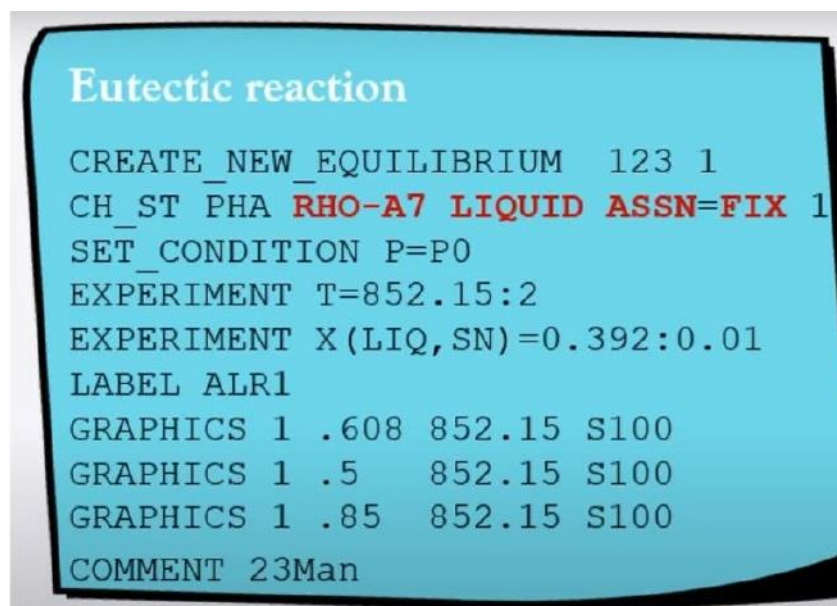
Enthalpy of formation

```
CREATE_NEW_EQUILIBRIUM 140,1
CHANGE_STATUS PHASE ASSN=FIX 1
SET_CONDITION P=1e5 T=723 X(SN)=0.5
SET_REFERENCE_STATE SN BCT_A5 * 1E5
SET_REFERENCE_STATE AS RHO_A7 * 1E5
EXPERIMENT HMR=-11500:2000
GRAPHICS 2 0.5 -11500 10
COMMENT 77Zal
LABEL A2
```

FIG.5 Enter the enthalpy of formation
data into the POP file

In the next LABEL, show the input eutectic reaction. In this case, all three phases involved in such reactions need to be fixed, which are Rhombohedral (RHO-A7), liquid phase, and AsSn phase. This reduces the number of degrees of freedom to 1, so only one condition needs to be set.

Eutectic reaction

```
CREATE_NEW_EQUILIBRIUM  123 1
CH_ST PHA RHO-A7 LIQUID ASSN=FIX 1
SET_CONDITION P=P0
EXPERIMENT T=852.15:2
EXPERIMENT X(LIQ,SN)=0.392:0.01
LABEL ALR1
GRAPHICS 1 .608 852.15 S100
GRAPHICS 1 .5   852.15 S100
GRAPHICS 1 .85  852.15 S100
COMMENT 23Man
```

FIG.6 Input eutectic reaction
data into POP file

The last LABEL is the consistent melting of the AsSn phase. The way to define the condition here is to set equal amounts of one component in both the liquid phase and the stoichiometric phase, in which case the composition of tin is equal in both phases.

Congruent melting

```
CREATE_NEW_EQUILIBRIUM   126 1
CH_ST PHASE LIQUID ASSN=FIX 1
SET_CONDITION P=P0
SET_CON X(LIQ,SN)-X(ASSN,SN)=0
LABEL A1L
EXPER T=868.15:2
EXPER X(SN)=.5:.01
GRAPHICS 1 .5 868.15 S100
COMMENT 68Per
```

FIG.7 Input consistent melting data for the **As-Sn** phase into POP file

For emphasis, other sentence meanings in the POP file can be referred to the Thermo-Calc Data Optimization User Guid

5. Evaluation

Once we have created a **SETUP** and a **POP** file, we are ready to evaluate in **PARROT**. It is worth mentioning that we can also prepare macro files, also known as **TCM** files. In order to easily draw the desired property or phase diagram during the optimization process and compare it with the experimental data. The steps are as follows:

(1) Create a working file, also known as a **PAR** file, from the **SETUP** file.

(2) Compile the **POP** file into a working file.

(3) Optimize in **PARROT**, or in other words, adjust the model coefficients.

(4) Phase maps and other properties are drawn during the evaluation process and compared to experimental data.

(5) Repeat **Step3** and **Step4** until satisfactory results are obtained.

FIG.8 CALPHAD evaluation process

6. Run the **SETUP** file

It is actually very easy to create a SETUP file from an existing TDB file. In this case, it is still necessary to manually add the stages and parameters by line using commands, this is done to understand what each command in the SETUP file means.

First, we enter the Gibbs module. We first enter the elements As and Sn. Then we modify the element description with the AMEND-ELEMENT-DATA command. Then we need to enter the Gibbs energy of each element in different states. An example of the reference Gibbs energy for input As is shown. We define this function as GHSERAS, and this function has two temperature ranges. All data for these functions and pure elements can be found in PURE5 installed by Thermo-Calc.

```
GES: am_el_d /- ELECTRON_GAS          0.0000E+00  0.0000E+00  0.0000E+00 1
  S: am_el_d VA  VACUUM                0.0000E+00  0.0000E+00  0.0000E+00 1
GES: am_el_d AS  RHOMBOHEDRAL_A7       7.4922E+01  0.0000E+00  0.0000E+00 2
GES: am_el_d SN  BCT_A5                1.1871E+02  6.3220E+03  5.1195E+01 2
GES: enter-symbol
 VARIABLE, FUNCTION, TABLE OR PARAMETER /FUNCTION/: fun
     : GHSERAS
LOW TEMPERATURE LIMIT /298 15/:
FUNCTION: -7270.447+122.211069*T-23.3144*T*LN(T)
&      -.00271613*T**2+11600*T**(-1);
HIGH TEMPERATURE LIMIT /6000/: 1090
ANY MORE RANGES /N/: y
FUNCTION: -10454.913+163.457433*T-29.216037*T*LN(T);
HIGH TEMPERATURE LIMIT /6000/:
ANY MORE RANGES /N/:
GES:
```

Next, shows how to get into the liquid phase. Give the phase name, then give the sublattice number, which in this case is 1. Then enter the components of each sublattice. The next step is to enter the interaction parameters of the liquid phase. Enter the L0 parameter and give its associated work. This continues until all elements, functions, stages, and interaction parameters are entered.

```
GES:ent-phase
NAME OF PHASE:liquid
TYPE CODE:
NUMBER OF SUBLATTICES /1/:
NAME OF CONSTITUENT:as sn
NAME OF CONSTITUENT:
WILL YOU ADD CONSTITUENTS LATER /NO/:
DO YOU WANT A LIST OF POSSIBLE PARAMETERS /NO/:
GES:ent-parameter
PARAMETER:L(LIQUID,AS,SN;0)
 L(LIQUID,AS,SN;0)
LOW TEMPERATURE LIMIT /298.15/:
FUNCTION:+V1+V2*T
&;
HIGH TEMPERATURE LIMIT /6000/:
ANY MORE RANGES /N/:
GES:
```

Once the **SETUP** file is ready, we go into the **PARROT** module and use the command CREATE-NEW-STORE-FILE

Or simply "**CREATE**" to create a working file.

```
GES:  go parrot

   PARROT  VERSION 5.3

    Global minimization used as test only
PARROT: @@ move "set-fix" lines here
PARROT:  create work
PARROT:  set-interactive
PARROT:
```

The next step is to COMPILE the **POP** file using the command "compile". We find the **POP** file from the browse window and press Enter several times.

```
PARROT:compile
OUTPUT TO SCREEN OR FILE /SCREEN/:
INITIATE STORE FILE: /Y/:
POP files may include graphics information using the
GRAPHICS_PLOT command. A file name for generating an ".exp" file must be given.
OUTPUT TO SCREEN OR FILE /SCREEN/:
  $
  $ As-Sn.POP (PARROT)
  $
```

Then we go to the submodule **EDIT**. From there, we can access the experiment. We can list all the balances and look them up

Look at the summary of the experimental data. In this submodule, we can manually add more balances, change weights, etc.

```
PARROT: edit
ED_EXP: read
Block number /1/:
ED_EXP: list-all-eq
  Eq  Lab   Iter Weight Temp   Exp  Fix phases or comments
    1 A1    ***   1.0    55.0       calorimetry - Demidenko ASSN
    2 A1    ***   1.0    60.0       CALORIMETRY - DEMIDENKO ASSN
    3 A1    ***   1.0    70.0       CALORIMETRY - DEMIDENKO ASSN
    4 A1    ***   1.0    80.0       CALORIMETRY - DEMIDENKO ASSN
    5 A1    ***   1.0    90.0       CALORIMETRY - DEMIDENKO ASSN
    6 A1    ***   1.0   100.0       CALORIMETRY - DEMIDENKO ASSN
    7 A1    ***   1.0   110.0       CALORIMETRY - DEMIDENKO ASSN
    8 A1    ***   1.0   120.0       CALORIMETRY - DEMIDENKO ASSN
    9 A1    ***   1.0   130.0       CALORIMETRY - DEMIDENKO ASSN
   10 A1    ***   1.0   140.0       CALORIMETRY - DEMIDENKO ASSN
   11 A1    ***   1.0   150.0       CALORIMETRY - DEMIDENKO ASSN
   12 A1    ***   1.0   160.0       CALORIMETRY - DEMIDENKO ASSN
   13 A1    ***   1.0   170.0       CALORIMETRY - DEMIDENKO ASSN
   14 A1    ***   1.0   180.0       CALORIMETRY - DEMIDENKO ASSN
   15 A1    ***   1.0   190.0       CALORIMETRY - DEMIDENKO ASSN
   16 A1    ***   1.0   200.0       CALORIMETRY - DEMIDENKO ASSN
   17 A1    ***   1.0   210.0       CALORIMETRY - DEMIDENKO ASSN
   18 A1    ***   1.0   220.0       CALORIMETRY - DEMIDENKO ASSN
```

Now that we have a working file, we can call it from the **PARROT** module using the command **SET-STORE-FILE** or S-S-F. We start the optimization by allowing the variables to change. As you can see here, there are no variables that might be used for optimization at first.

```
SYS: go par

 PARROT  VERSION 5.3

   Global minimization used as test only
PARROT: s-s-f
PARROT: l-a-v
OUTPUT TO SCREEN OR FILE /SCREEN/:

  == OPTIMIZING VARIABLES ==

  AVAILABLE VARIABLES ARE V1   TO V00

  VAR.    VALUE              START VALUE       SCALING FACTOR    REL.STAND.DEV

  NUMBER OF OPTIMIZING VARIABLES :    0
  ALL OTHER VARIABLES ARE FIX WITH THE VALUE ZERO
PARROT:
```

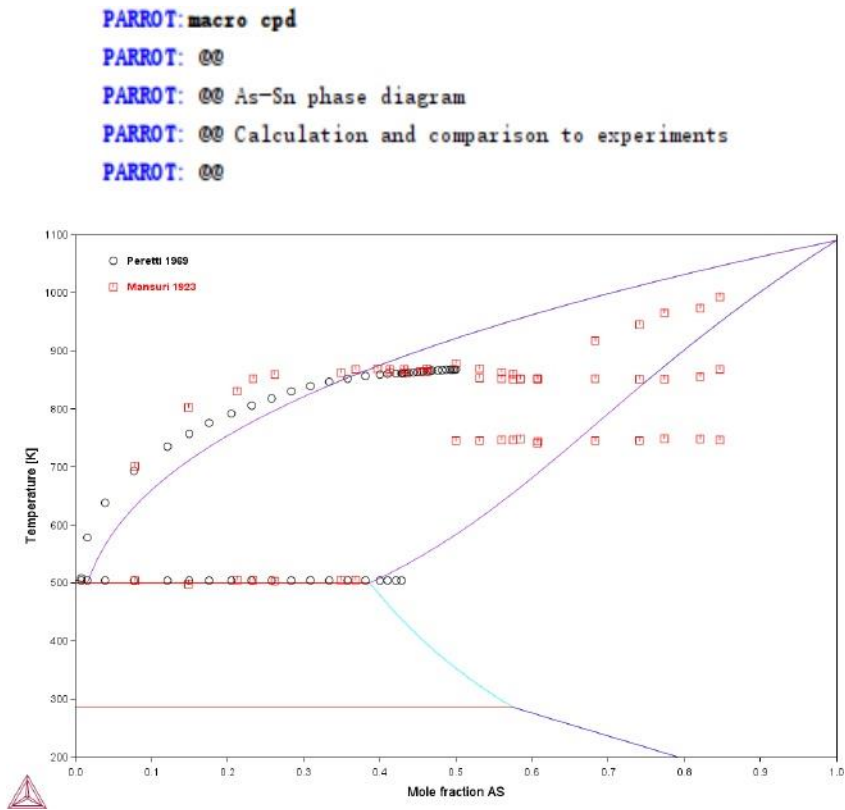First let's draw a phase diagram to see what it looks like
when all model coefficients or variables are zero.

```
PARROT: macro cpd
PARROT: @@
PARROT: @@ As-Sn phase diagram
PARROT: @@ Calculation and comparison to experiments
PARROT: @@
```


FIG.9 As-Sn phase diagram when all coefficients or variables are zero

We first fit the heat capacity of the AsSn phase. The variables from V20 to
V23 are optimized in this step. We need to use the command "set-optimizing -
VARIABLE" to SET some starting values for these variables. This is done to
facilitate the fit.

```
PARROT: s-o-v 20 -70
PARROT: s-o-v 21 1e-3
PARROT: s-o-v 22 1e5
PARROT: s-o-v 23 1e-6
```

After entering the starting value, we must go to the **EDIT** submodule to select the relevant experiment. First, we set all the balanced weights to zero, and then set the balanced weights related to the heat capacity of the AsSn to 1, in this case the numbers 1 to 30.

```
ED_EXP: set-we 0 first-lat
ED_EXP: set-we 0 first-last
ED_EXP: set-we 1 1-30
ED_EXP: select-eq fi
  Equilibrium number                        1, label A1
ED_EXP: c-a
```

Now if we look at the list again, we can see that in addition to those equilibria related to the **Cp** of **AsSn**, All of the equilibria are not used.

3 A1	2	1.	70.0	CALORIMETRY - DEMIDENKO ASSN
4 A1	2	1.	80.0	CALORIMETRY - DEMIDENKO ASSN
5 A1	2	1.	90.0	CALORIMETRY - DEMIDENKO ASSN
6 A1	2	1.	100.0	CALORIMETRY - DEMIDENKO ASSN
7 A1	2	1.	110.0	CALORIMETRY - DEMIDENKO ASSN
8 A1	2	1.	120.0	CALORIMETRY - DEMIDENKO ASSN
9 A1	2	1.	130.0	CALORIMETRY - DEMIDENKO ASSN
10 A1	2	1.	140.0	CALORIMETRY - DEMIDENKO ASSN
11 A1	2	1.	150.0	CALORIMETRY - DEMIDENKO ASSN
12 A1	2	1.	160.0	CALORIMETRY - DEMIDENKO ASSN
13 A1	2	1.	170.0	CALORIMETRY - DEMIDENKO ASSN
14 A1	2	1.	180.0	CALORIMETRY - DEMIDENKO ASSN
15 A1	2	1.	190.0	CALORIMETRY - DEMIDENKO ASSN
16 A1	2	1.	200.0	CALORIMETRY - DEMIDENKO ASSN
17 A1	2	1.	210.0	CALORIMETRY - DEMIDENKO ASSN
18 A1	2	1.	220.0	CALORIMETRY - DEMIDENKO ASSN
19 A1	2	1.	230.0	CALORIMETRY - DEMIDENKO AsSN
20 A1	2	1.	240.0	CALORIMETRY - DEMIDENKO ASSN
21 A1	2	1.	250.0	CALORIMETRY - DEMIDENKO ASSN
22 A1	2	1.	260.0	CALORIMETRY - DEMIDENKO ASSN
23 A1	2	1.	270.0	CALORIMETRY - DEMIDENKO ASSN
24 A1	2	1.	273.1	CALORIMETRY - DEMIDENKO ASSN
25 A1	2	1.	280.0	CALORIMETRY - DEMIDENKO ASSN
26 A1	2	1.	290.0	CALORIMETRY - DEMIDENKO ASSN
27 A1	2	1.	298.1	CALORIMETRY - DEMIDENKO ASSN
28 A1	2	1.	300.0	CALORIMETRY - DEMIDENKO ASSN
29 A1	2	1.	310.0	CALORIMETRY - DEMIDENKO ASSN
30 A1	2	1.	1500.0	CALORIMETRY - DEMIDENKO ASSN
31 A2	< unused >		55.0	CALORIMETRY - DEMIDENKO AS3SN4
32 A2	< unused >		60.0	CALORIMETRY - DEMIDENKO AS3SN4

We "save" and return PARROT. We then use the command "OPTIMIZE" to run the optimization and set up the iteration.

The number of times, in this case 20.

```
ED_EXP:save
ED_EXP:ba
PARROT:op 20
   Use      30 experiments, maximum is       2000
   Use     314 real workspace, maximum is    50000
        The following output is provided by subroutine VA05A
```

By listing the variables, we can see how the value changes.

```
PARROT:l-a-v
OUTPUT TO SCREEN OR FILE /SCREEN/:

 == OPTIMIZING VARIABLES ==

AVAILABLE VARIABLES ARE V1  TO V00

VAR.    VALUE          START VALUE        SCALING FACTOR     REL.STAND.DEV
V20    -4.43042446E+01  -7.00000000E+01   -7.00000000E+01    3.07858370E-03
V21    -1.44592886E-02   1.00000000E-03    1.00000000E-03    5.15543324E-01
V22     3.06972295E+04   1.00000000E+05    1.00000000E+05    4.01686426E-03
V23     1.53467749E-06   1.00000000E-06    1.00000000E-06    1.01021304E-01

NUMBER OF OPTIMIZING VARIABLES :    4
ALL OTHER VARIABLES ARE FIX WITH THE VALUE ZERO
THE SUM OF SQUARES HAS CHANGED FROM   1.59002535E+05 TO   1.19221270E+02
DEGREES OF FREEDOM   26.  REDUCED SUM OF SQUARES   4.58543347E+00
```

We can also plot the heat capacity of that phase and compare it to the experimental data.

```
PARROT:macro AsSn
PARROT: @@
PARROT: @@ AsSn (Fcc) heat capacity
PARROT: @@ Calculation and comparison to expeiments
PARROT: @@
```
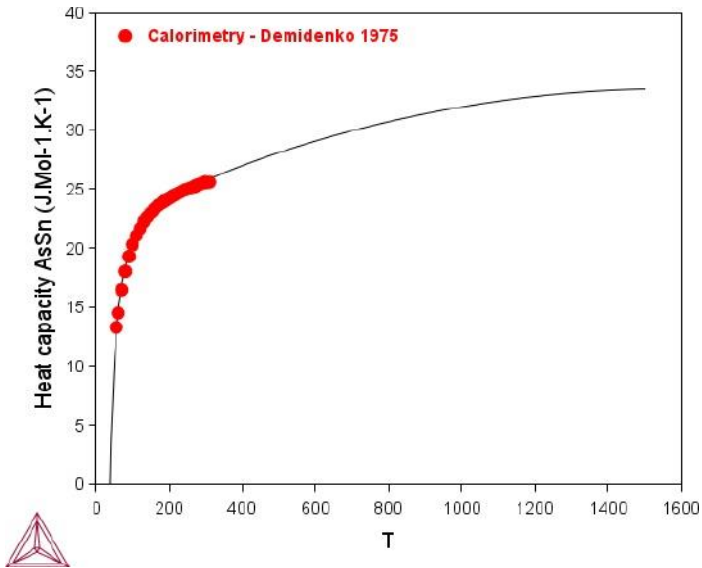
FIG. 10 Heat capacity of As-Sn phase
compared with experimental data

We then draw the phase diagram and we can see that the AsSn phase has now appeared
in the phase diagram.

POST:ba
POLY:ba

 PARROT VERSION 5.3

PARROT:macro cpd
PARROT: @@
PARROT: @@ As-Sn phase diagram
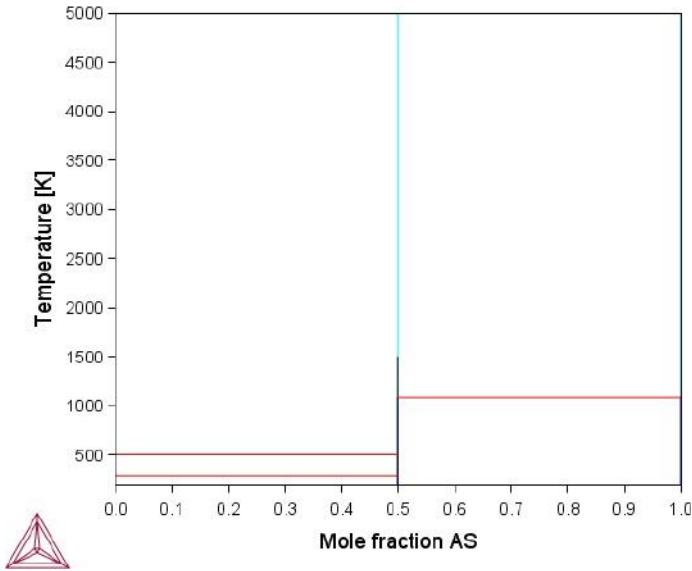PARROT: @@ Calculation and comparison to experiments
PARROT: @@

FIG. 11 As-Sn phase diagram after optimizing the C_p-
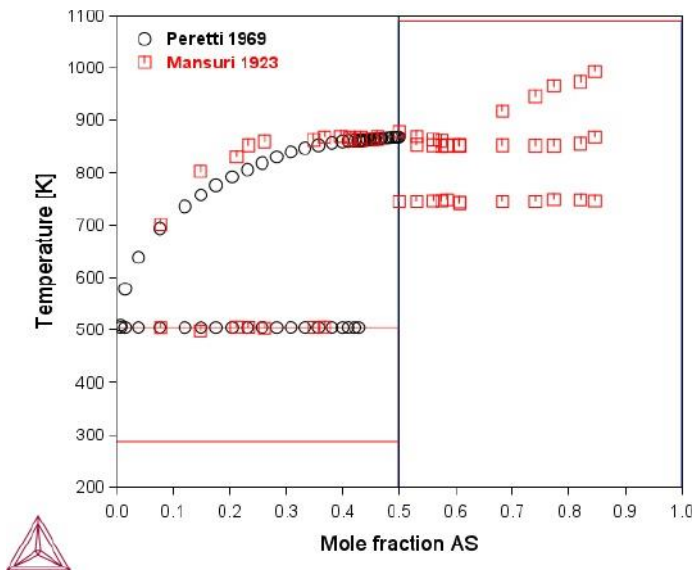related parameters of the As-Sn phase

FIG.12 Comparison between As-Sn phase diagram and experimental
data after optimizing C_P-related parameters of AsSn phase

Repeat this operation for the next stoichiometric phase As_3Sn_4 . Two stoichiometric phases now appear, and you can see the heat capacity of the second stoichiometric phase compared to the experimental data.
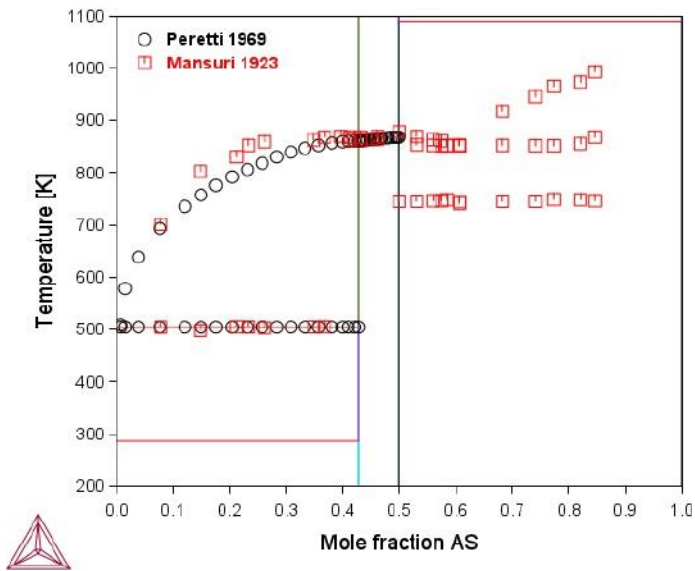

FIG.13 The As-Sn phase diagram after optimizing the C_P-related
parameters of the AsSn phase is compared with the experimental data

In the next step, fit the enthalpy of formation of As_3Sn_4 and AsSn phase. Now let's look at the enthalpy of formation diagram as well as the phase diagram after these changes.
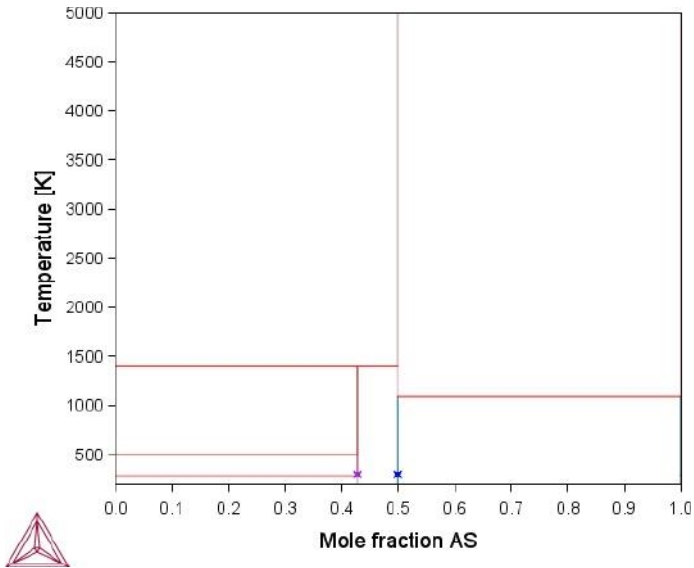
FIG. 14 As-Sn phase diagram after optimizing enthalpy of formation related parameters of As_3Sn_4 and $AsSn$ phase
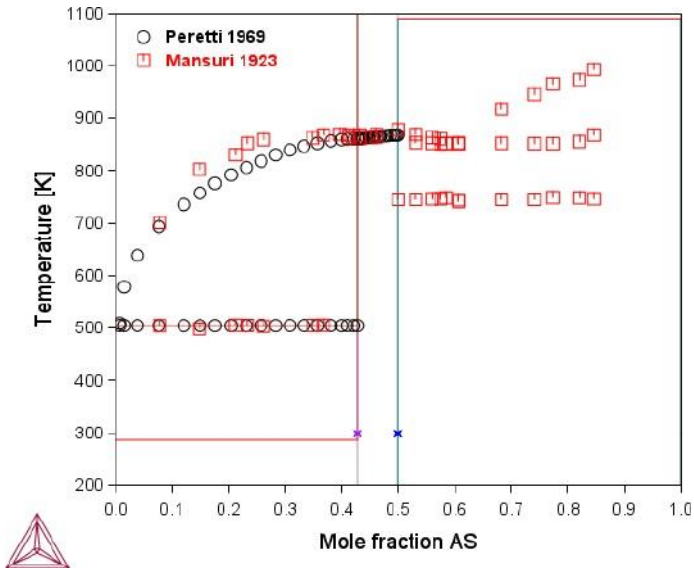

FIG. 15 Comparison between As-Sn phase diagram and experimental data after optimizing enthalpy correlation parameters of As_3Sn_4 and $AsSn$ phase
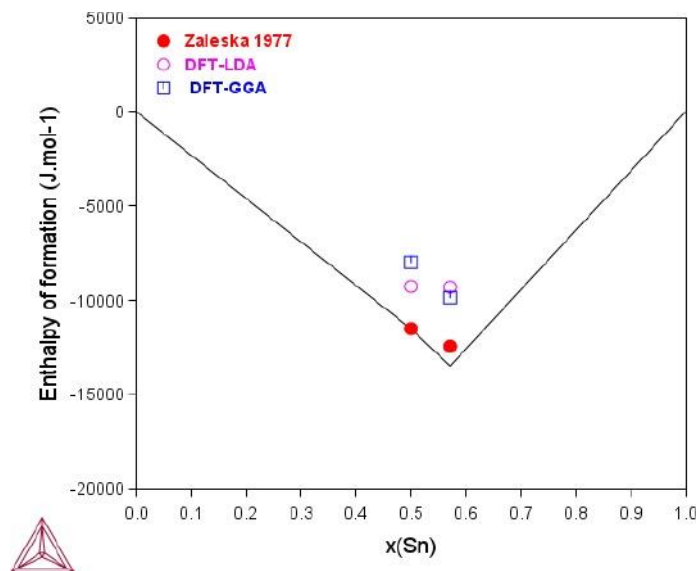
FIG.16 Comparison between enthalpy of formation of optimized As₃Sn₄ and AsSn phase and experimental data

After that, the melting point and liquidus parameters are adjusted. After this step, the phase diagram looks very close to the experimental data, only the variables need to be fine-tuned.
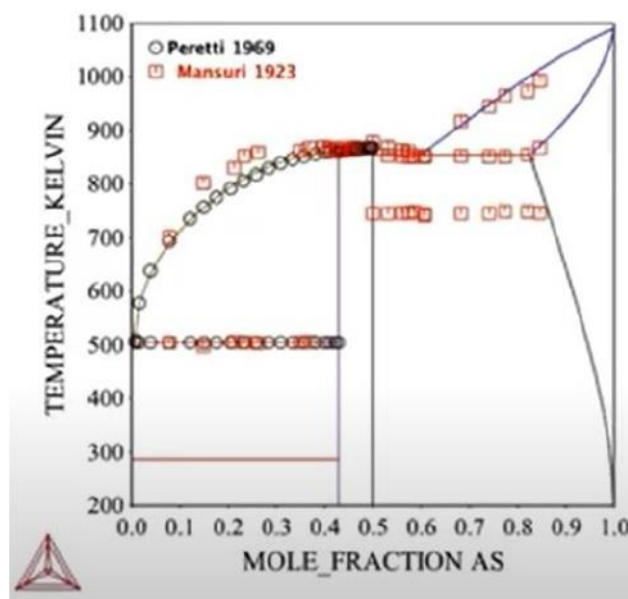

FIG.17 Comparison of As-Sn binary phase diagram with experimental values before the variables were fine-tuned

At the end of the evaluation, usually, all variables are optimized together one or more times by using different weights on different datasets