A thermodynamic database for solder systems:

COST 531 and the benefits of international collaboration

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Teddington, UK

GTT Workshop, Herzogenrath, Germany

4-6 June 2008

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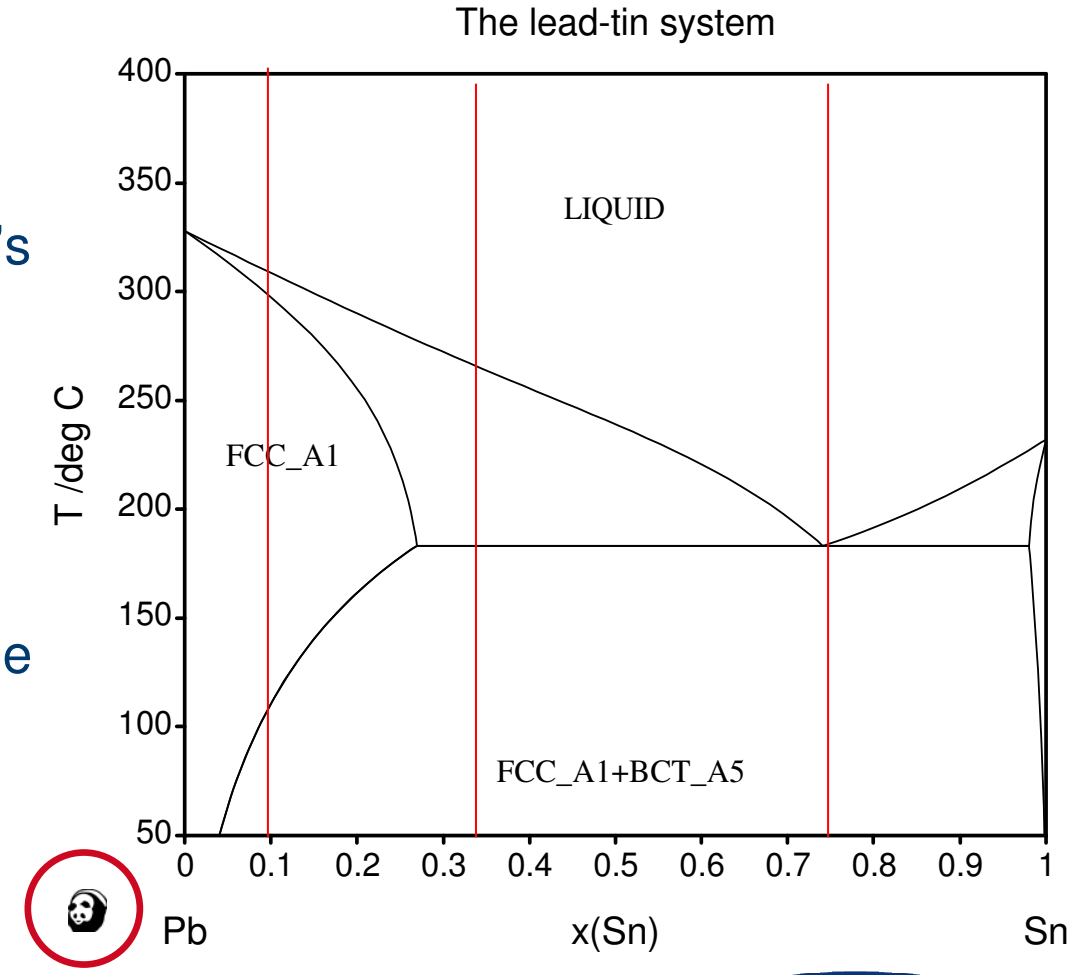
Outline

- The need for Lead free solders
- COST (COST531 and MP0602)
- Thermodynamic database for lead free solders
- Scope and Standards
- Need for consistency
- Applications
- How you can access the database
- Conclusions

The need for Lead free solders

The need for Lead-free Solders

- Traditional solder
  - Pb-Sn
  - Electrician's solder (tinman's solder)
    - Eutectic Composition
    - Rapid solidification
  - Plumber's solder
    - ~Pb:Sn 2:1
    - Large solidification range
      - *Pasty range*
  - High-temperature solders
    - *(under-bonnet applications)*



Problems with Lead

- **Environmental issues**
  - Toxic
    - Incorporated into bone marrow, nerve tissue, brain, kidneys..
    - Low levels affect the brain, central nervous system, lead to learning difficulties in children, impair physical and mental development
  - Disposal of electrical and electronic equipment
    - Lead leaching into groundwater from landfill
  - European legislation
    - Waste Electrical and Electronic Equipment (WEEE) Directive
      - Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment Regulations 2006 (RoHS) *– 1st July 2006*
  - Need for coordinated European research in support of European industry

What is COST ?

What is COST ?

- European COoperation in the field of Scientific and Technical research
- Mission: To strengthen Europe in scientific and technical research for peaceful purposes through the support of cooperation and interaction between European researchers
- 34 COST member states plus 1 cooperating member
- Supported by the European Commission through the Framework Programme
- Works through a series of actions in the form of networked research projects
- Aims to coordinate nationally funded research at a European level

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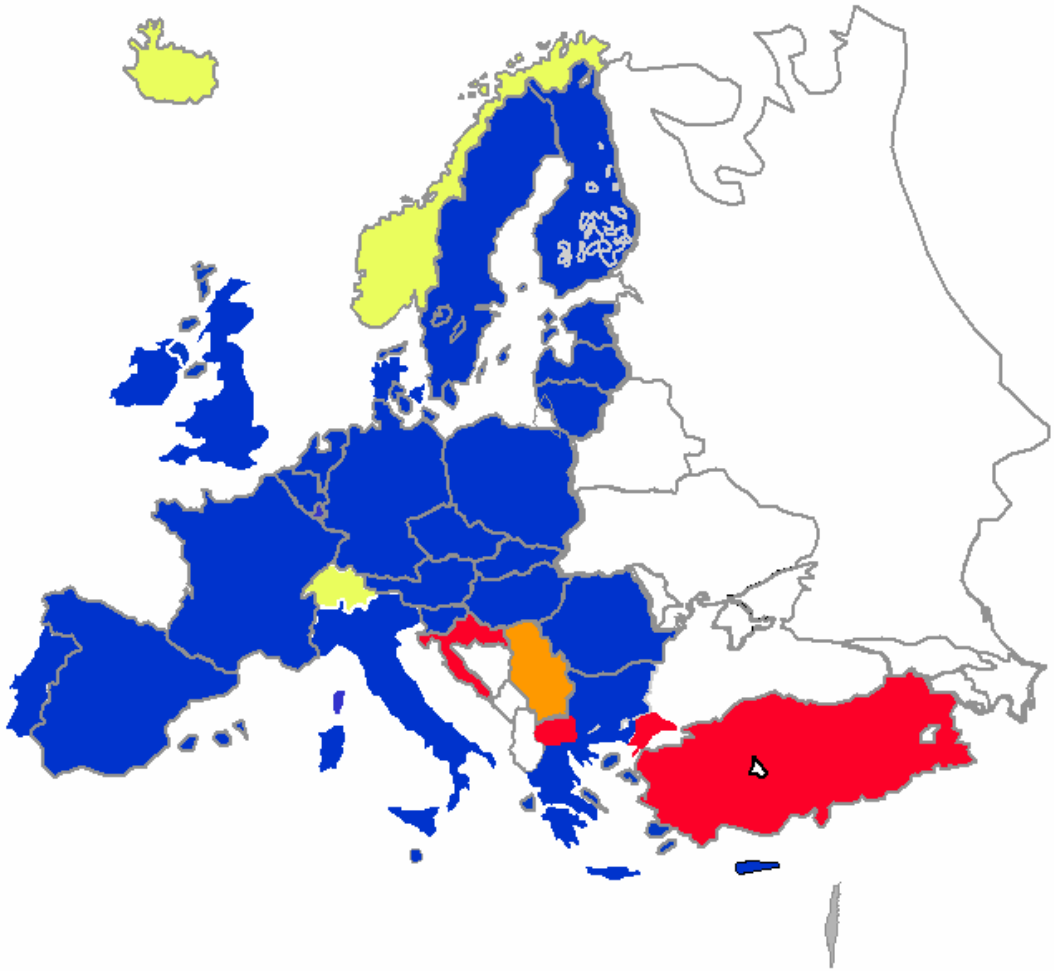
COST Countries



- 27 EU Member States
- Candidate countries
  - Croatia*
  - Former Yugoslav Republic of Macedonia (FYROM)*
  - Turkey
- EFTA Member States
  - Iceland
  - Norway
  - Switzerland
- Other European Countries
  - Republic of Serbia*
- COST Cooperating States
  - Israel

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COST531

- A European Action on Lead-free Soldering

  (March 2002 to March 2007)

  "*....to increase the basic knowledge on possible alloy systems that can be used as lead-free solder materials and to provide a scientific basis for a decision which of these materials to use for different soldering purposes in order to replace the currently used lead-containing solders in the future.*"

- 45 research institutes from 17 countries
- Working Groups
  - Groups 1&2: Thermochemistry and Phase Diagrams (Experimental + Modelling)
  - Groups 3-6: Physical, Chemical Properties, Reliability Issues

COST531 Outputs

- Thermodynamic database
  - Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn, Zn
- Database of Physical Properties of Lead-free Solder Alloys
  - physical and mechanical properties of bulk solders and solder joints
- SURDAT Database of Lead-free Soldering Materials
- ATLAS of Microstructures of Pb-free solders and solder joints
- Synt@all" (SYNthesis of ALLoys)
- Publication (June 2008)
  - Volume 1: COST 531 Atlas of Phase Diagrams
  - Volume 2: COST 531/ELFNET Handbook of Solder Alloy Properties

COST531 database managed by:

- Aleš Kroupa
- Adéla Zemanová
- Jan Vreštál
- Jirí Vízdal
- Andy Watson
- Alan Dinsdale

"SOLDERS" is now available for lease with all major software for calculation of phase equilibria

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Atlas of Solder Phase Diagrams

Bi-Zn system

Several authors worked on the theoretical description of the Bi-Zn system – e.g. Malakhov [00Mal], Oleari et al. [55Ole], Bale et al. [77Bal], Girard [85Gir] nebo Wang et al. [93Wan]. Kim and Sanders [03Kim] attempted to describe properly the segregation region in the liquid, using two interaction parameters LIZ only instead of six used by Malakhov. Unfortunately, their description is not consistent with unary parameters ( ) of the „COST531" database and therefore the data from Malakhov [00Mal] were used for this system. The changes of unary data were introduced and new value of G(HCP_ZN,BI:VA;0) from work of Moelans [03Moe] was accepted. New data were also introduced to model new experimental data from Vizdal et al. [07Viz] for solubility of Bi in HCP_ZN Zn (G(HCP_ZN,BI,ZN:VA;0)).

References:

[55Ole] Oleari, L., Fiorani, M., Valenti, V.: La Metallurgia Italiana, 1955, vol. 46, p. 773.

[77Bal] Bale, C. W., Pelton, A. D., Rigaud, M.: Z. Metallkd., 1977, vol. 68, p. 69.

[85Gir] Girard, C.: Ph.D. Thesis, Universite de Provence, Marseille, 1985

[93Wan] Wang, Z. C., Yu, S. K., Sommer, F.: J. Chimie Phys. Physico-Chimie Biol., 1993, vol. 90, p. 379.

[00Mal] Malakhov, D. V.: CALPHAD, 2000, vol. 24, p. 1

[03Kim] Kim, S. S., Sanders, T. H. Jr.: Z. Metallkd., 2003, vol. 94, p. 390.

[03Moe] Moelans, N., Kumar, K. C. H., Wollants, P.: J. All. and Comp., 2003, vol. 360, p. 98.

[07Viz] Vizdal, J., Braga, M. H., Kroupa, A., Richter, K. W., Soares, D., Malheiros, L. F., Ferreira, J.: CALPHAD – sent for publication, 2007

Table of invariant reactions

T / °C	Phases			Compositions / x_{Bi}		
254.5	RHOMBO_A7	LIQUID	HCP_ZN	0.016	0.081	0.998
271.4	LIQUID	RHOMBO_A7				
418.3	LIQUID 1	LIQUID 2	HCP_ZN	0.374	0.992	0.996
419.5	HCP_ZN	LIQUID				

Phase information

Phase Name	Common Name	Structure Type	Pearson Symbol
LIQUID	Liquid		
RHOMBO_A7	(Bi)	A7	hR2
HCP_ZN	(Zn)	A3 mod	hP2

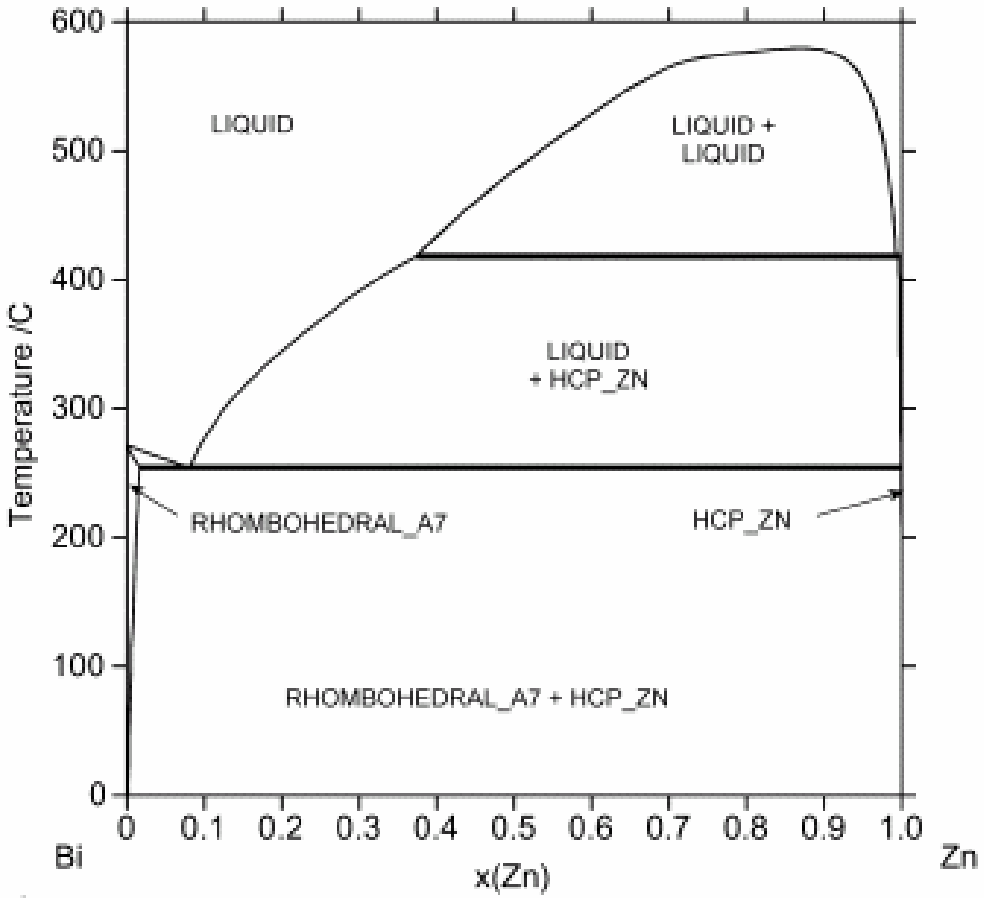
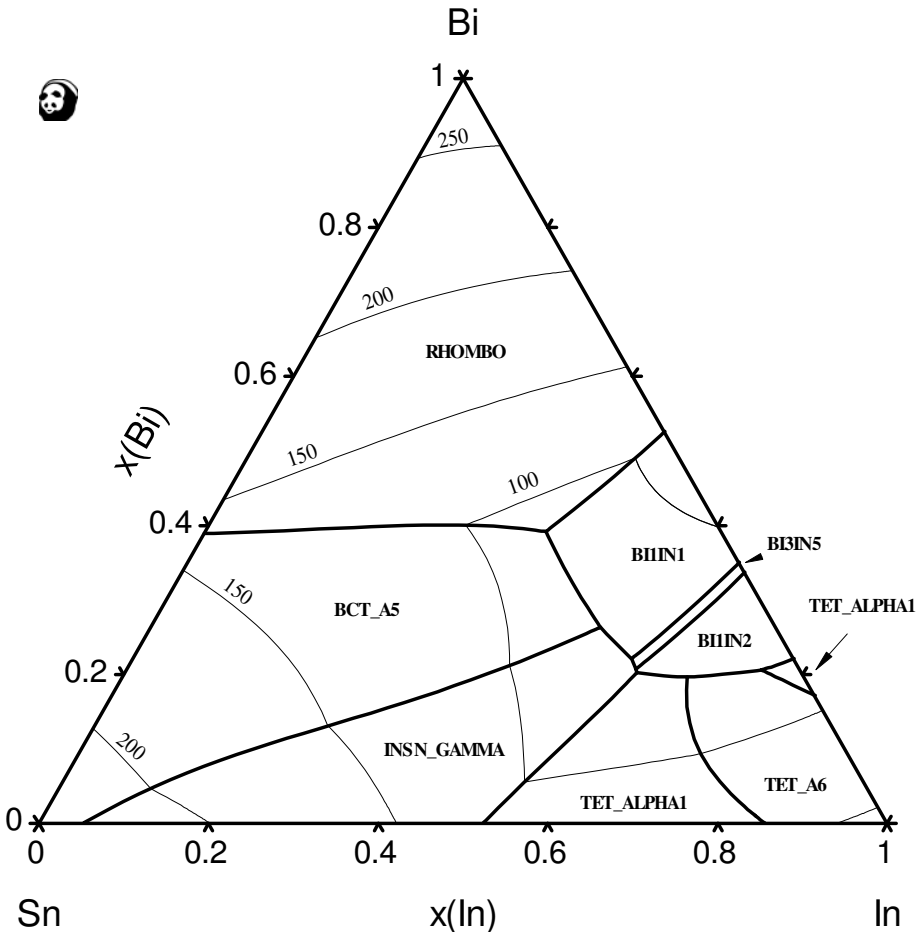
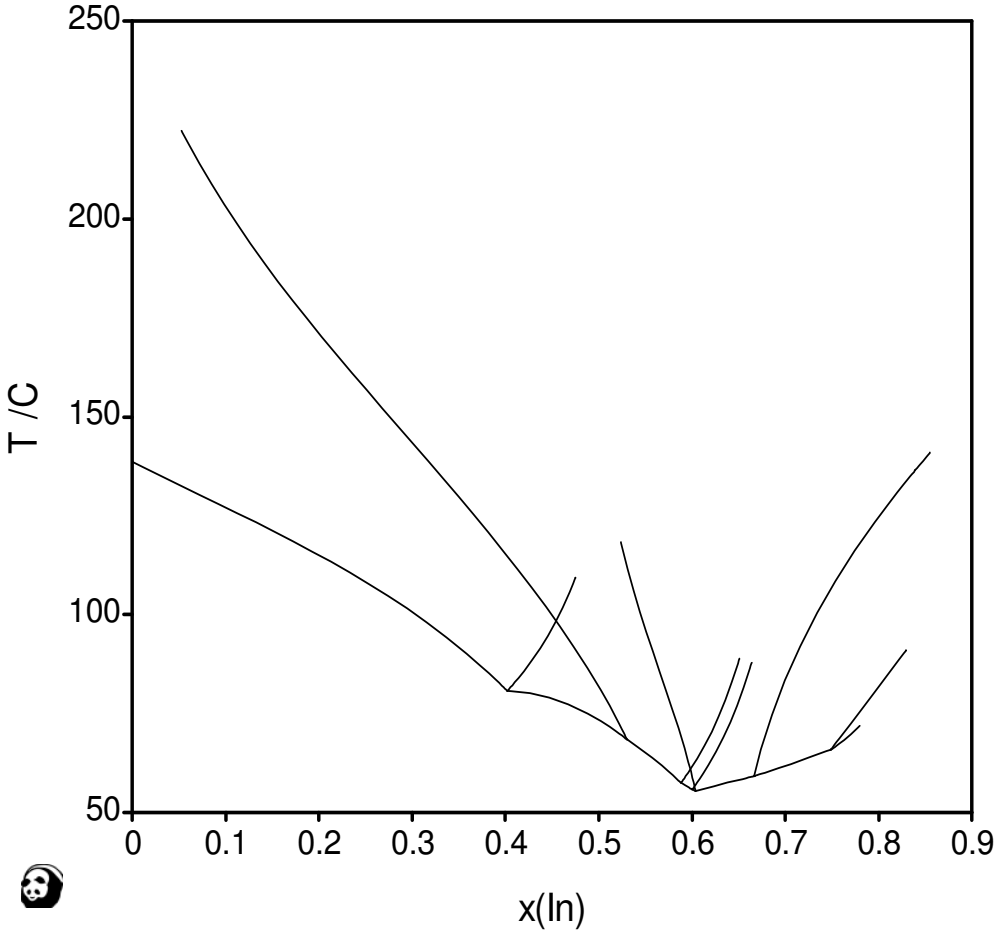


Fig. 1: ...

A different view of liquidus projections





HISOLD:

Advanced Solder Materials for High Temperature Application

HISOLD: Main drivers

- We need replacement for high temperature, high-Pb containing alloys - Lead is toxic !
- Currently exempt from RoHS legislation ….. but future EU legislation is likely
- Preparation by the scientific and industrial community is important
- Research for replacements underway in Japan and USA (and in China)
- Major research programme in Japan funded by main Japanese car manufactures.
- Currently no ‘drop-in’ lead-free alternative

High temperature solders

- **Solders with Tm ≥ 230°C**
  - Electronics industry for advanced packaging technologies
  - Power circuits (very high levels of conductivity required)
  - Automotive industry under bonnet applications
    - high current and low voltage, high temperatures within the engine area
  - Multi-chip modelling (MCM)
    - step soldering approach - soldering of various levels of the package with different solders with different melting points
    - upper limit around 350°C (limit set by polymer used in substrate)

HISOLD: Scientific programme

- Multidisciplinary and multiscale approach
- Establishment of materials property databases
  - thermodynamics and kinetics
  - materials properties (structural, physical, electrical, mechanical …)
  - process related properties of the solder and joint materials
- Model
  - formation of intermetallic compounds at solder/substrate interface
  - development of texture of reaction products in concentration gradients and of defect structures in vicinity of reaction interface
  - competitive nucleation and growth of intermediate phases
  - prediction of corrosion behaviour, deformation processes, failure modes etc. during fabrication and service
- Understand
  - thermo-mechanical fatigue
  - durability of interfaces and intermetallics
- Identify optimum process conditions.

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What are we hoping to achieve ?

- To identify a number of environmentally friendly lead-free solder systems suitable for high-temperature applications
- To define a comprehensive set of data for these potential solders
- To improve collaboration within Europe between academic institutions and industry
- To gain a market lead for European Electronic Manufacturers over competitors from Japan, China and United States, especially in areas where environmentally friendly and recyclable products are concerned
- To strengthen the position of the Universities and Research Institutions involved in materials science.

Potential systems for high temperature Pb free solders

- Zn-Al with Mg, Ge, Ga, Bi, Sn
- Sn-Sb with Bi, Ag, Cu
- Ag-Bi with Au, Sn
- Au-Sn with ?
- Zn-Sn with Bi, Ag, Cu

Development of a Thermodynamic database for lead free solders

Database overview

- Why we need a thermodynamic database
- Methodology
- Issues of consistency
- Status of COST531 database for lead free solders
- Examples of assessment issues

Why we need a thermodynamic database for solders

- Predict phase equilibria in multicomponent solders
- Model formation of the intermetallics at interface between substrate and the solder
- Understand issues of contamination of lead free solder through reworking of old solder joints
- Understand solidification properties
  - Liquidus and solidus temperatures of candidate solders
  - Solidification paths
  - Liquidus surface
  - Scheil simulation
- Predict physical properties
  - Surface tension and interfacial tensions – Butler equation
  - Volumes and densities – changes on solidification

Methodology

- Choose unary data
  - SGTE unary database v4.4
- Search for binary data
  - SGTE/NPL solders database
  - Brno solders database
  - Literature
  - Data generated by COST 531
- Test for consistency/compatibility
  - MTDATA
  - ThermoCalc
  - Pandat

  - "Competitive" software can be complementary

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CALPHAD approach

- Selection of appropriate models for phases
- Critical assessment of data for lower order systems
- Use well tested, reliable models to extrapolate from binary systems into ternary and higher order systems
- Introduce high order parameters where necessary
- Testing to ensure that extrapolations in temperature and composition are reasonable
  - Miscibility gaps
  - Inverted compound melting

Models

The temperature and concentration dependency of Gibbs energy of studied phase:

$$G_m^f = G_{ref}^f + G_{id}^f + G_E^f + G_{mag}^f + G_P^f + \ldots \ ,$$

G_{ref} - the reference level for the molar Gibbs energy of the phase

G_{id} - the contribution from the ideal mixing

G_{ex} - excess Gibbs energy, which describes the influence of non-ideal behaviour on the thermodynamic properties of the phase

Other terms can be added related to contributions from e.g. the interface energy, energy of plastic deformation, magnetism, pressure etc.

Excess Gibbs energy – Redlich-Kister-Muggianu polynomial

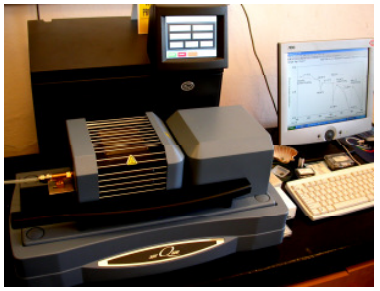
$$^{E}G = x_i x_j \sum_{k=0}^{n} {}^{k}L(x_i - x_j)^k$$

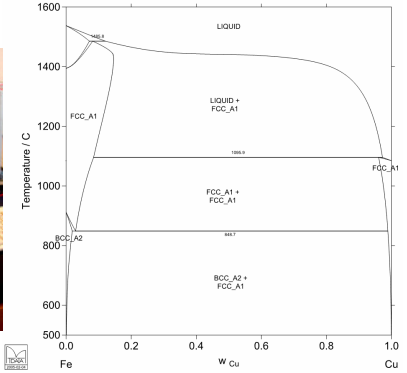
Analysis of crystalline phases structure – selection of appropriate sublattice description

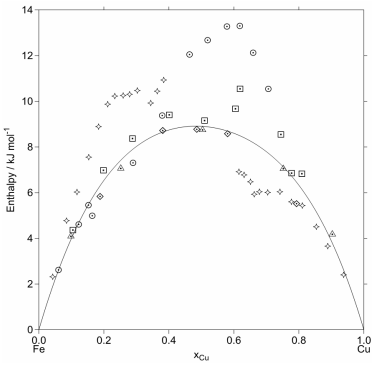
Phase Name	Number of sublattices	Stoichiometry				Constituents			
AUZN_GAMMA	4	0.15385	0.15385	0.23077	0.46153	Au, Zn	Au	Au, Zn	Zn
CUIN_GAMMA	3	0.654	0.115	0.231		Ag, Cu	Ag,Cu In	In, Sn	
BETA_INPD2	2	0.34	0.66			In	Pd		
INNI_CHI	3	1	1	1		Ni, Va	Ni	In, Ni	
IN3PD2	2	0.6	0.4			In	Ag,Pd		
LAVES_C15	2	2	1			Cu, Zn	Cu,Zn		
NI3SN2	3	0.5	0.25	0.25		Ni, Sn	Au,Ni	Au,Ni	
PDZN_GAMMA	2	2	9			Pd, Zn	Pd,Zn		
SBSN	2	1	1			Bi,Pb, Sb,Sn	Sb,Sn		
ZETA_AGZN	2	1	2			Zn	Ag, Zn		

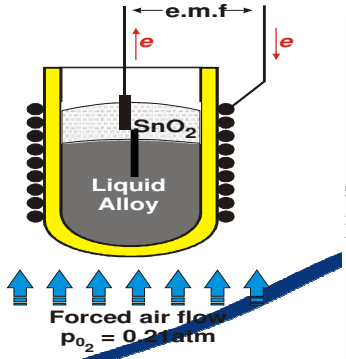
What do we mean by critical assessment ?

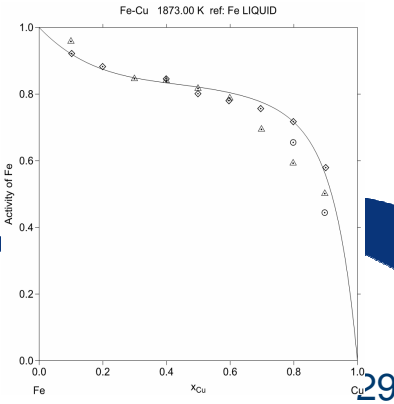
- Critical assessment is a process to generate a set of reliable data or diagrams which are self consistent and represent all the available experimental data for the system eg phase diagram, enthalpies of mixing, vapour pressures, …
- It involves a critical analysis of the experimental data (Hultgren, Massalski etc)
- ….. followed by a computer based optimisation process to reduce the experimental data into a small number of model parameters
- ….. using rigorous theoretical basis underlying thermodynamics











Example of consistency problem

Issues of consistency

- Often a problem combining assessments
  - eg Cu-Ni, Cu-Sn and Ni-Sn to give Cu-Ni-Sn
- Potentially different unary data used for different assessments
  - Sn fcc and hcp
- Possibly different models used for crystalline phases
  - gamma brass
- Metastable phases might extrapolate badly
  - liquid phase data extrapolated over wide range of temperatures

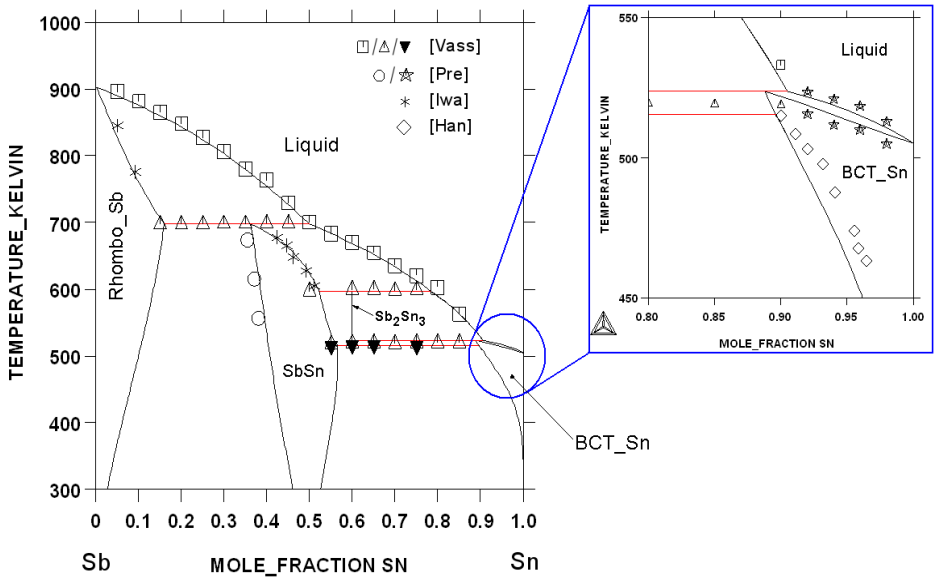
The reassessment of the Sb-Sn system

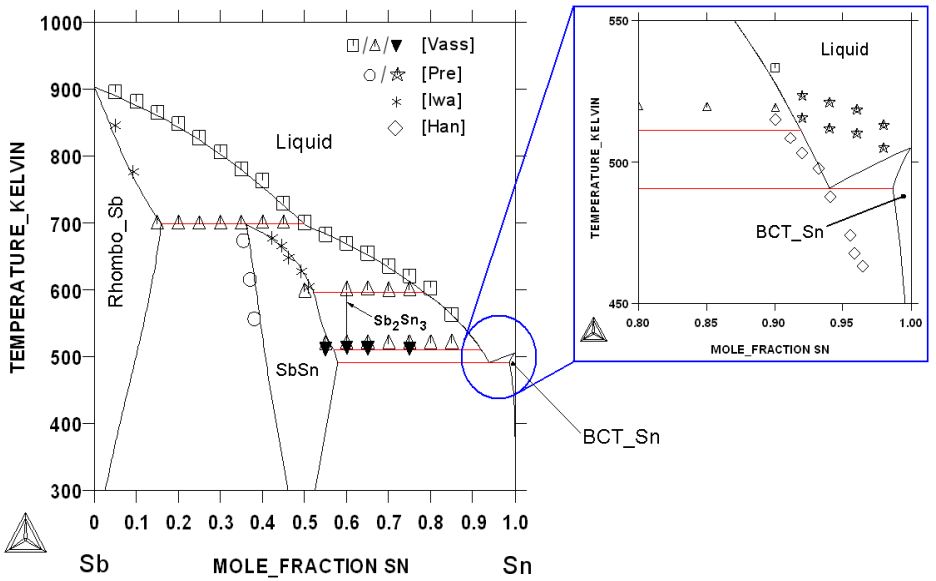
Calculated according to **Oh** utilizing unary data from

SGTE version 1.0 (original paper) and **version 4.4**

G(BCT_A5,SB;0) 1000 + GHSERSB

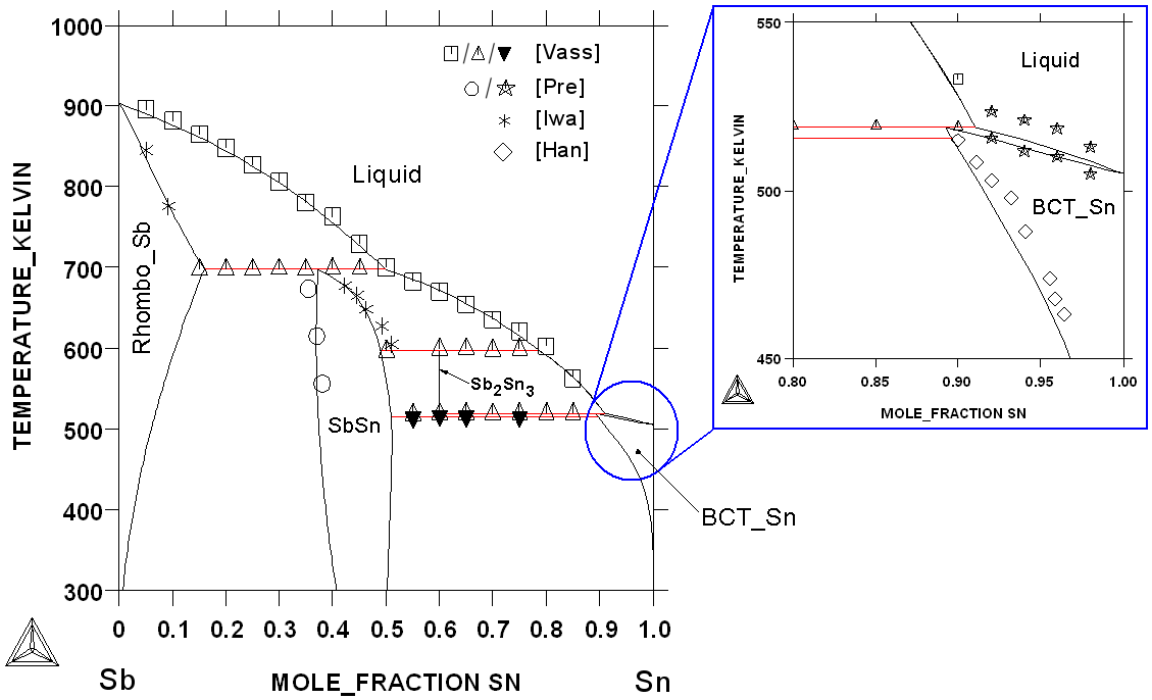
13000-8*T + GHSERSB





The reassessment of the Sb-Sn system

Calculated according to our reassessment utilizing unary data from **SGTE version 4.4**



Sources of experimental data

[Vass] Vassiliev, V., Feutelais, Y., Sghaier, M., Legendre, B.: *J. Alloys Comp.* 314, pp. 198-205, 2001.

[Pre] Predel, B., Schwermann, W.: *J. Inst. Met.* 99, pp. 169-173, 1971.

[Iwa] Iwasé, K., Aoki, N., Osava, A.: *Sci. Rep. Res. Inst.* 20, Tôhoku Univ., pp. 353-368, 1931.

[Han] Hanson, D., Pell-Wallpole, W. T.: *J. Inst. Met.* 58, pp. 299-310, 1936.

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Current status of the SOLDERS database

Scope: 11 elements

Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn, Zn

Binary systems: All 55 binary systems except

Ni-Sb and Pd-Sb

Selected ternary systems:

Ag-Au-Bi, Ag-Au-Sb, Ag-Bi-Sn, Ag-Cu-Ni, Ag-Cu-Pb,
Ag-Cu-Sn, Ag-In-Sn, Ag-Ni-Sn
Au-Bi-Sb, Au-In-Sb, Au-In-Sn, Au-Ni-Sn
Bi-In-Sn, Bi-Sb-Sn, Bi-Sn-Zn
Cu-In-Sn, Cu-Ni-Pb, Cu-Ni-Sn
In-Sb-Sn, In-Sn-Zn

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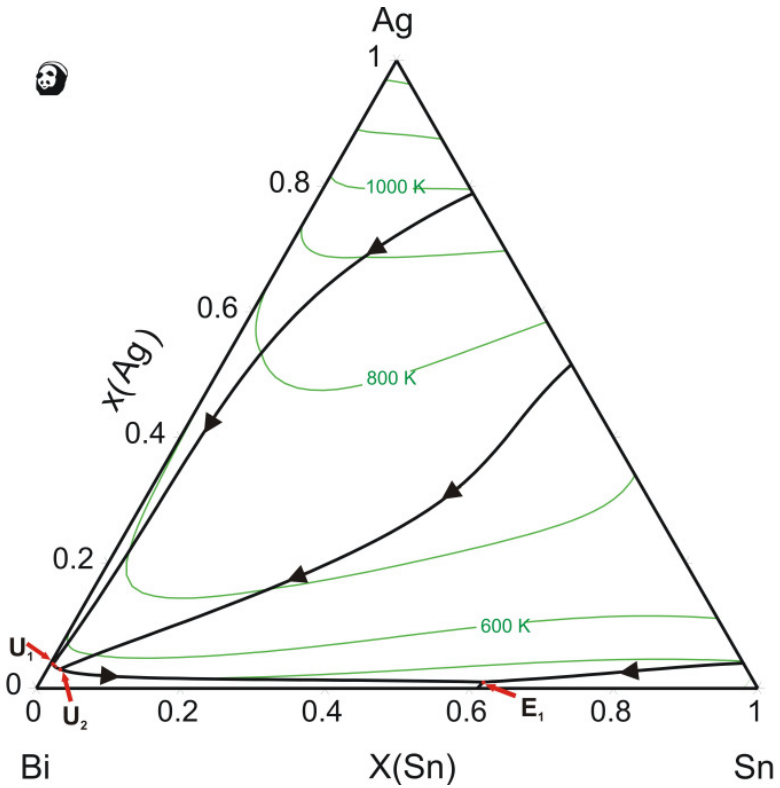
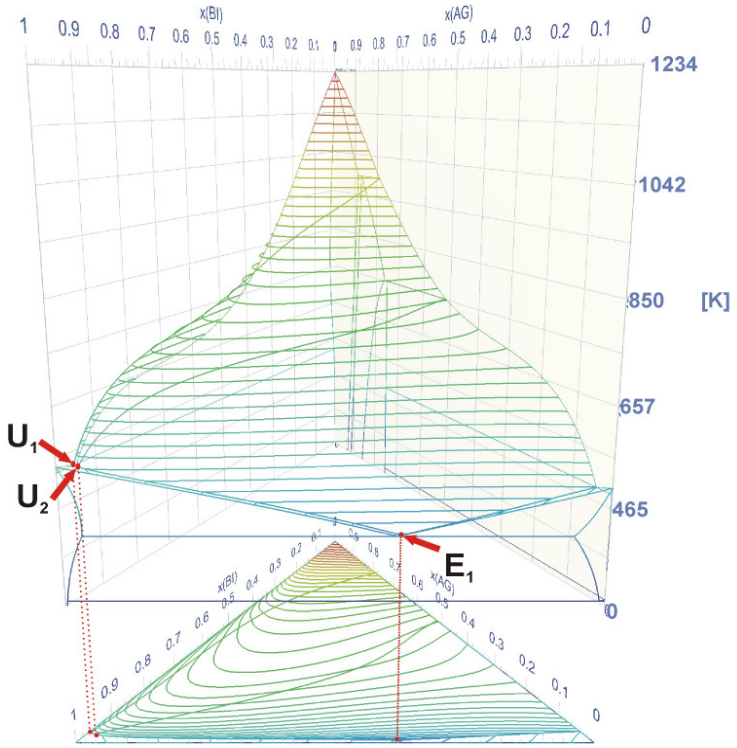
Assessments !!!

Ag-Bi-Sn

Phase diagram calculations



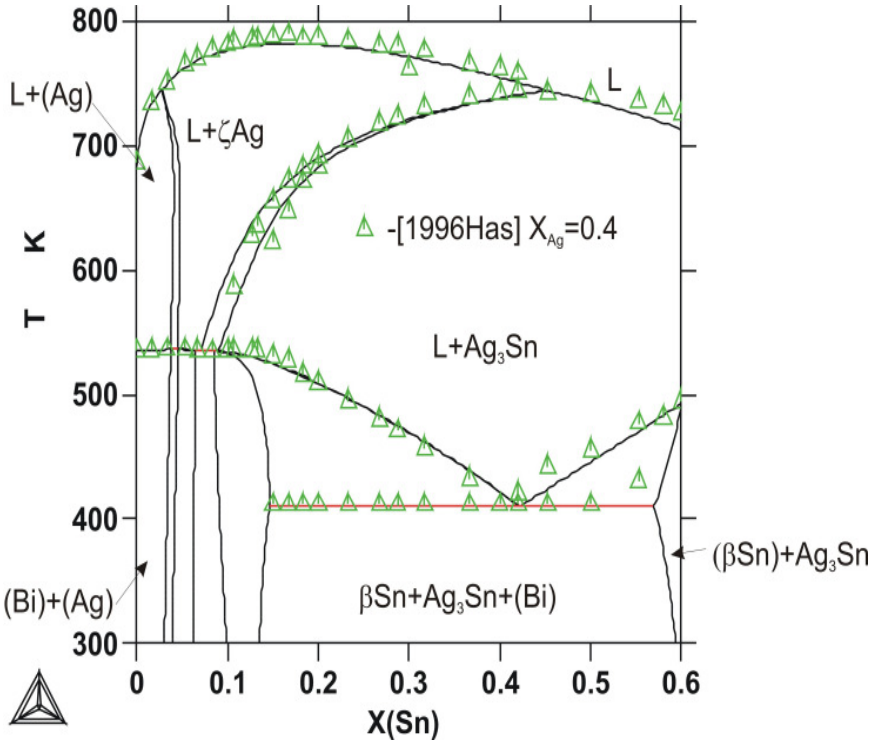
Polythermal projection of liquidus surface

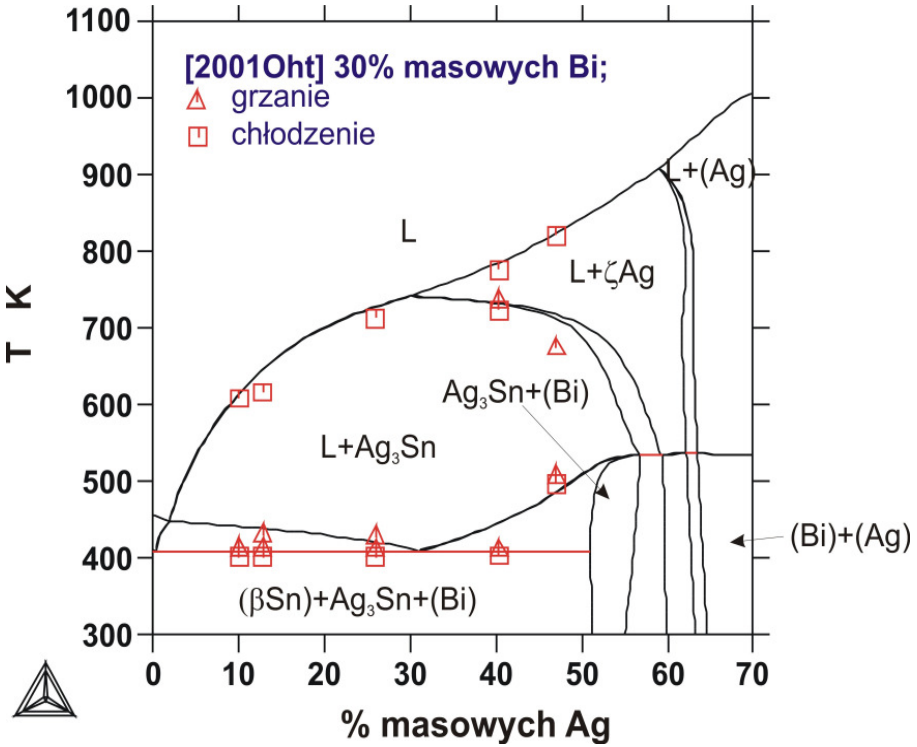


Ag-Bi-Sn 3D phase diagram

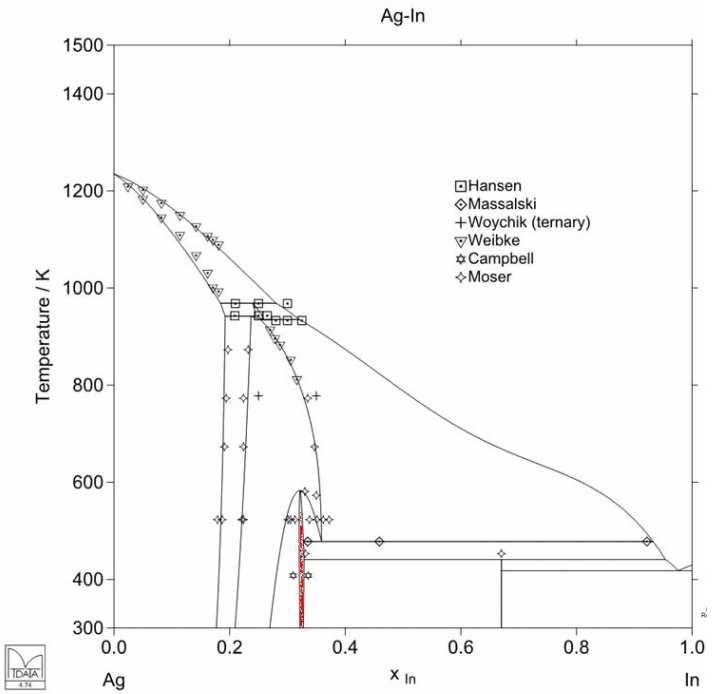
Ag-Bi-Sn

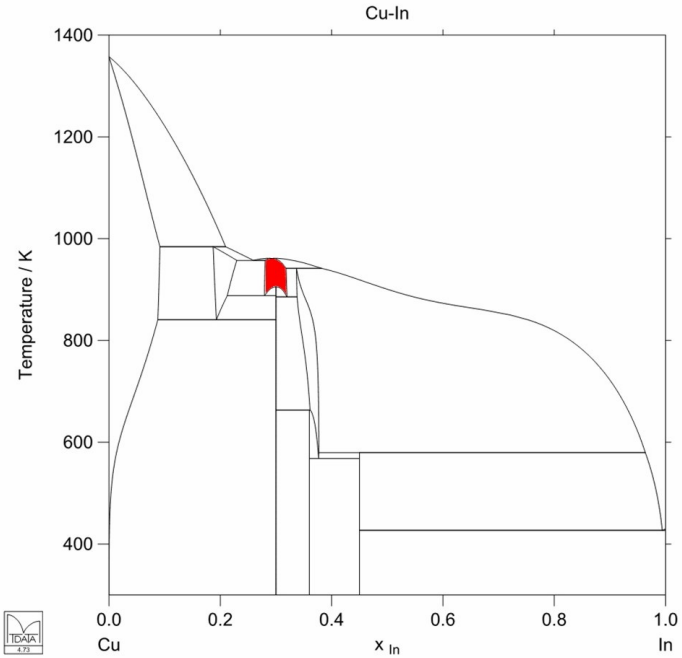
Isopleths





Ag-Cu-In





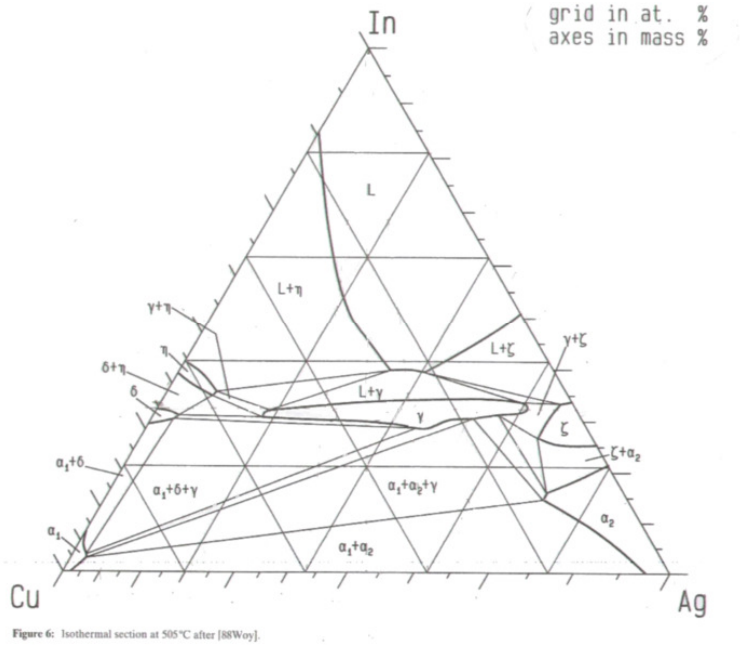
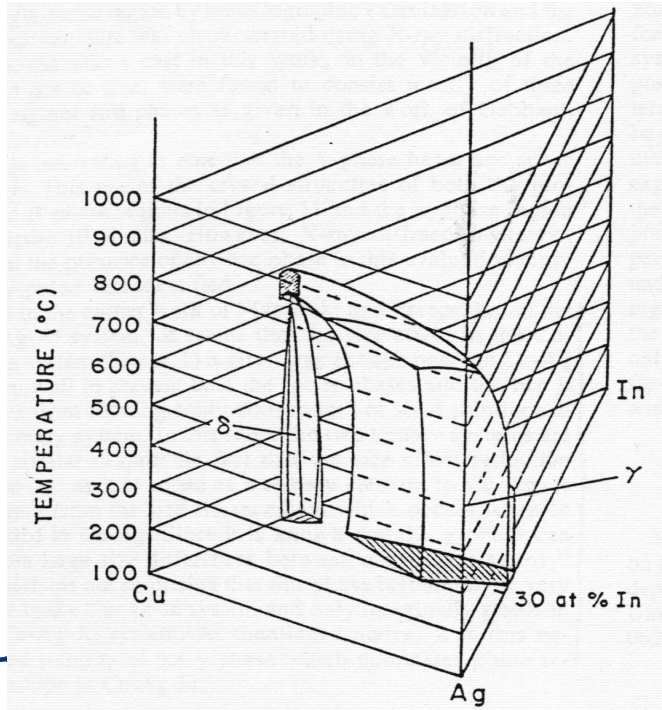
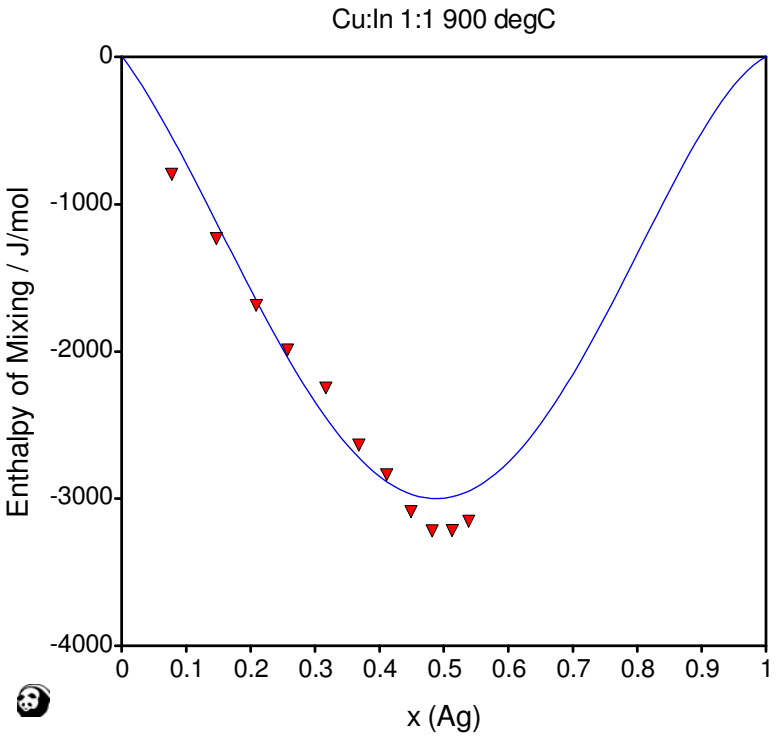
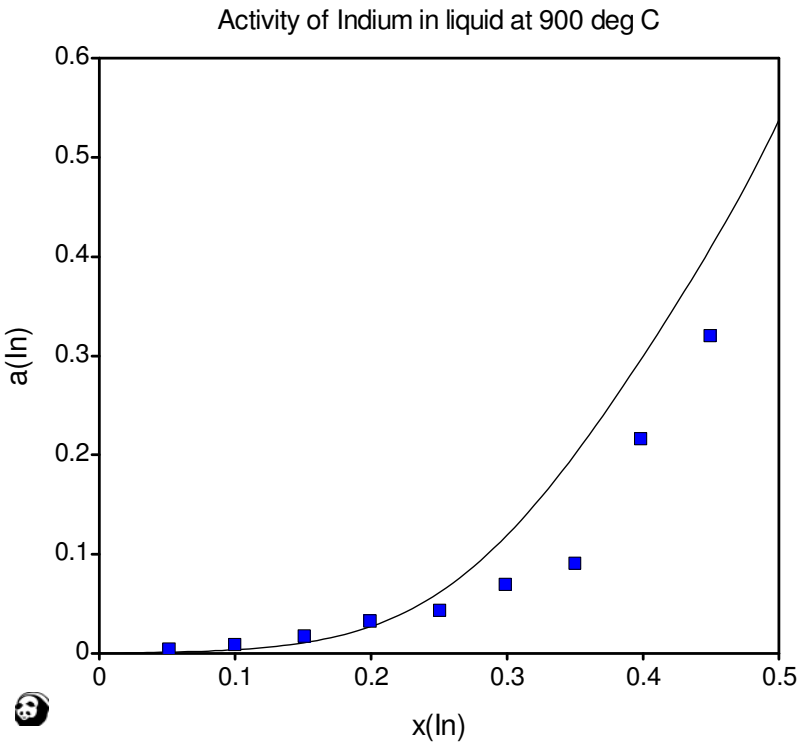


Figure 6: Isothermal section at 505 °C after [88Woy].



Ag-Cu-In


Cu:In 1:1 900 degC
Enthalpy of Mixing / J/mol
0
-1000
-2000
-3000
-4000
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
x (Ag)


Activity of Indium in liquid at 900 deg C
a(In)
0.6
0.5
0.4
0.3
0.2
0.1
0
0 0.1 0.2 0.3 0.4 0.5
x(In)

Ag-Cu-Sn: Experimental studies

• 59GEB/PET	Liquidus surface and primary phase fields
• 69SHE, 69SHE/SPE	Enthalpies of solution of Ag and Cu at 720 K
• 81,82FED/OSI	Determination of temperature-composition sections
• 94MIL/AND	Characterisation of the ternary eutectic
• 99CHA/LAU	Solubility of Cu in Sn-Ag liquids containing 3.5 wt% Ag
• 00LOO/FIN	Determination of ternary eutectic temperature and composition
00MOO/BOE	Phase equilibria for Sn rich compositions. Data assessment for Sn rich compositions.

Recent work

Ipser et al. (2004)	Enthalpies of mixing of Ag-Sn, Cu-Sn, Ag-Cu-Sn liquid alloys
Zabdyr et al.	E.m.f. measurements on Ag-Cu-Sn liquids
Yen and Chen (2004)	Phase equilibria

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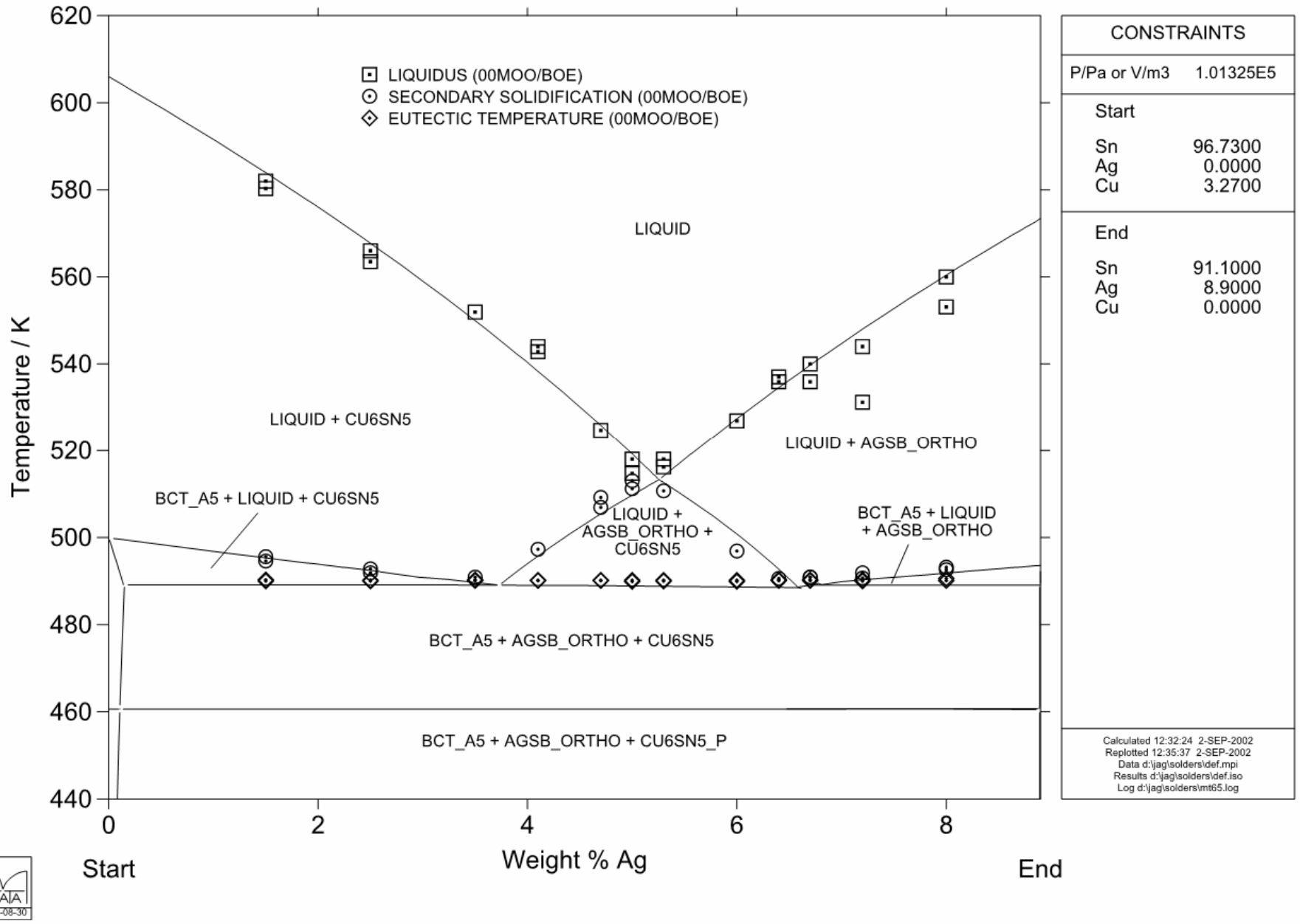
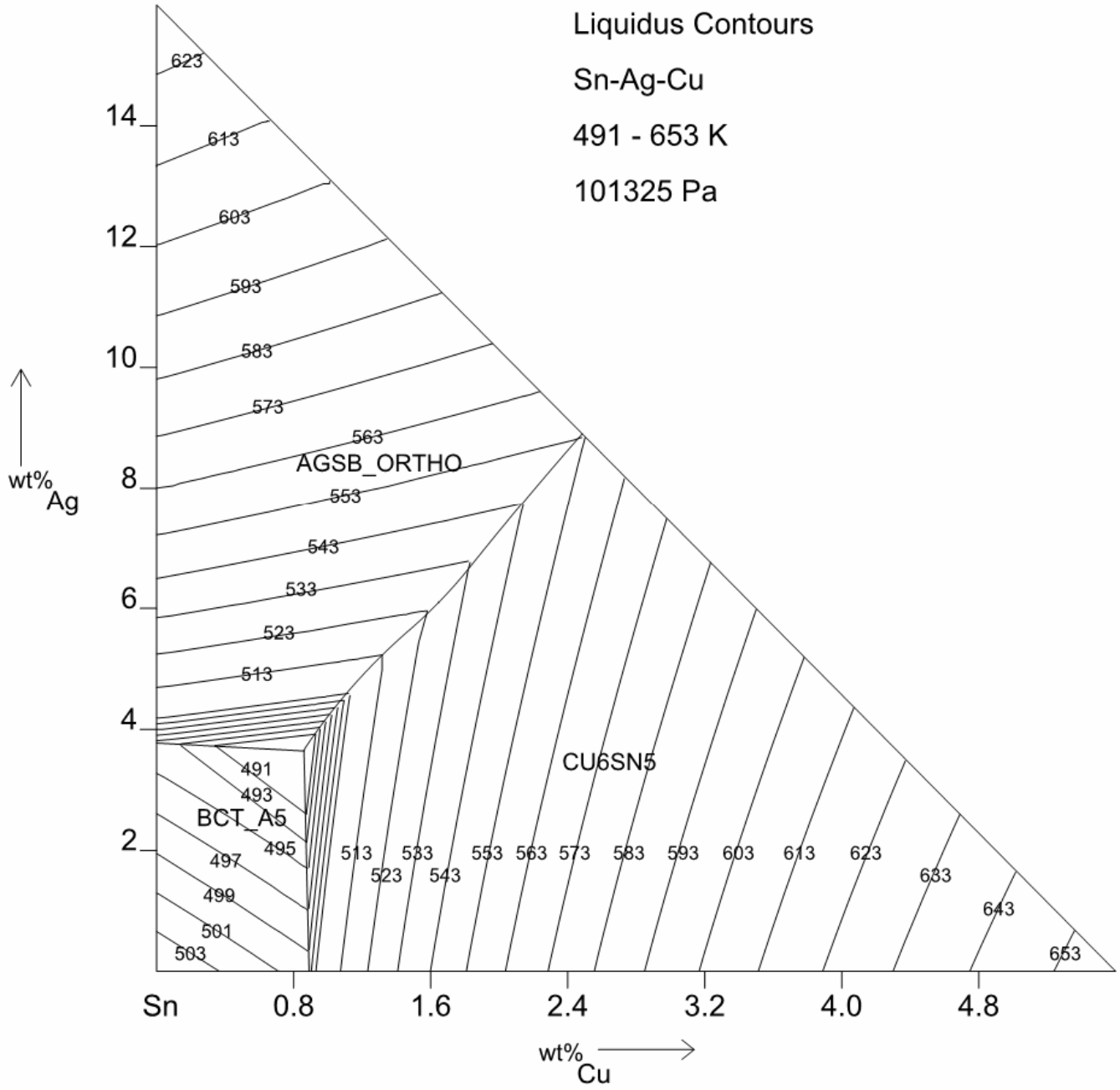
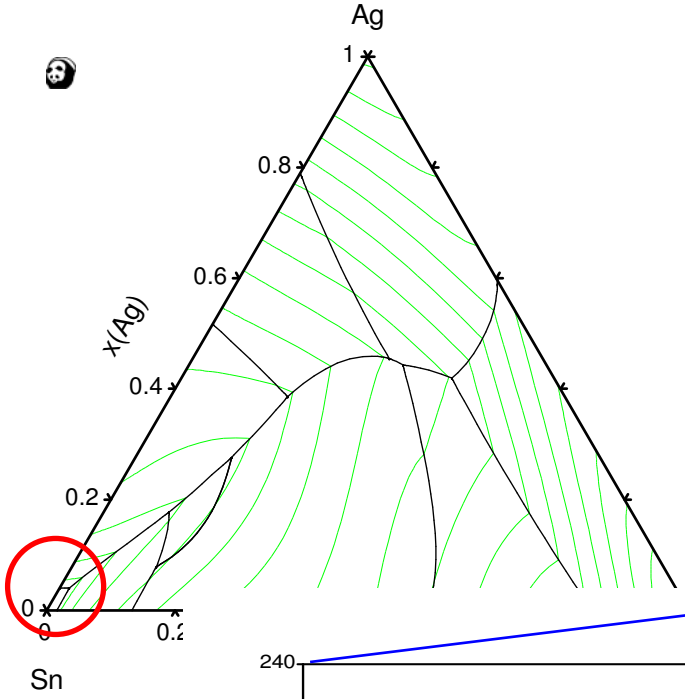
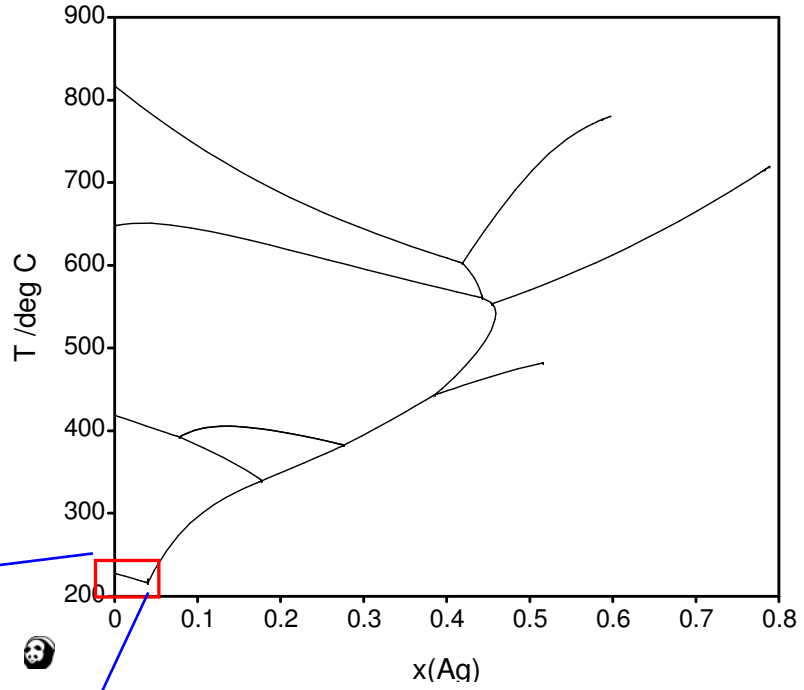

LIQUIDUS (00MOO/BOE)
SECONDARY SOLIDIFICATION (00MOO/BOE)
EUTECTIC TEMPERATURE (00MOO/BOE)
LIQUID
LIQUID + CU6SN5
LIQUID + AGSB_ORTHO
BCT_A5 + LIQUID + CU6SN5
LIQUID + AGSB_ORTHO + CU6SN5
BCT_A5 + LIQUID + AGSB_ORTHO
BCT_A5 + AGSB_ORTHO + CU6SN5
BCT_A5 + AGSB_ORTHO + CU6SN5_P
Temperature / K
620
600
580
560
540
520
500
480
460
440
0
2
4
6
8
Start
Weight % Ag
End
CONSTRAINTS
P/Pa or V/m3 1.01325E5
Start
Sn 96.7300
Ag 0.0000
Cu 3.2700
End
Sn 91.1000
Ag 8.9000
Cu 0.0000
Calculated 12:32:24 2-SEP-2002
Replotted 12:35:37 2-SEP-2002
Data d:\jag\solders\def.mpi
Results d:\jag\solders\def.iso
Log d:\jag\solders\mt65.log
TDATA
2002-08-30

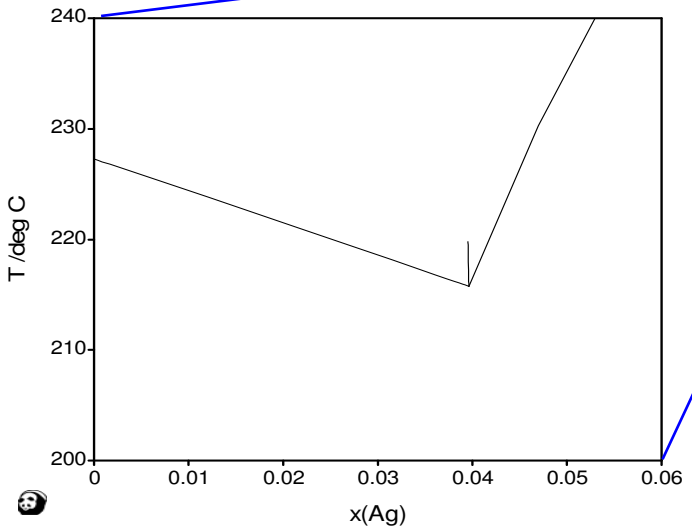


IDAIA
2002-08-30

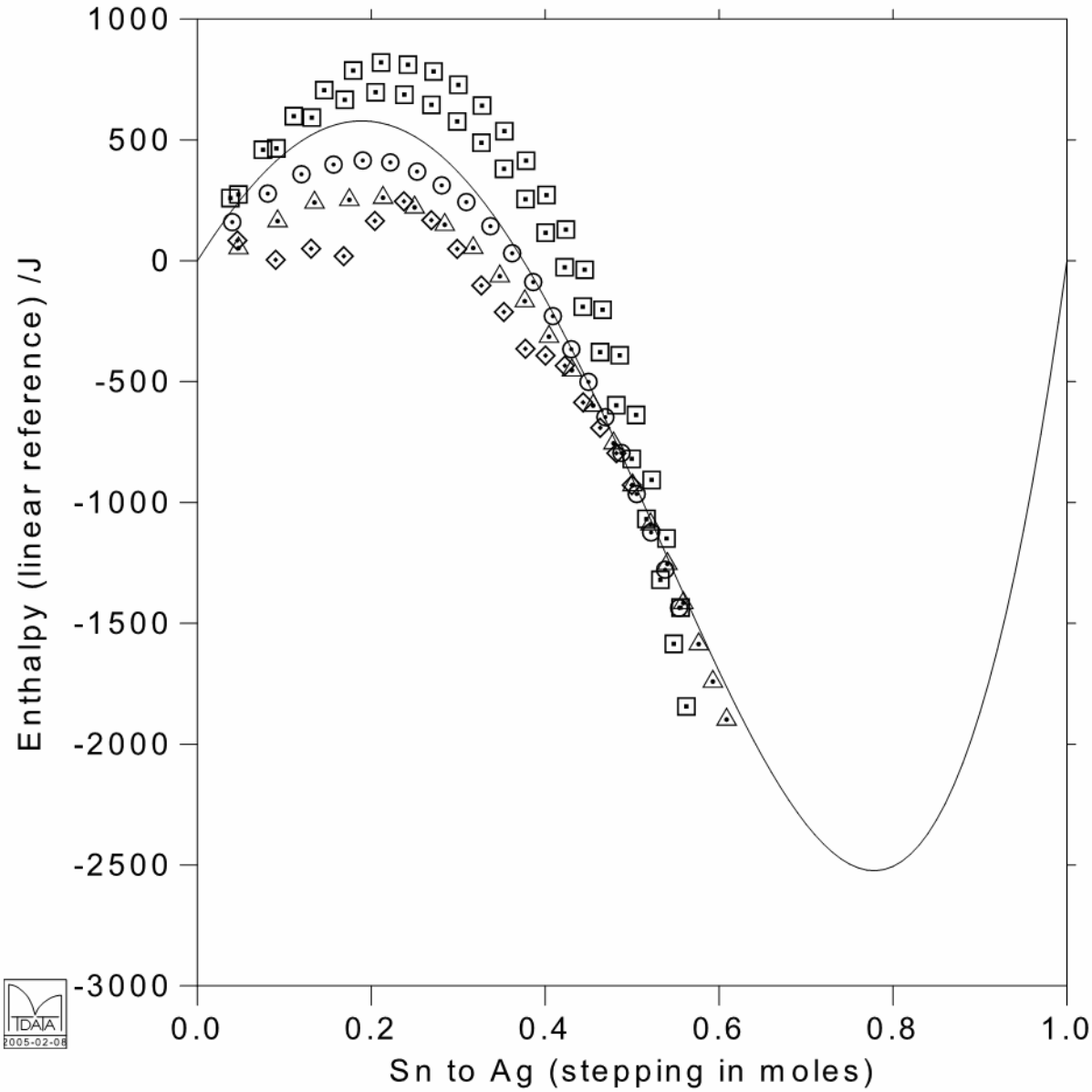
Ag-Cu-Sn


Ag
1
0.8
0.6
0.4
0.2
0
x(Ag)
Sn

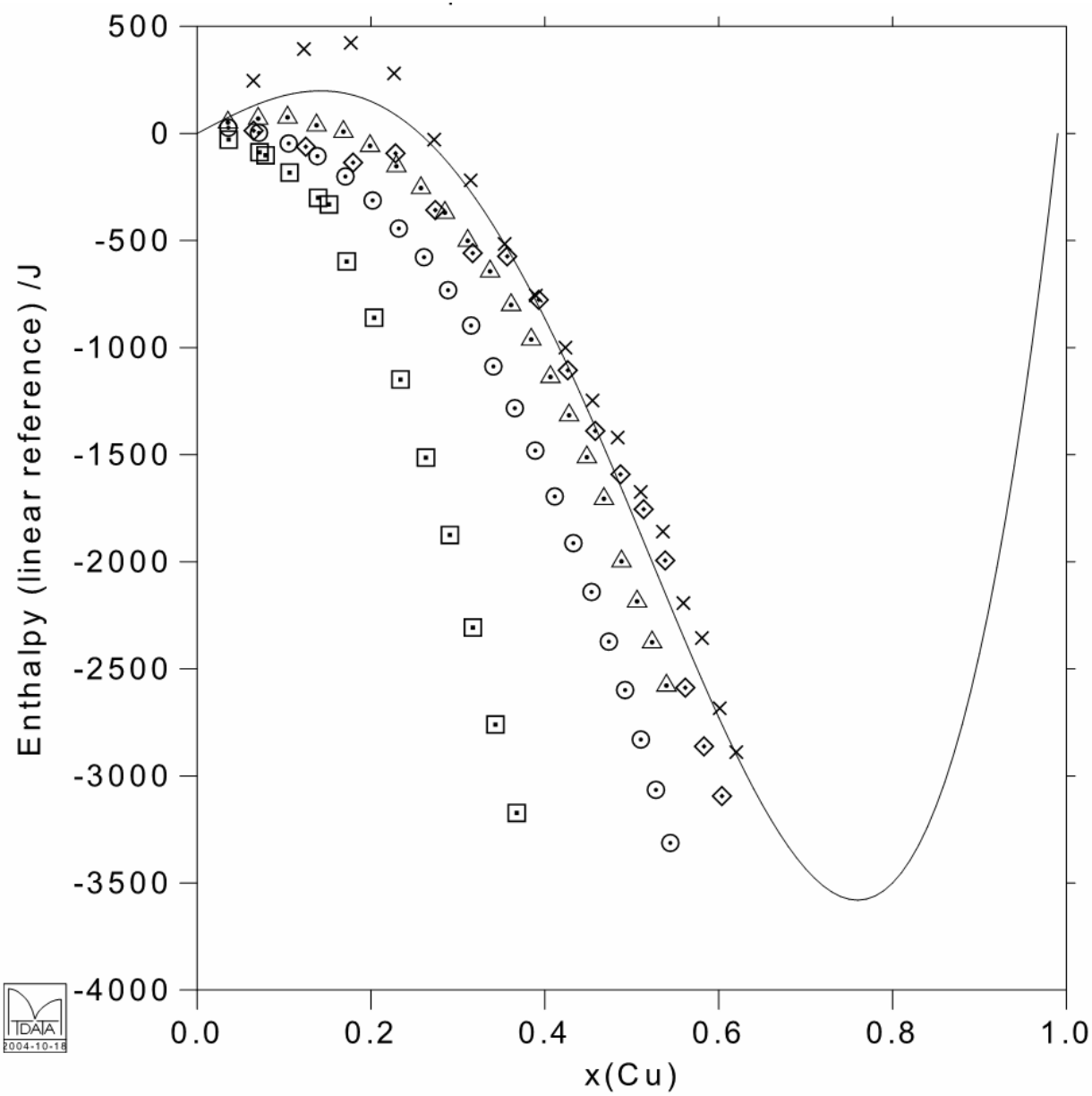

900
800
700
600
500
400
300
200
T /deg C
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x(Ag)


240
230
220
210
200
T /deg C
0
0.01
0.02
0.03
0.04
0.05
0.06
x(Ag)

Enthalpy of mixing - Ag-Sn



Enthalpies of mixing – Cu-Sn



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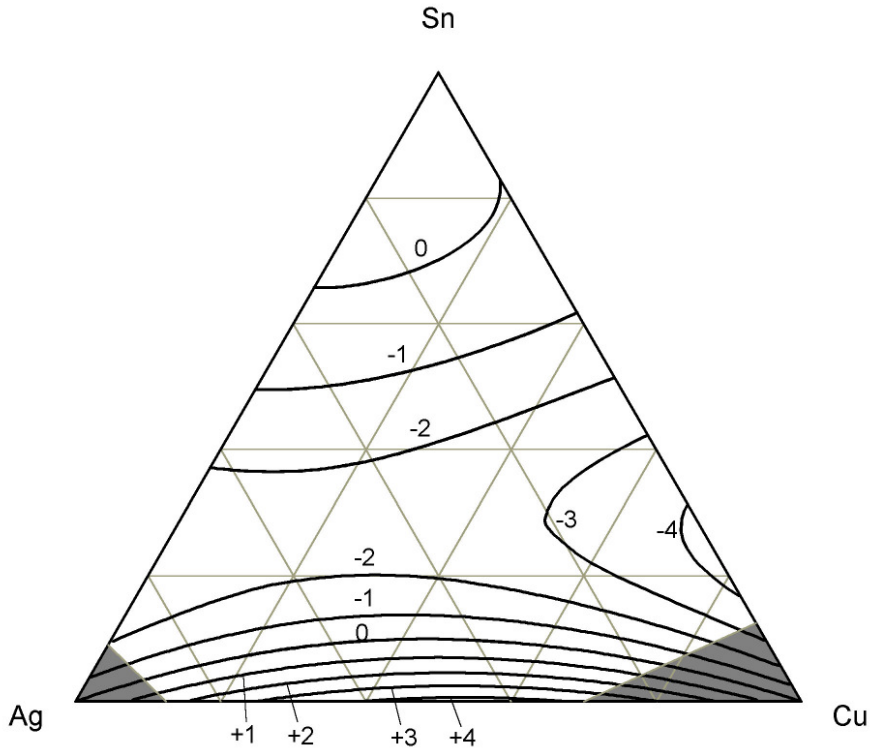
Ag-Sn, Cu-Sn, Ag-Cu-Sn

ΔH_{mix} at 500, 700, and 900°C by drop calorimetry.

C. Luef et al.,
Z. Metallkd. 95 (2004)
151-163.

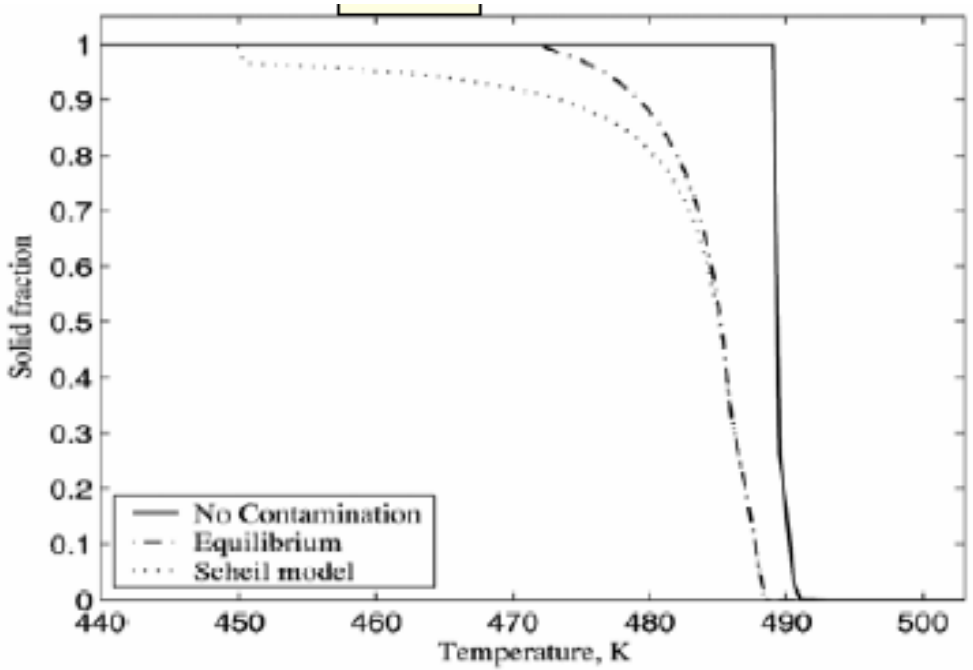


APPLICATIONS

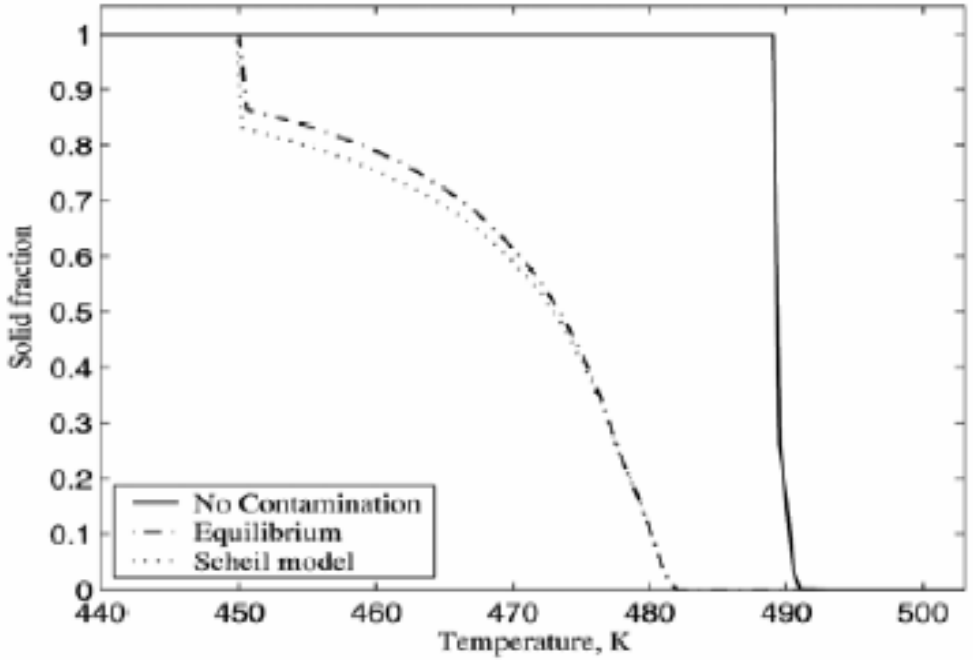
Applications

- Understand issues of contamination of lead free solder through reworking of old solder joints
- Understand volume changes associated with solidification reaction – tin pest
- Predict liquidus and solidus temperatures of candidate solders
- Model formation of the intermetallics at interface between substrate and the solder
- Model surface tension

Contamination of lead free joints

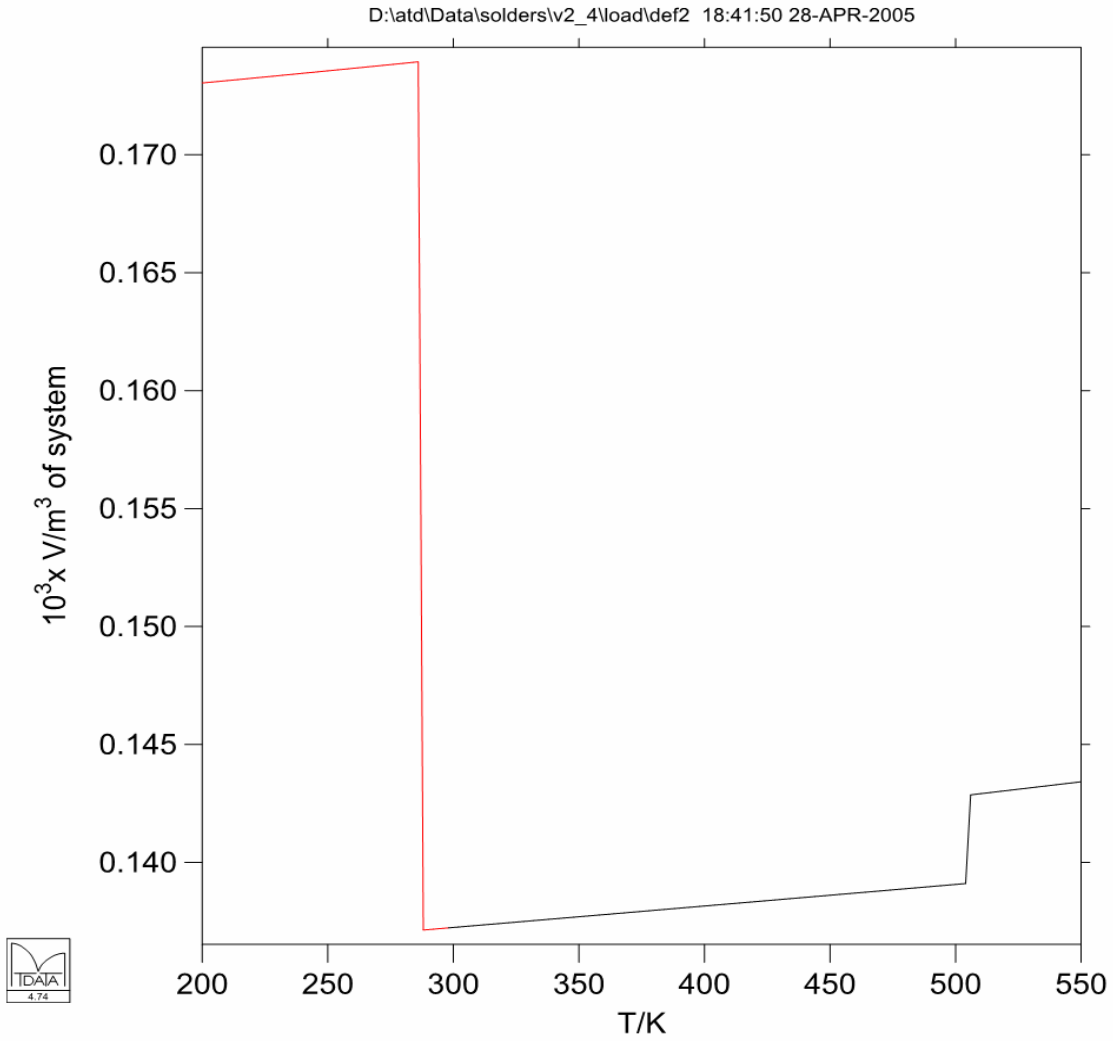


a) 405 + 5 wt.% Sn-37Pb



b) 405 + 20 wt.% Sn-37Pb

Volume changes on solidification - Pure Sn



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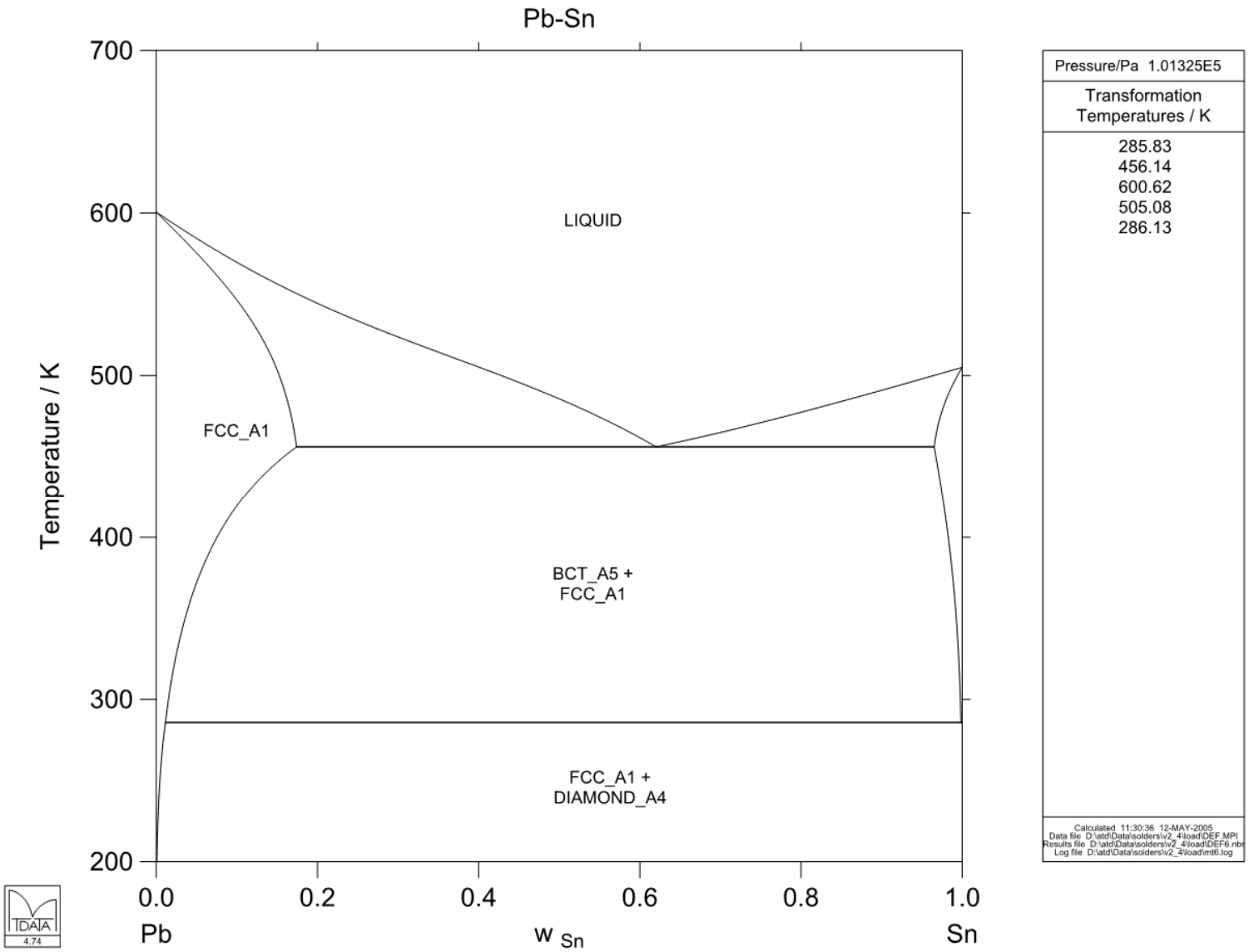
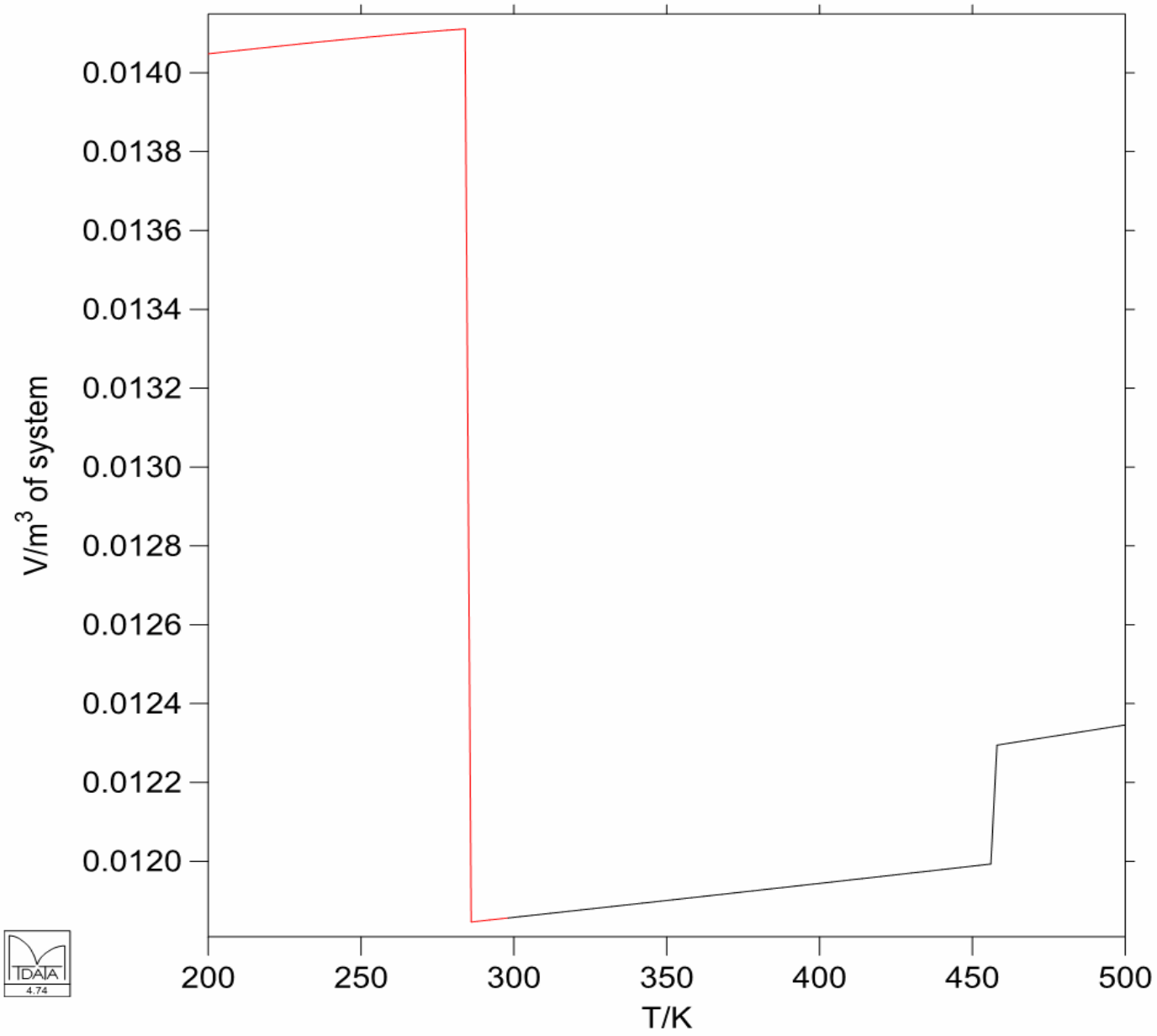
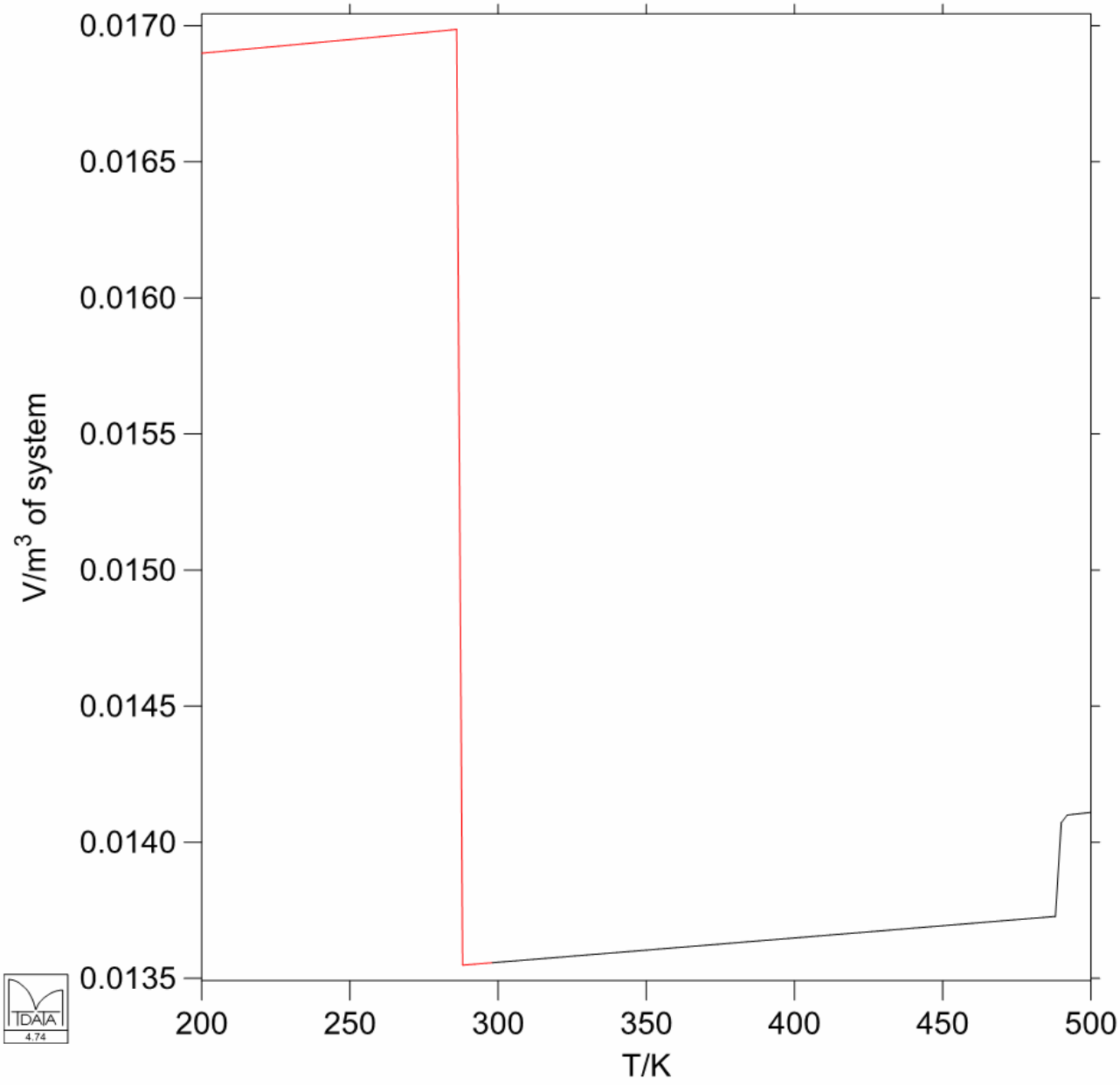
Pb-Sn phase diagram



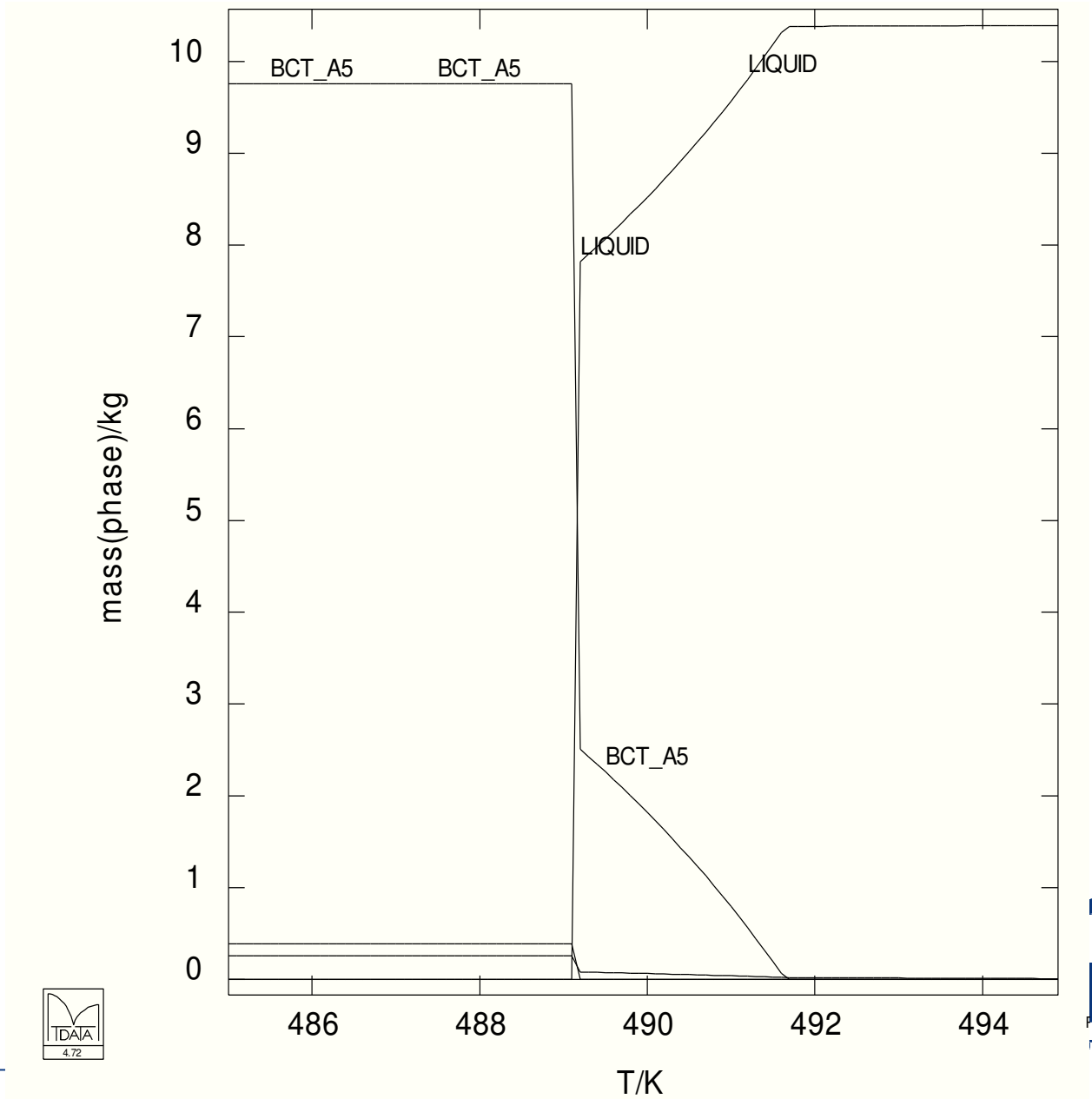
Sn-38%Pb


0.0140
0.0138
0.0136
0.0134
0.0132
0.0130
0.0128
0.0126
0.0124
0.0122
0.0120
V/m3 of system
200
250
300
350
400
450
500
T/K

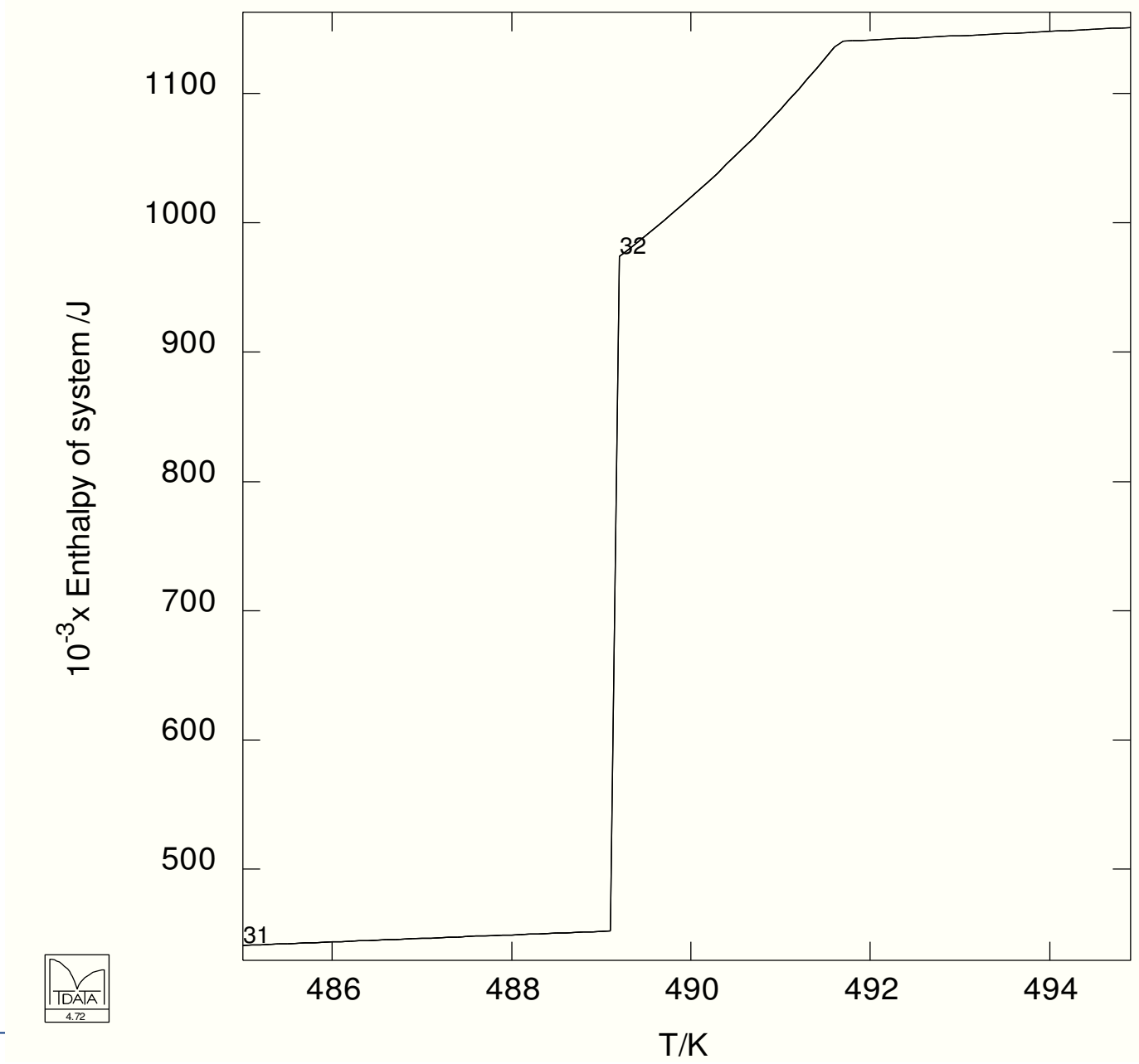
Sn-3.5%Ag-0.7%Cu


0.0170
0.0165
0.0160
0.0155
0.0150
0.0145
0.0140
0.0135
V/m3 of system
200
250
300
350
400
450
500
T/K

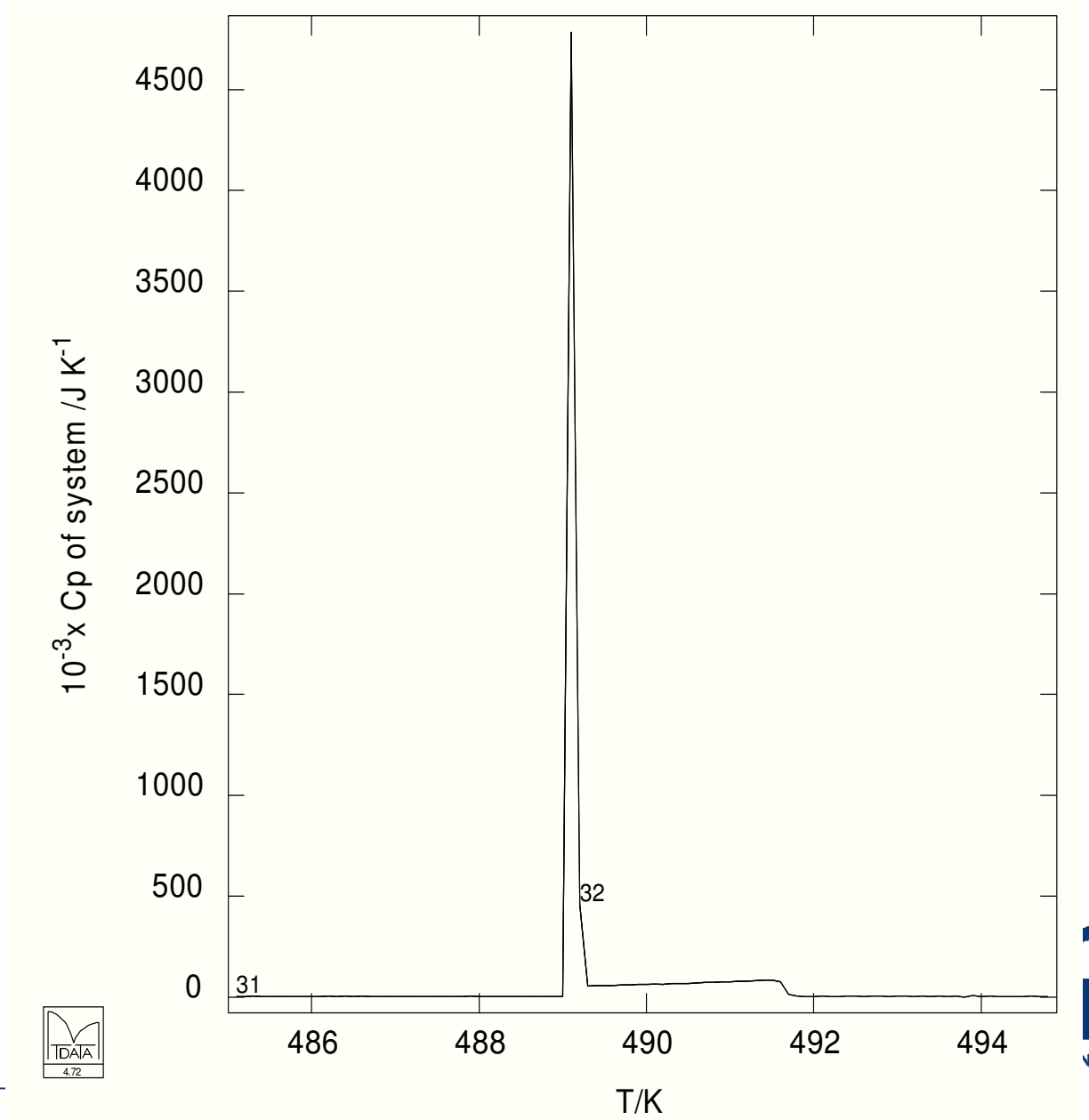
Sn-3.5%Ag-0.7%Cu


BCT_A5
BCT_A5
LIQUID
LIQUID
BCT_A5
mass(phase)/kg
T/K
0
1
2
3
4
5
6
7
8
9
10
486
488
490
492
494

Enthalpy release



Calculated heat capacity



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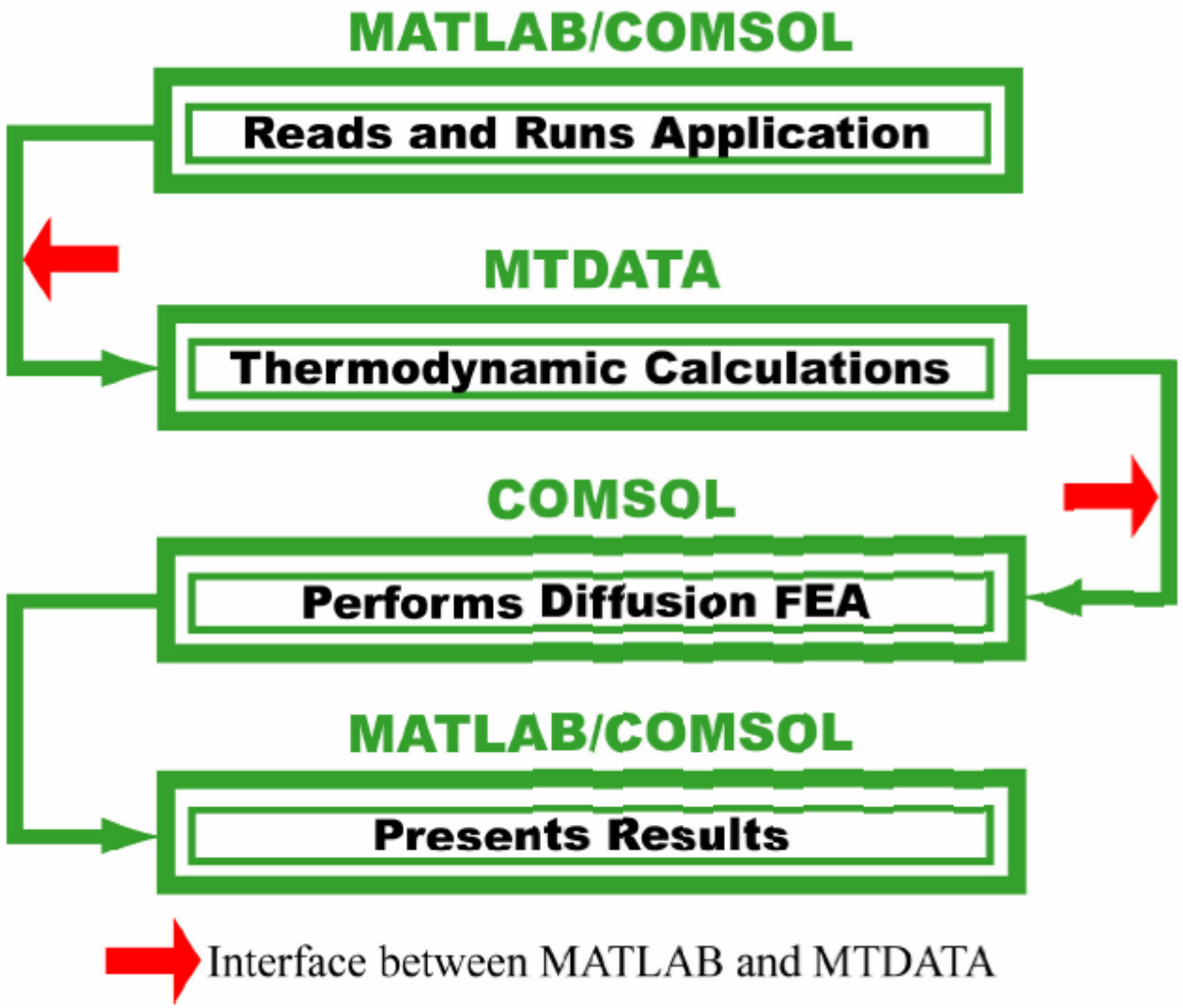
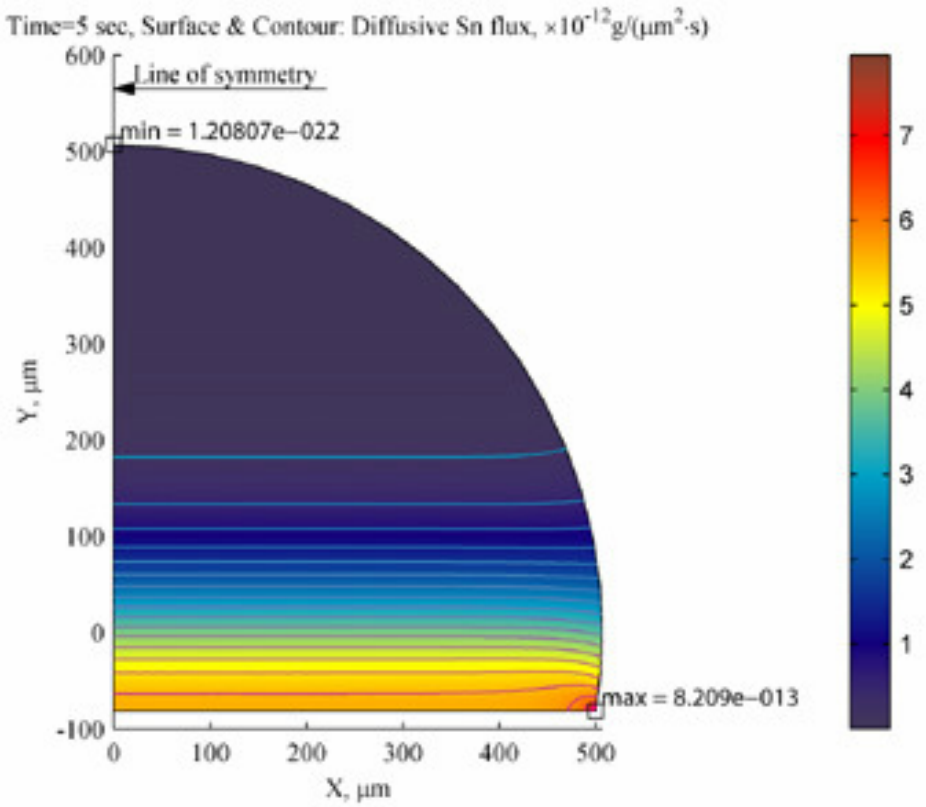
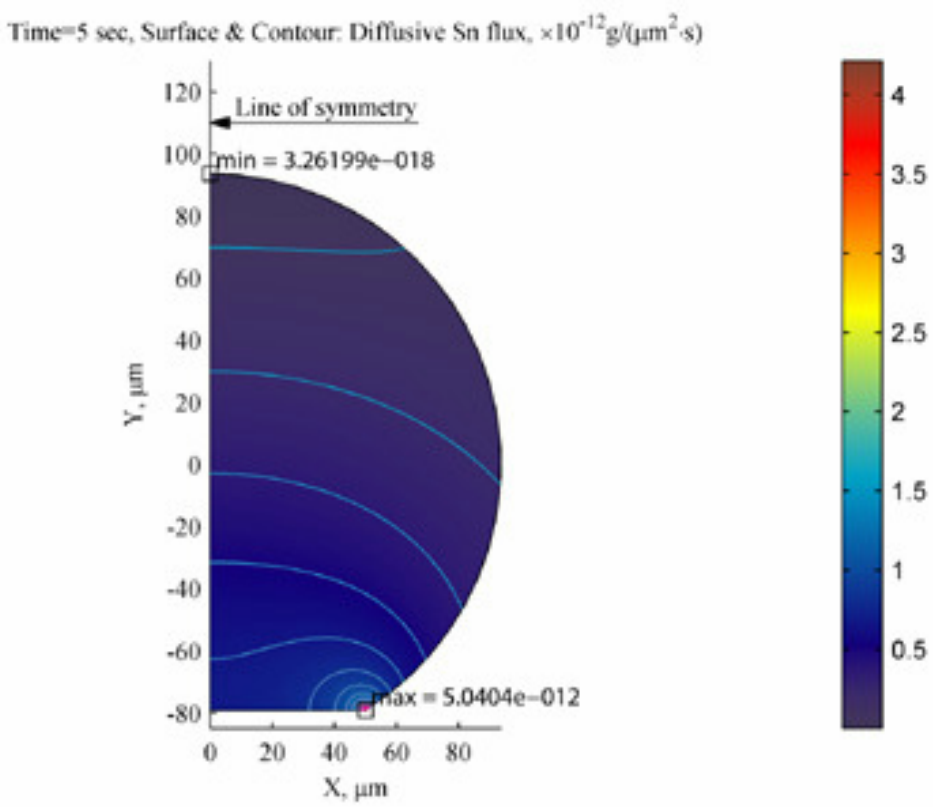
Model formation of the intermetallics at interface

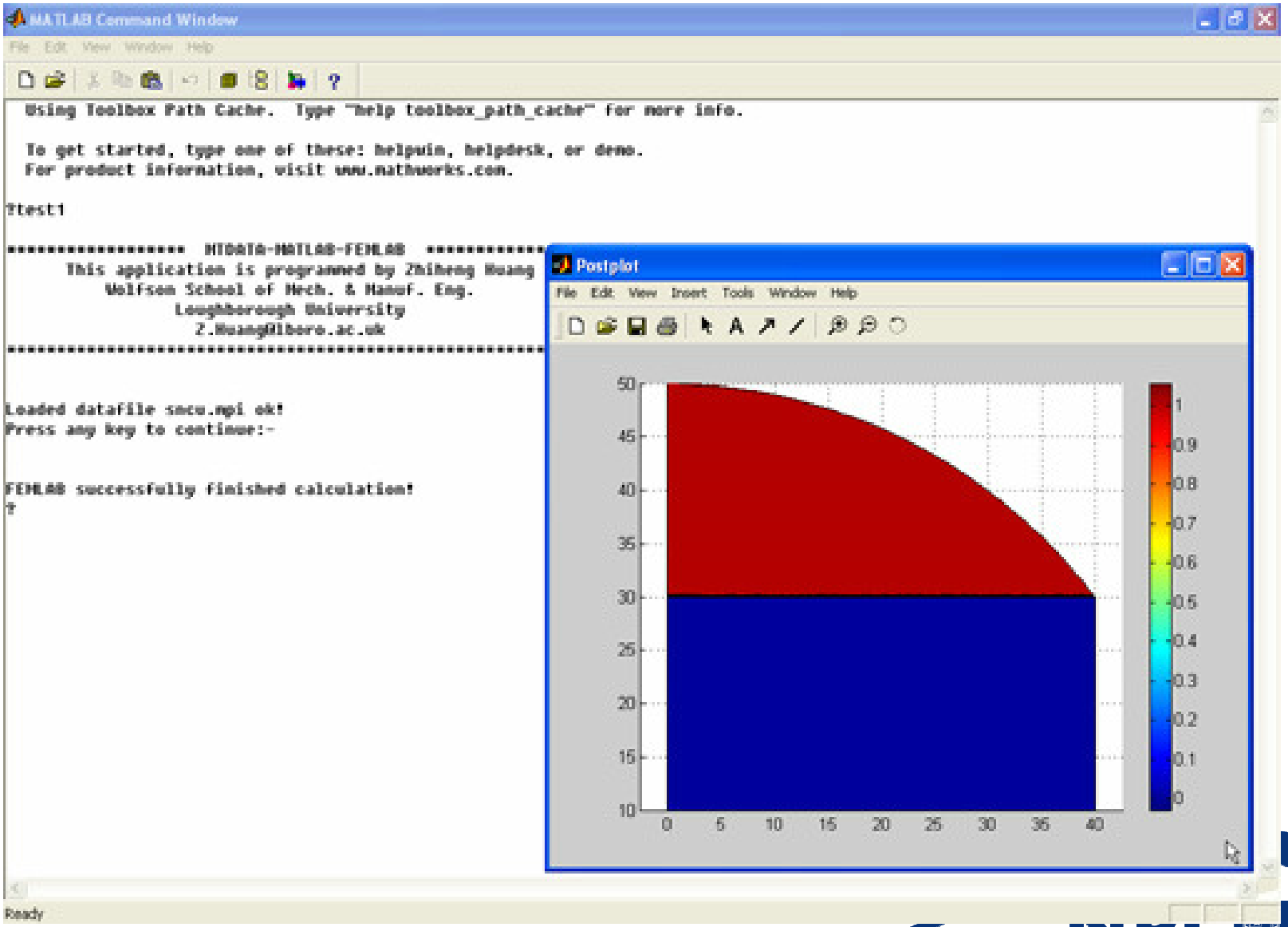


Modelling diffusive Sn flux





MTDATA-MATLAB-COMSOL interface



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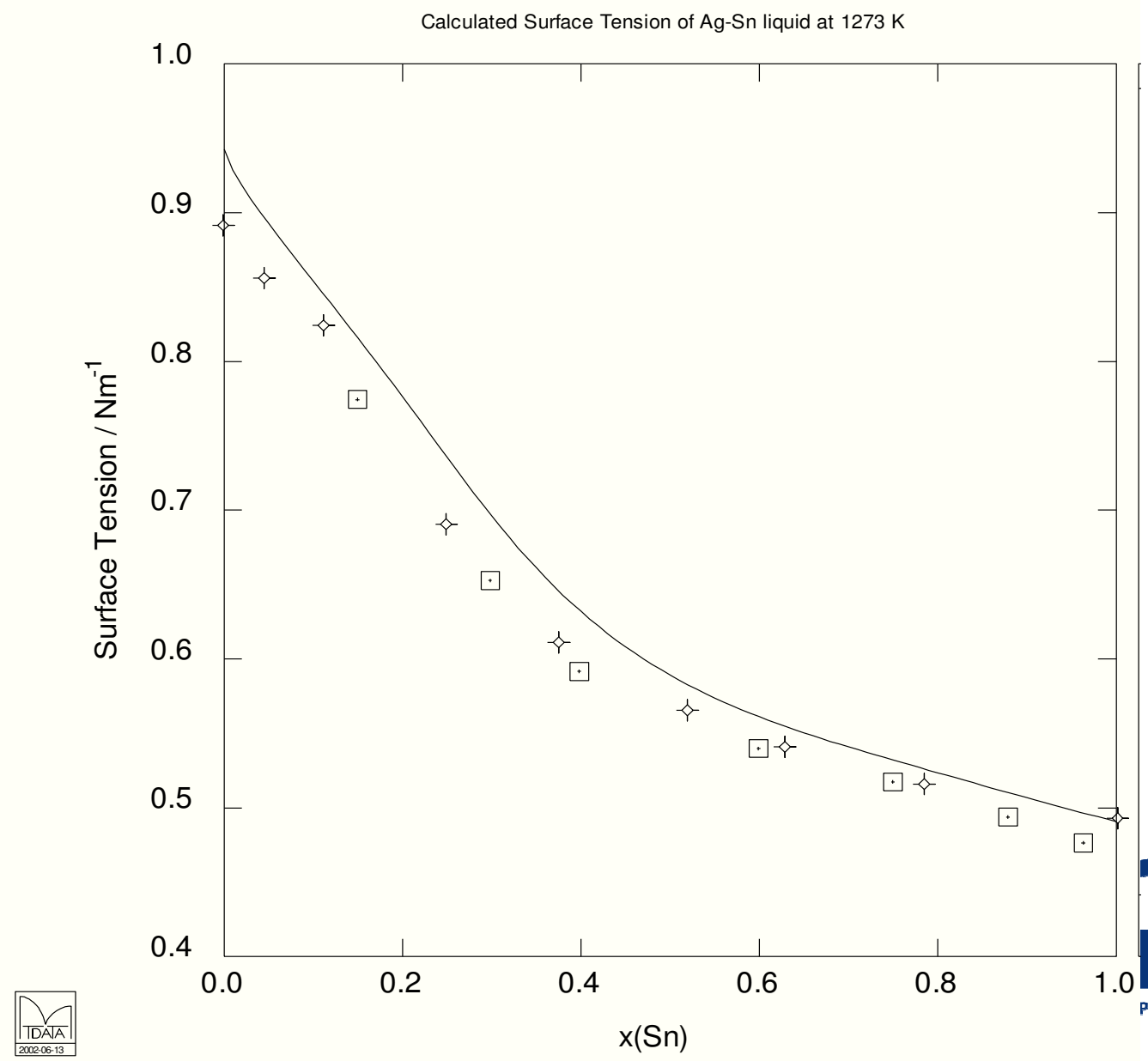
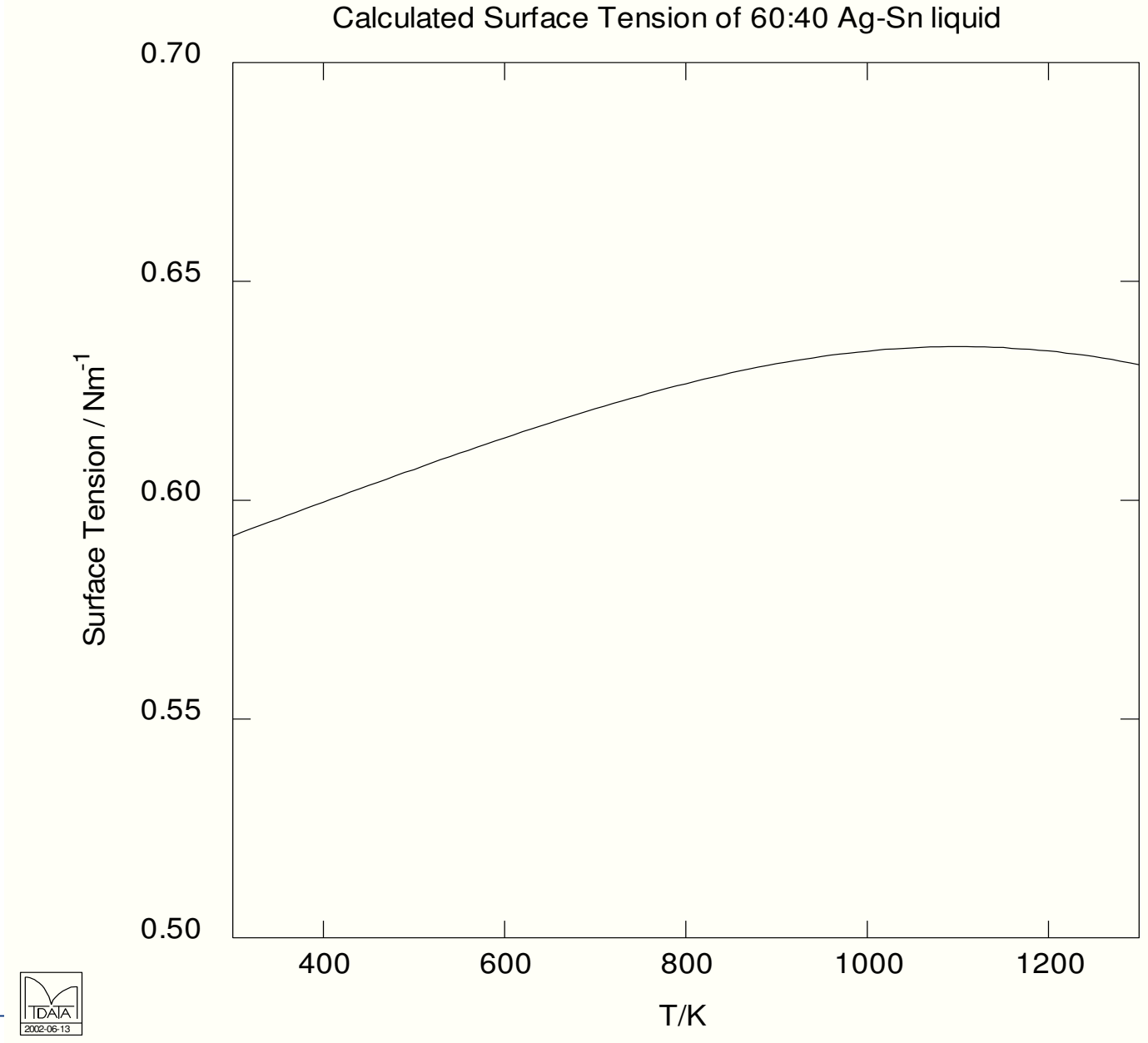
Use thermodynamic properties to model surface tension

- Based on the approach of Tanaka using the Butler equation
- Assumes an equilibrium between the bulk liquid and the surface liquid
- Easily generalised and extended to cover multicomponent systems
- Butler equation shows relation between the surface tension of the binary alloy to the surface tension of the pure components and the thermodynamic properties of the bulk and the surface monolayer
- Equivalent to expressing chemical equilibrium between the bulk liquid and the surface
- Bulk liquid properties modelled from solders database
- Non-ideal interactions in the surface monolayer taken to be a proportion of those for bulk liquid

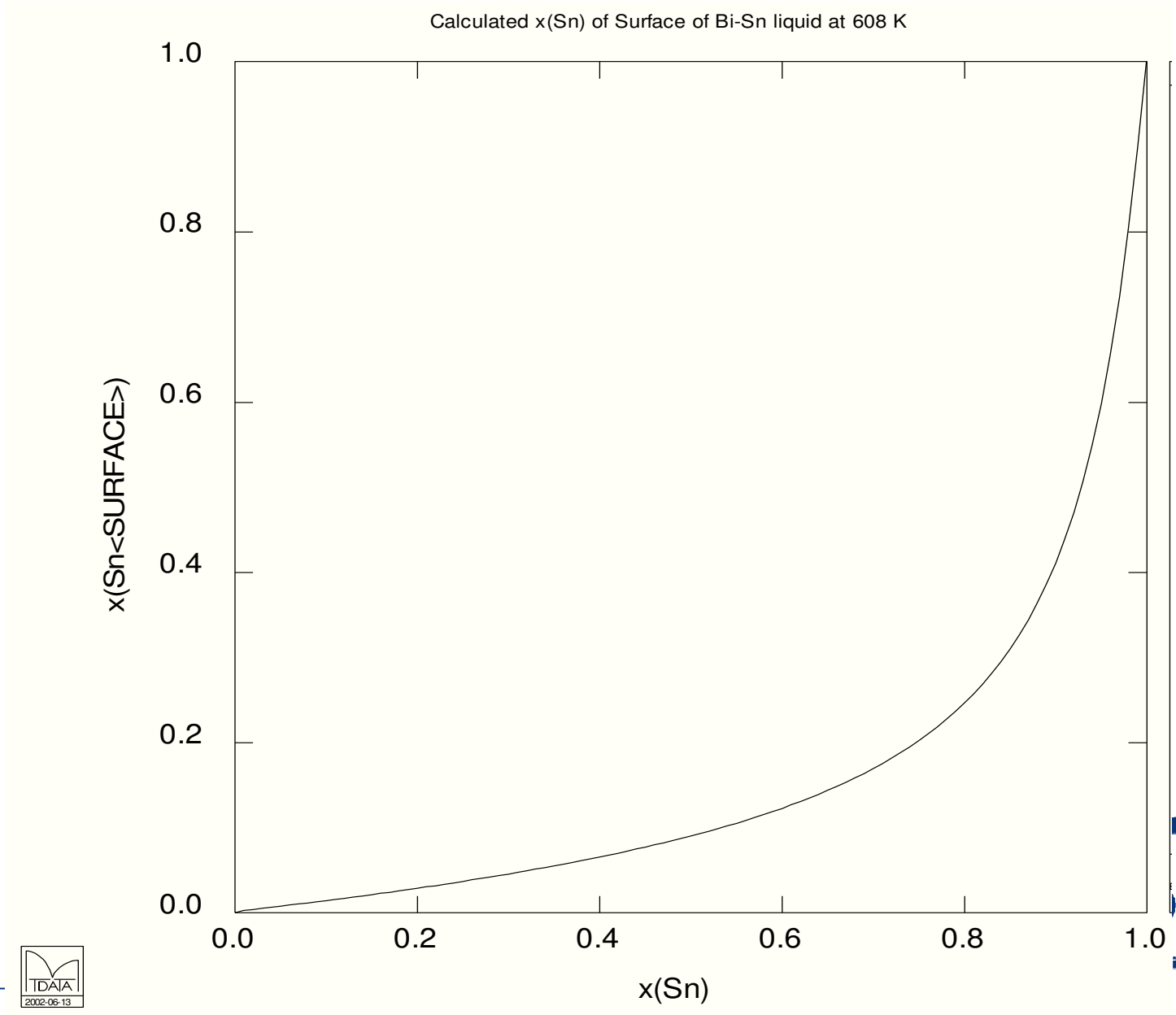
Ag-Sn 1273 K


Calculated Surface Tension of Ag-Sn liquid at 1273 K
Surface Tension / Nm-1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.0
0.2
0.4
0.6
0.8
1.0
x(Sn)

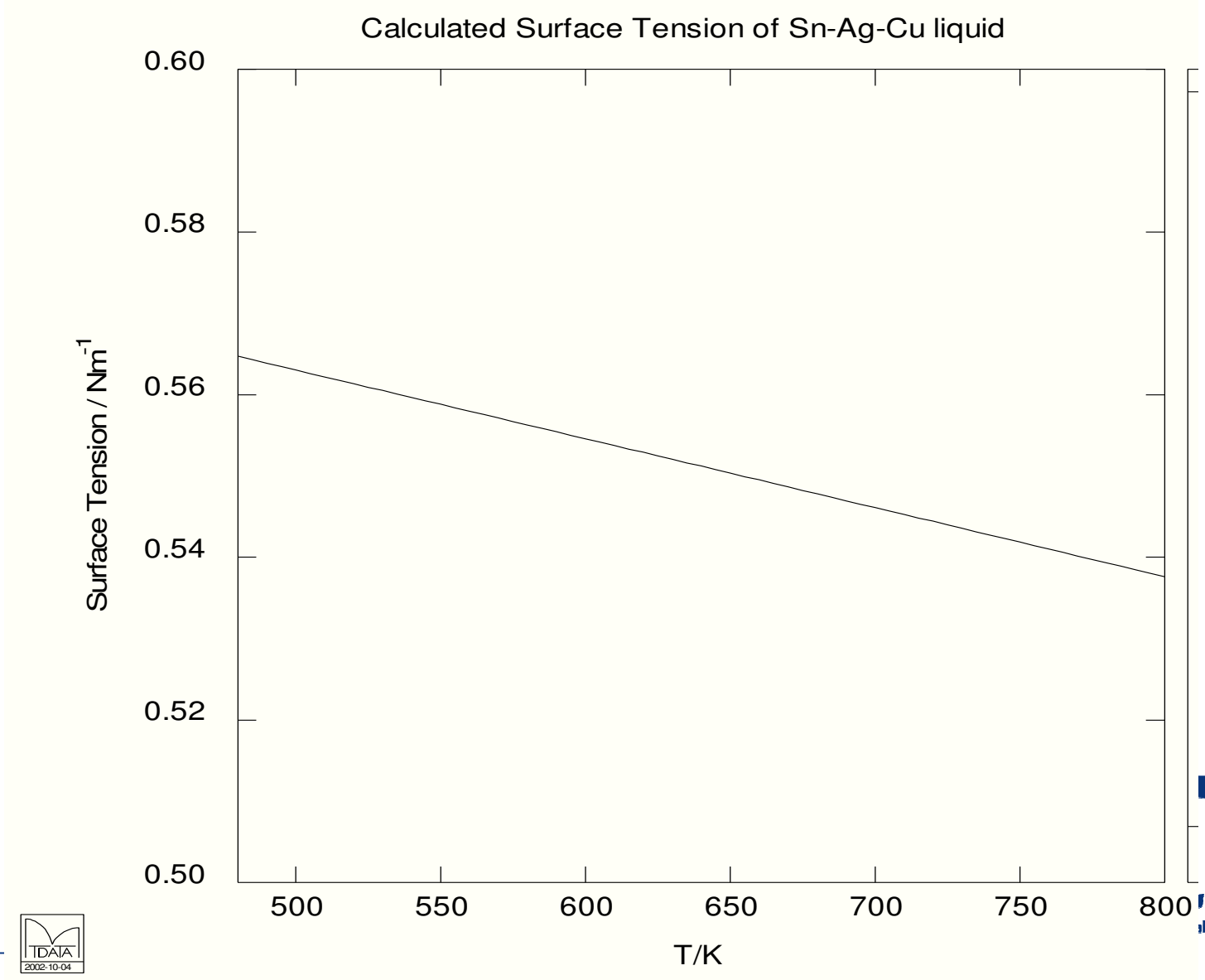
Ag-Sn 40%Sn : effect of temperature



Surface composition: Bi-Sn 608 K



Sn-Ag-Cu: variation with temperature



How you can access the database

- Database will not be published as such (ie as for COST507)
- Will be available to COST531 and MP0602 partners for internal use
- Now available through software providers (eg TCSAB, NPL, GTT) in association with SGTE
- Income will be used to support further database development

Conclusions and Future work

- COST
  - COST531
  - MP0602 - HISOLD
- COST531 thermodynamic database
  - Scope of the database
  - Emphasis on consistency
- How the database can be used
  - Understanding of the interface between substrate and the solder
  - Predict liquidus and solidus temperatures of candidate solders
  - Modelling surface tension
  - Understand volume changes associated with solidification
  - Understand issues of contamination of lead free solder

Thank you for your attention