

# **TCS Solder Alloy Solutions Database (TCSLD)**

## **Examples Collection**



## Contents

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<b>About the Database Examples</b> .....	<b>3</b>
<b>TCS Solder Alloy Solutions Database (TCSLD) Resources</b> .....	<b>4</b>
<b>TCSLD Calculation Examples</b> .....	<b>5</b>
Binary Phase Diagrams .....	6
Ternary Isothermal Section .....	8
Solidification Simulations .....	9
Formation of Interfacial Products .....	11
Surface Tension: Ag-Cu, Ag-Sn, Cu-Sn, and Ag-Cu-Sn .....	13
Viscosity: Ag-Cu, Ag-Sn, and Sn-Ag-Cu .....	17
<b>TCSLD Validation Examples</b> .....	<b>20</b>
Effect of Alloying Element on Melting .....	21
Liquidus and Solidus Temperatures .....	22
Liquidus Projection .....	23
Surface Tension of Cu-Sn-Bi-In-Pb Alloy .....	26
Viscosity of SAC Alloy .....	28

## About the Database Examples

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There are examples available to demonstrate both the *validity* of the database itself as well as to demonstrate some of its *calculation* capabilities when combined with Thermo-Calc software and its Add-on Modules and features.



For each database, the type and number of available examples varies. In some cases an example can belong to both a validation and calculation type.

- *Validation* examples generally include experimental data in the plot or diagram to show how close to the predicted data sets the Thermo-Calc calculations are. It uses the most recent version of the software and relevant database(s) unless otherwise specified.
- *Calculation* examples are intended to demonstrate a use case of the database. This might be showing a binary or ternary system calculated in a phase diagram, or demonstrate how the database and relevant software features would be applied to a heat treatment application, process metallurgy, soldering process, and so forth. In the case of heat treatment, it might include the result of calculating solidification segregation, determining homogenization temperature and then predicting the time needed to homogenize. There are many other examples specifically related to each database.



Where relevant, most references related to each example set are included at the end of the individual section. You can also find additional references specific to the database itself when using the database within Thermo-Calc. You can also contact us directly should you have any questions.



If you are interested in sharing your own examples using Thermo-Calc products in unique or surprising ways, or if you want to share your results from a peer reviewed paper, send an email to [info@thermocalc.com](mailto:info@thermocalc.com).

## TCS Solder Alloy Solutions Database (TCSLD) Resources

Information about the database is available on our website and in the Thermo-Calc software online Help.

- **Website:** On our website the information is both searchable and the database specific PDFs are available to download.
- **Online Help:** Technical database information is included with the Thermo-Calc software online Help. When in Thermo-Calc, press F1 to search for the same information as is contained in the PDF documents described. Depending on the database, there are additional examples available on the website.

### Database Specific Documentation

- The *TCS Solder Alloy Solutions Database (TCSLD) Technical Information* PDF document contains version specific information such as the binary and ternary assessed systems, phases and models. It also includes details about the properties data (e.g. viscosity, surface tension, etc.), a list of the included elements, and summaries of the database revision history by version.
- The *TCS Solder Alloy Solutions Database (TCSLD) Examples Collection* PDF document contains a series of validation examples using experimental data, and a set of calculation examples showing some of the ways the database can be used.



Go to the [Solder Alloys Databases](#) page on our website where you can access an examples collection and the technical information plus learn more about the compatible kinetic database. Also explore further [applications of Thermo-Calc to solders](#) including links to resources such as examples, publications, and more.



Learn more on our website about the [CALPHAD Method](#) and how it is applied to the Thermo-Calc databases.

## TCSLD Calculation Examples

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Some diagrams are calculated with earlier versions of the database. Negligible differences might be observed if these are recalculated with the most recent version. The diagrams are updated when there are considerable or significant improvements.

### In this section:

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Binary Phase Diagrams .....	6
Ternary Isothermal Section .....	8
Solidification Simulations .....	9
Formation of Interfacial Products .....	11
Surface Tension: Ag-Cu, Ag-Sn, Cu-Sn, and Ag-Cu-Sn .....	13
Viscosity: Ag-Cu, Ag-Sn, and Sn-Ag-Cu .....	17

## Binary Phase Diagrams

Included binary systems in the TCS Solder Alloy Solutions Database (TCSLD) are critically assessed based on available experimental and theoretical data for phase diagram and thermodynamic properties.

Some important key binary systems for lead-free solders are shown here, for example, Ag-Sn and Cu-Sn are sub-systems of the SnAgCu solder alloys, and Cu is commonly used in substrate materials.  $\text{Ag}_3\text{Sn}$  is often observed in solidified solder bulk alloys,  $\text{Cu}_6\text{Sn}_5\text{-HT}$  and  $\text{Cu}_3\text{Sn}$  are commonly interfacial reaction products.



Learn more on our website about the [CALPHAD Method](#) and how it is applied to the Thermo-Calc databases.



When working in Thermo-Calc with binary diagrams you use either the Binary Calculator (in Graphical Mode) or the Binary module (in Console Mode). The fundamental calculation engine is the same but you access the settings in different ways.

### Ag-Sn

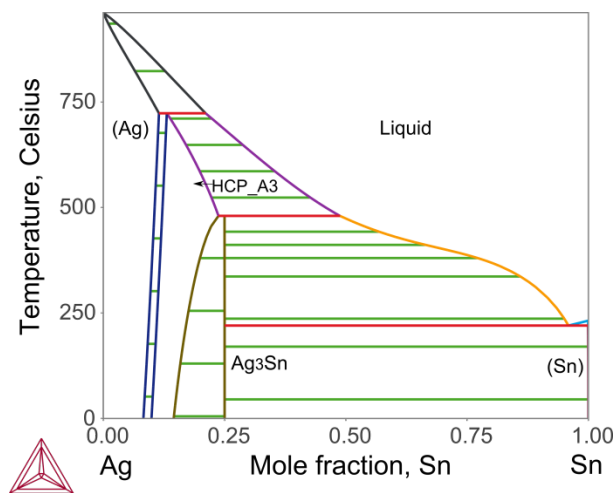


Figure 1: Calculated Ag-Sn phase diagram [1996Oh].

## Cu-Sn

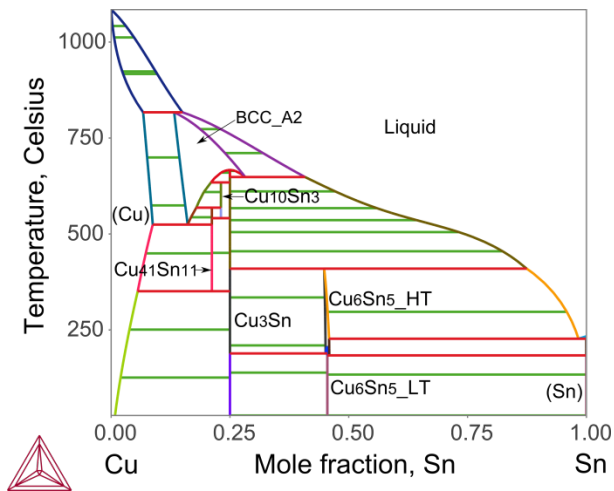


Figure 2: Calculated Cu-Sn phase diagram [2001Liu].

## References

- [1996Oh] C.-S. Oh, J.-H. Shim, B.-J. Lee, A thermodynamic study on the Ag-Sb-Sn system. *J. Alloys Compd.* 238, 155–166 (1996).
- [2001Liu] X. J. Liu et al., Experimental determination and thermodynamic calculation of the phase equilibria in the Cu-In-Sn system. *J. Electron. Mater.* 30, 1093–1103 (2001). The Cu<sub>6</sub>Sn<sub>5</sub>\_HT phase was modified in TCSLD2, Thermo-Calc Software AB, Sweden (2014).

## Ternary Isothermal Section

Cu-Ni-Sn is a key system in understanding the interactions between the SnAgCu (SAC) solder and Ni substrate. The Cu-Ni-Sn ternary system has been re-assessed in the TCS Solder Alloy Solutions Database (TCSLD) by taking into account recent experimental observations.

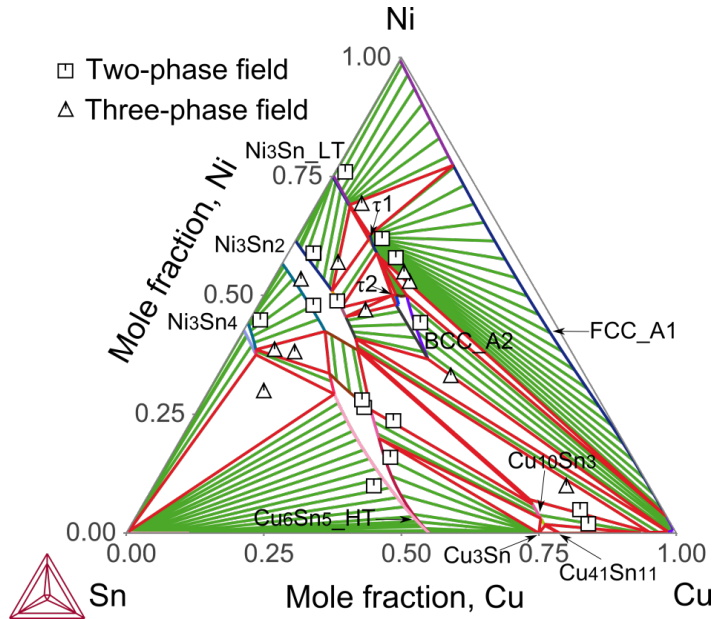


Figure 3: Calculated Cu-Ni-Sn isothermal section at 400 °C compared to experimental data from [2008Sch].

### Reference

[2008Sch] C. Schmetterer, H. Flandorfer, C. Luef, A. Kodentsov, H. Ipser, Cu-Ni-Sn: A Key System for Lead-Free Soldering. *J. Electron. Mater.* 38, 10–24 (2008).



## Solidification Simulations

The final step of the reflow process is the solidification of the solder. Though the solidification behavior of solder is also influenced by the consuming of elements during interface reactions, the analysis of the solidification of solder itself can still provide insight on the actual solidification process of the solder. With solidification simulations, the phase formation sequence, phase fraction, phase transformation temperatures and so forth, can be predicted using Thermo-Calc and the TCS Solder Alloy Solutions Database (TCSLD).

In industry application, non-equilibrium solidification rather than equilibrium solidification is usually observed. The plot simulates both the equilibrium solidification and Scheil (non-equilibrium) solidification of a Sn-Ag-Cu-In alloy.

The calculated Scheil solidification path, including the solidified phases and the phase transformation temperatures, agrees well with the experimental data. It should be noted that the fraction of the  $\text{Cu}_2\text{In}_3\text{Sn}$  phase was very small which is difficult to be detected in the experiment.



Read more about [Scheil Solidification Simulations](#) on our website. If you are in Thermo-Calc, press F1 to search the help to learn about using Scheil.

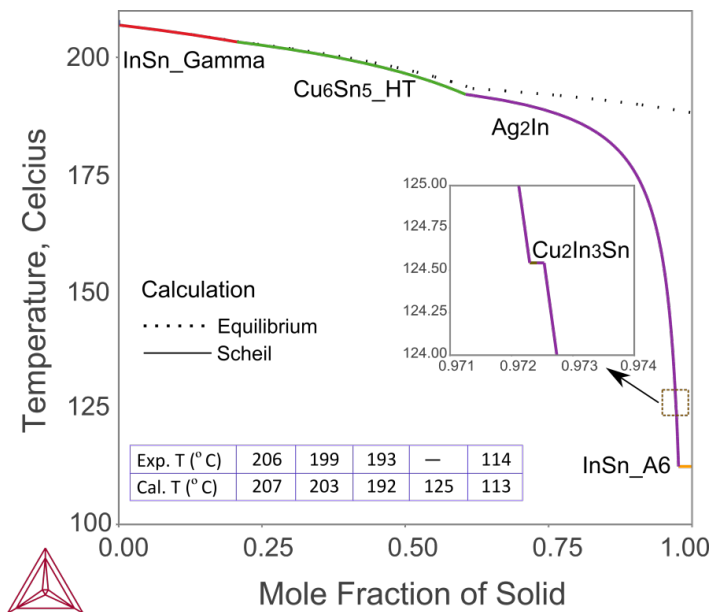


Figure 4: Equilibrium solidification and Scheil solidification simulations of a new type of solder patented in Korea with composition Sn-1.5Ag-0.7Cu-9.5In (wt.%) [2008Lee] compared with experimental results [2010Sop].

## References

- [2008Lee] J.-H. Lee, C.-W. Lee, J. H. Kim, J. H. Kim, Quaternary Pb-free solder composition incorporating Sn-Ag-Cu-In (2008), (available at <http://www.patentsencyclopedia.com/app/20080292493>).
- [2010Sop] J. Sopoušek, M. Palcut, E. Hodúlová, J. Janovec, Thermal Analysis of the Sn-Ag-Cu-In Solder Alloy. J. Electron. Mater. 39, 312–317 (2010).

## Formation of Interfacial Products

The reliability of the joints in the functionality and reliability of electronic components are strongly dependent on the interface reactions that occur between solders and substrate materials. The intermetallic compounds at the interface, especially the one that forms first, is critical to the mechanical performance of the soldered joints. Here, using the TCS Solder Alloy Solutions Database (TCSLD), the calculation tries to predict the first formed interfacial compound during soldering through calculating and comparing the driving force of formation.

This scheme for predicting the first formed compound was proposed by [1997Lee], who suggested that during soldering, the phase which forms first at the interface is the phase with the highest driving force of nucleation from the solder liquid in metastable equilibrium with the substrate. The driving force is thus the Gibbs free energy difference between the set equilibria, i.e. metastable local equilibrium at the interface between the substrate and liquid solder, and the possible forming phases.

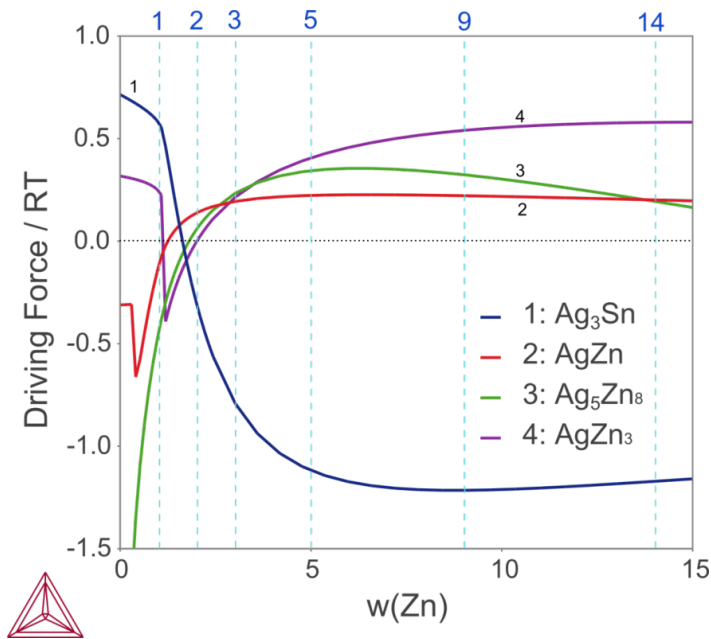


Figure 5: Calculated driving force of formation of the phases in the Sn-xZn/Ag ( $x=1, 2, 3, 5, 9, 14$ , wt.%) couples at 260 °C.

The table lists predicted first formed interface reaction product compared with experiments [2008Jao; 2010Jee]. The calculations successfully predict for all compositions except for the Sn-3 wt.%Zn alloy. It should be noted that at  $w(\text{Zn})=3\%$ , the driving forces of  $\text{Ag}_5\text{Zn}_8$  and  $\text{AgZn}$  are very close to each other, as shown in the figure above. In such a case, other effects, e.g., interfacial energy, misfit strain energy etc., should also be considered. Nevertheless, thermodynamic calculations are a very good starting point to obtain information on possible IMC formations and to understand the interface reactions.

<i>Sn-xZn/Ag couple, 260 °C</i>		
<i>Alloy</i>	<i>Calculation</i>	<i>Experiment (22,23)</i>
Sn-1 wt.%Zn	Ag3Sn	Ag3Sn
Sn-2 wt.%Zn	AgZn	AgZn
Sn-3 wt.%Zn	Ag5Zn8	AgZn
Sn-5 wt.%Zn	AgZn3	AgZn3
Sn-9 wt.%Zn	AgZn3	AgZn3
Sn-14 wt.%Zn	AgZn3	AgZn3

## References

- [1997Lee] B.-J. Lee, N.-M. Hwang, H.-M. Lee, Prediction of interface reaction products between Cu and various solder alloys by thermodynamic calculation. *Acta Mater.* 45, 1867–1874 (1997).
- [2008Jao] C.-C. Jao, Y.-W. Yen, C.-Y. Lin, C. Lee, Phase equilibria of the Sn–Zn–Ag system and interfacial reactions in Sn–Zn/Ag couples. *Intermetallics.* 16, 463–469 (2008).
- [2010Jee] Y. K. Jee, J. Yu, Interfacial Reactions and Joint Strengths of Sn-xZn Solders with Immersion Ag UBM. *J. Electron. Mater.* 39, 2286–2291 (2010).

## Surface Tension: Ag-Cu, Ag-Sn, Cu-Sn, and Ag-Cu-Sn

The surface tension thermophysical property data is included with the TCS Solder Alloy Solutions Database (TCSLD) starting with version 4 (TCSLD4).

For more information about the various thermophysical models, and when in Thermo-Calc, press F1 to search the online help. The details are found under a *General Reference* section.



You can find information on our website about the [properties that can be calculated](#) with Thermo-Calc and the Add-on Modules. Additional resources are added on a regular basis so keep checking back or [subscribe to our newsletter](#).

### Ag-Cu, Ag-Sn, and Cu-Sn

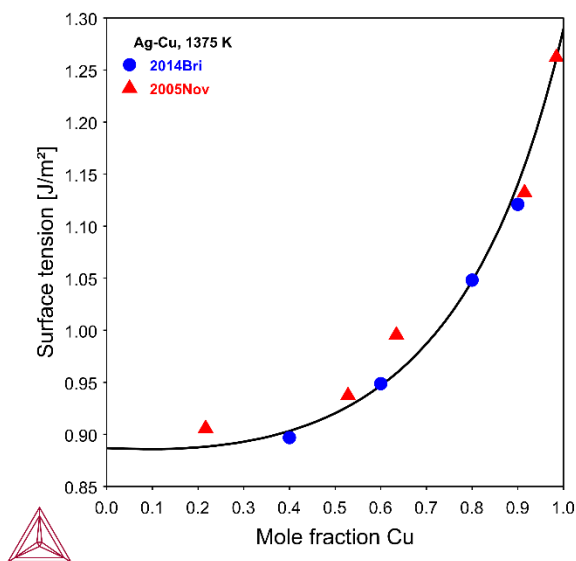


Figure 6: Surface tension of Ag-Cu at 1375 K. Experimental data are taken from [2005Nov; 2014Bri].

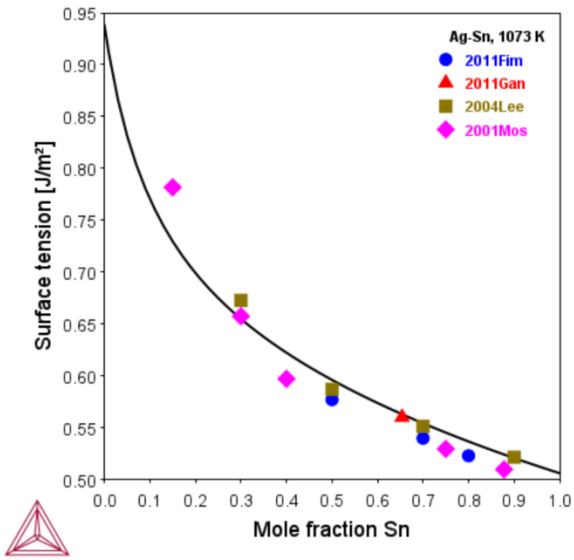


Figure 7: Surface tension of Ag-Sn at 1073 K with experimental data from [2001Mos; 2004Lee; 2011Fim; 2011Gan].

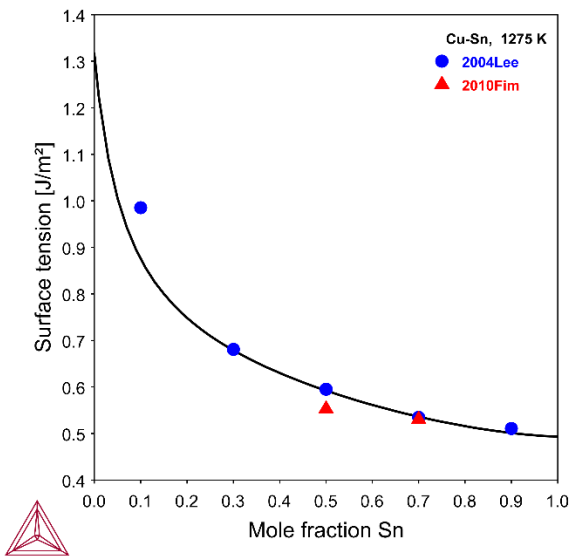


Figure 8: Surface tension of Cu-Sn at 1275 K with experimental data from [2004Lee; 2010Fim].

## **(Ag<sub>7</sub>-Cu<sub>3</sub>-Sn)<sub>100-x</sub>Sn<sub>x</sub>**

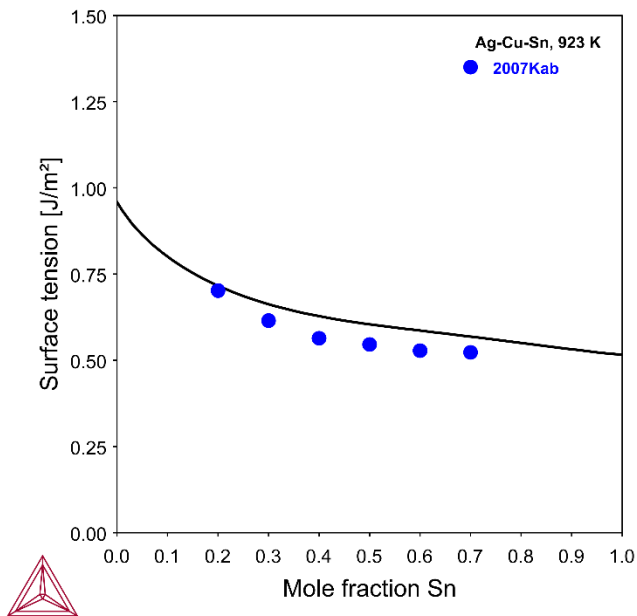


Figure 9: Surface tension of  $(\text{Ag}_7\text{Cu}_3)_{100-x}\text{Sn}_x$  as a function of Sn composition at 923 K. Experimental data are taken from [2007Kab].

## **References**

- [2001Mos] Z. Moser, W. Gasior, J. Pstrus, Surface tension measurements of the Bi-Sn and Sn-Bi-Ag liquid alloys. *J. Electron. Mater.* 30, 1104–1111 (2001).
- [2004Lee] J. Lee, W. Shimoda, T. Tanaka, Surface Tension and its Temperature Coefficient of Liquid Sn-X (X=Ag, Cu) Alloys. *Mater. Trans.* 45, 2864–2870 (2004).
- [2005Nov] R. Novakovic, E. Ricci, D. Giuranno, A. Passerone, Surface and transport properties of Ag–Cu liquid alloys. *Surf. Sci.* 576, 175–187 (2005).
- [2007Kab] I. Kaban, S. Gruner, W. Hoyer, Surface tension and density in liquid Ag–Cu–Sn alloys. *J. Non. Cryst. Solids.* 353, 3717–3721 (2007).
- [2010Fim] P. Fima, Surface tension and density of liquid Sn-Cu alloys. *Appl. Surf. Sci.* 257, 468–471 (2010).
- [2011Fim] P. Fima, Surface tension and density of liquid Sn–Ag alloys. *Appl. Surf. Sci.* 257, 3265–3268 (2011).
- [2011Gan] T. Gancarz, Z. Moser, W. Gasior, J. Pstruś, H. Henein, A Comparison of Surface Tension, Viscosity, and Density of Sn and Sn–Ag Alloys Using Different Measurement Techniques. *Int. J. Thermophys.* 32, 1210–1233 (2011).

[2014Bri] J. Brillo, G. Lauletta, L. Vaianella, E. Arato, D. Giuranno, R. Novakovic, E. Ricci, Surface Tension of Liquid Ag–Cu Binary Alloys. *ISIJ Int.* 54, 2115–2119 (2014).



## Viscosity: Ag-Cu, Ag-Sn, and Sn-Ag-Cu

The viscosity thermophysical property data is included with the TCS Solder Alloy Solutions Database (TCSLD) starting with version 4 (TCSLD4).

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### Ag-Cu and Ag-Sn

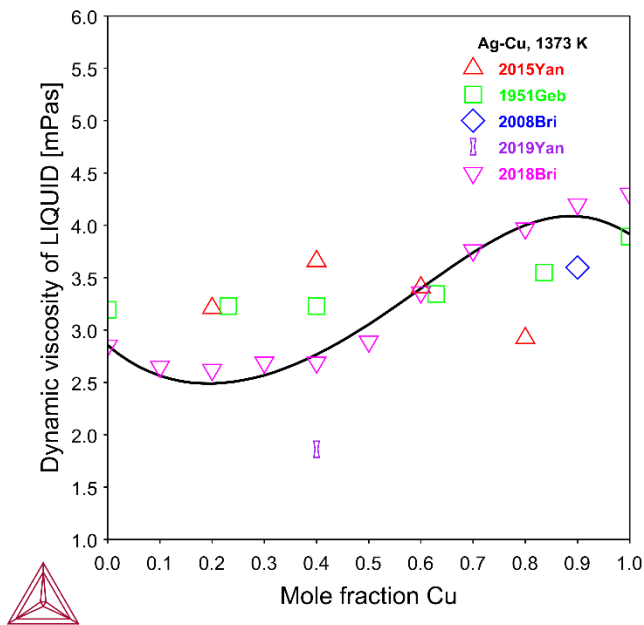


Figure 10: Calculated dynamic viscosity of Ag-Cu at 1371 K with experimental data from [1994See; 2008Bri; 2015Zha; 2018Bri; 2019Yan].

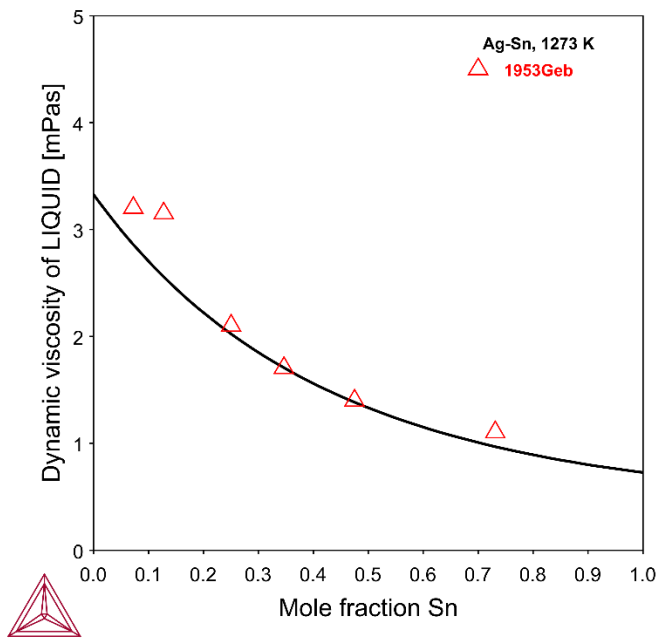


Figure 11: Calculated dynamic viscosity of Ag-Sn at 1273 K.

## Sn-Ag-Cu

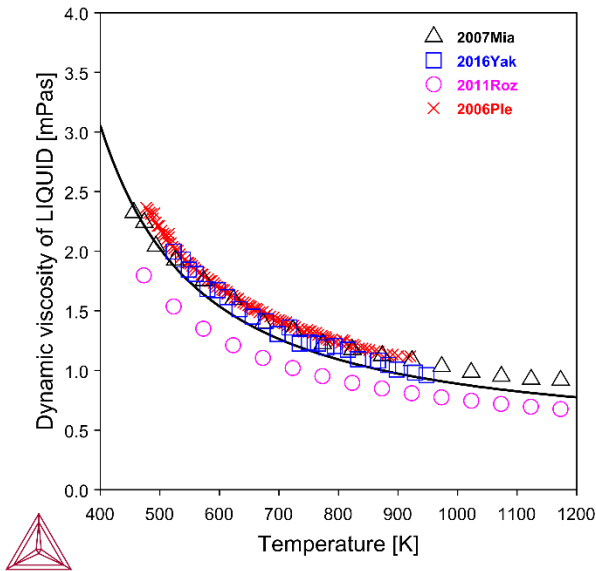


Figure 12: Viscosity of Sn-3.8Ag-0.7Cu alloy. Experimental data are from [2006Ple; 2011Roz].

## References

[1994See] S. Seetharaman, D. Sichen, Estimation of the viscosities of binary metallic melts using Gibbs energies of mixing. Metall. Mater. Trans. B. 25, 589–595 (1994).

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- [2006Ple] Y. Plevachuk, V. Sklyarchuk, W. Hoyer, I. Kaban, Electrical conductivity, thermoelectric power and viscosity of liquid Sn-based alloys. *J. Mater. Sci.* 41, 4632–4635 (2006).
- [2008Bri] J. Brillo, R. Brooks, I. Egry, P. Quedstedt, Density and viscosity of liquid ternary Al-Cu-Ag alloys. *High Temp. - High Press.* 37, 371–381 (2008).
- [2011Roz] E. V. Rozhitsina, S. Gruner, I. Kaban, W. Hoyer, V. E. Sidorov, P. S. Popel', Dynamic viscosities of pure tin and Sn-Ag, Sn-Cu, and Sn-Ag-Cu eutectic melts. *Russ. Metall.* 2011, 118–121 (2011).
- [2015Zha] Y. Zhao, X.-X. Hou, Viscosities and their correlations with structures of Cu–Ag melts. *Chinese Phys. B.* 24, 096601 (2015).
- [2018Bri] J. Brillo, E. Arato, D. Giuranno, H. Kobatake, C. Maran, R. Novakovic, E. Ricci, D. Rosello, Viscosity of liquid Ag-Cu alloys and the competition between kinetics and thermodynamics. *High Temp. - High Press.* 47, 417–441 (2018).
- [2019Yan] J. Yang, Y. Wang, J. Huang, W. Wang, Z. Ye, S. Chen, Y. Zhao, Investigation on viscosity, surface tension and non-reactive wettability of melting Ag-Cu-Xwt%Ti active filler metals. *J. Alloys Compd.* 772, 438–446 (2019).

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## TCSLD Validation Examples

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Some diagrams are calculated with earlier versions of the database. Negligible differences might be observed if these are recalculated with the most recent version. The diagrams are updated when there are considerable or significant improvements.

### In this section:

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Effect of Alloying Element on Melting .....	21
Liquidus and Solidus Temperatures .....	22
Liquidus Projection .....	23
Surface Tension of Cu–Sn–Bi–In–Pb Alloy .....	26
Viscosity of SAC Alloy .....	28

## Effect of Alloying Element on Melting

Knowledge on the effect of alloying elements on the melting behavior of lead-free solders is of great importance to the development of new solder alloys and the improvement of existing alloys.

Using the TCS Solder Alloy Solutions Database (TCSLD), this example shows the effect of Zn addition on the melting temperatures of Sn-Zn-Al solder alloys at different fixed Al content. The calculation suggests that the addition of Zn decreases the melting temperature up to a certain amount, and higher Al content in the alloy leads to a higher melting point.

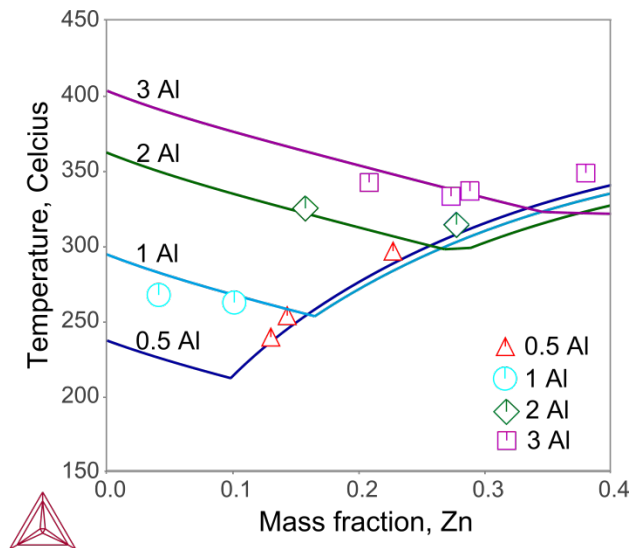


Figure 13: The effect of Zn content on the melting temperatures of Sn-Zn-Al solder alloys at different fixed Al content. Experimental data are from [2012Sme].

### Reference

[2012Sme] B. Smetana, S. Zlá, A. Kroupa, M. Žaludová, J. Drápala, R. Burkovič, D. Petlák, Phase transition temperatures of Sn-Zn-Al system and their comparison with calculated phase diagrams. *J. Therm. Anal. Calorim.* 110, 369–378 (2012).

## Liquidus and Solidus Temperatures

Melting temperature and melting range are basic consideration criterion when selecting solder alloys or designing a new solder. The liquidus and solidus temperatures of a large number of commercial solder alloys have been collected and compared to the calculated temperatures using the TCS Solder Alloy Solutions Database (TCSLD).

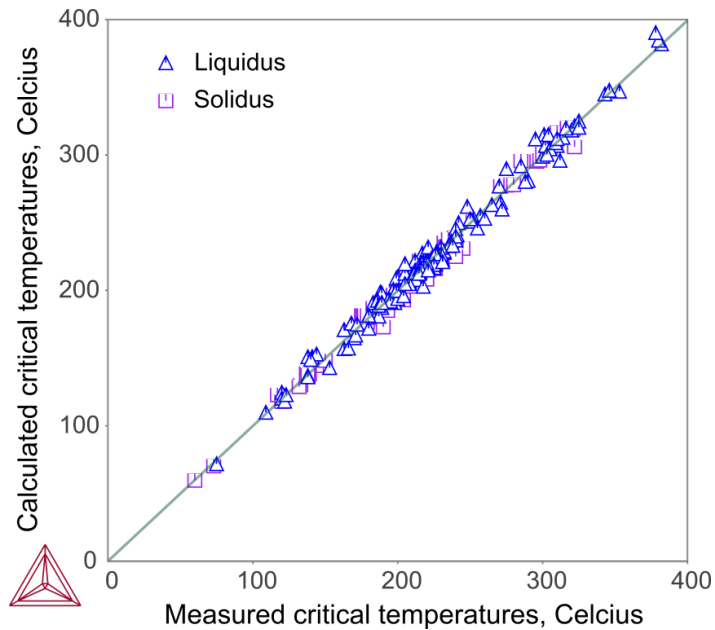


Figure 14: Comparison of experimental and calculated liquidus and solidus temperatures for various solder alloys. Critical temperatures refers to either the liquidus or the solidus temperatures. Good agreement between calculations and experiments is observed.



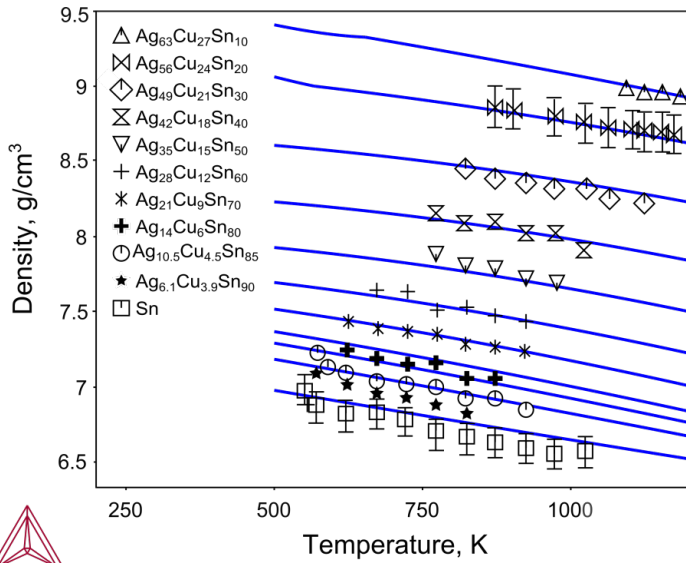


Figure 16: Calculated density of liquid Sn-Ag-Cu alloys compared to experimental data.

### Sn-Ag-Bi

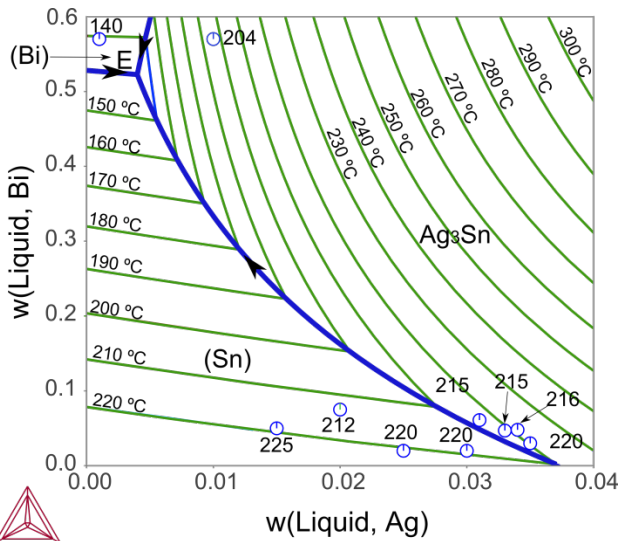


Figure 17: Calculated Sn-Ag-Bi liquidus projection at Sn-rich corner. The reported liquidus temperatures of SnAgBi solder alloys are shown for comparison. Ternary eutectic reaction E:  $T_{cal.}=137.5\text{ °C}$ ,  $T_{exp.}=138.4\text{ °C}$ .



## Sn-Ag-In

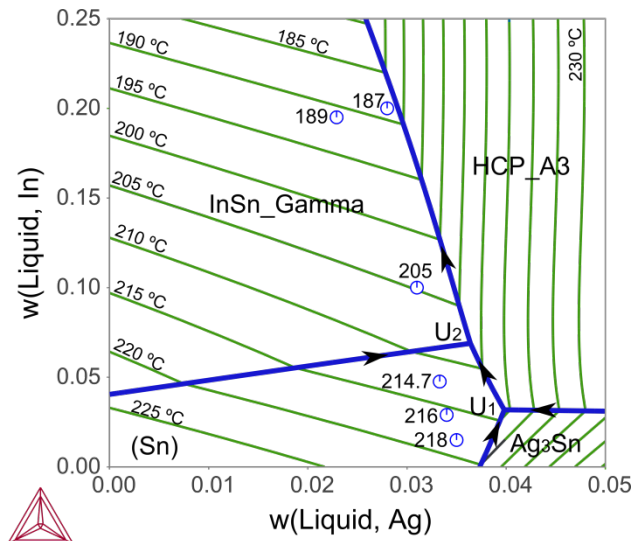


Figure 18: Calculated Sn-Ag-In liquidus projection at Sn-rich corner. The reported liquidus temperatures of SnAgIn solder alloys are shown for comparison. The difference is less than 2 °C.  $U_1$ :  $T_{cal}=214$  °C,  $T_{exp}=215$  °C ;  $U_2$ :  $T_{cal}=207.5$  °C,  $T_{exp}=206$  °C.

## Surface Tension of Cu–Sn–Bi–In–Pb Alloy

The surface tension thermophysical property data is included with the TCS Solder Alloy Solutions Database (TCSLD) starting with version 4 (TCSLD4).

For more information about the various thermophysical models, and when in Thermo-Calc, press F1 to search the online help. The details are found under a *General Reference* section.



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Surface tension plays an important role in wetting of solders. Good wetting of the part by the solder is critical to ensuring joint quality. The chemistry and temperature effect on surface tension can be calculated with Thermo-Calc.

The temperature dependencies of the surface tension of liquid high- entropy equiatomic Cu–Sn–Bi–In–Pb alloy on heating and cooling is shown.

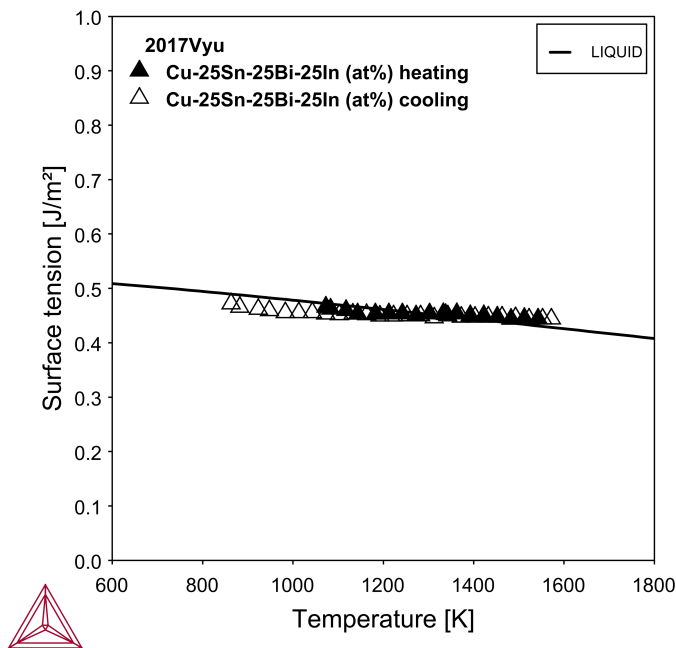


Figure 19: Calculated surface tension of equiatomic Cu–Sn–Bi–In–Pb alloy along with experimental data from [2017V'yu].

## Reference

[2017 V'yu] V. V. V'yukhin, O. A. Chikova, V. S. Tsepelev, Surface tension of liquid high-entropy equiatomic alloys of a Cu–Sn–Bi–In–Pb system. *Russ. J. Phys. Chem. A.* 91, 613–616 (2017).

## Viscosity of SAC Alloy

The viscosity thermophysical property data is included with the TCS Solder Alloy Solutions Database (TCSLD) starting with version 4 (TCSLD4).

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The viscosity is a critical material property needed when performing finite element simulations of soldering processes. Thermophysical data found in handbooks and finite element (FE) codes typically does not capture chemistry variation or data for novel/experimental materials. Below is the calculated viscosity for a specific chemistry of SAC compared with some measured values.

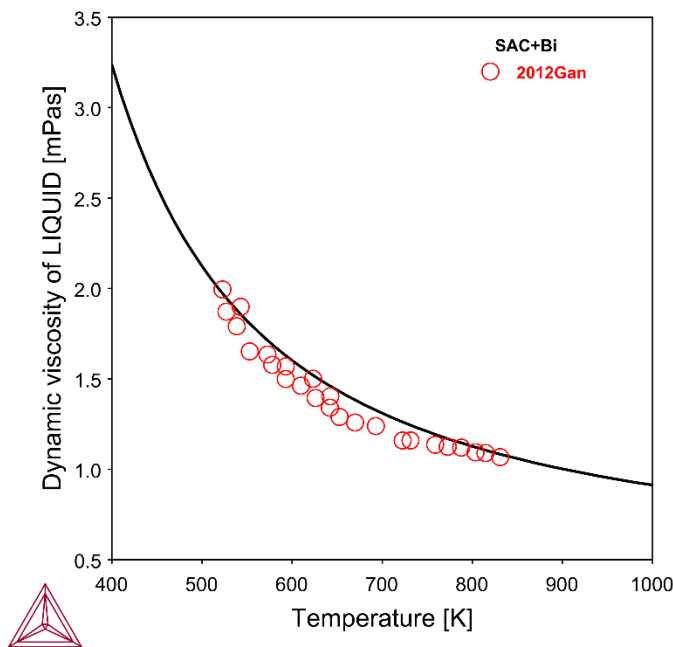


Figure 20: Viscosity of SAC alloy plus 3.07 wt% Bi along with experimental data from [2013Gan].

### Reference

[2013Gan] T. Gancarz, J. Pstruś, W. Gąsior, H. Henein, Physicochemical Properties of Sn-Zn and SAC + Bi Alloys. *J. Electron. Mater.* 42, 288–293 (2013).