Karlsruhe Institute of Technology

WeNDeLIB SPP 1473 DFG

IAM Institute for Applied Materials

Thermodynamic Modeling and Experiments in Systems Evaluated in the WeNDeLIB priority program for Li-ion batteries

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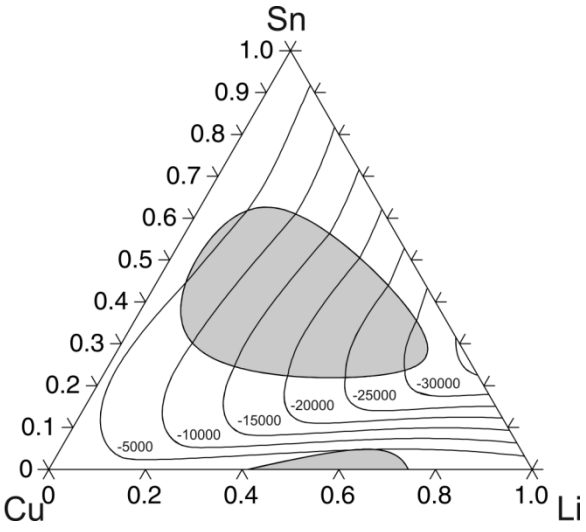
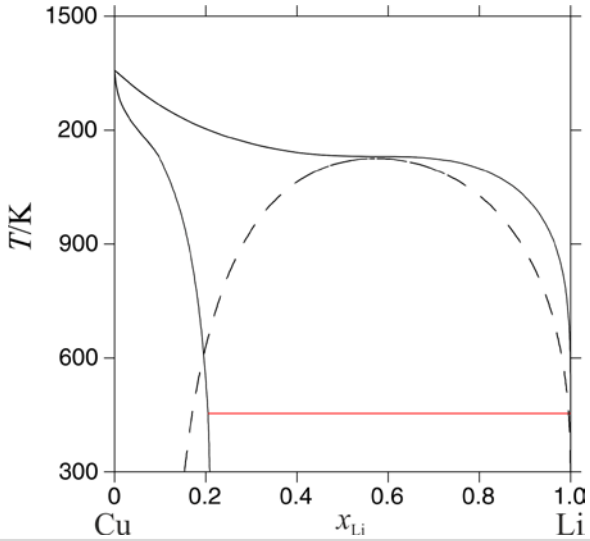
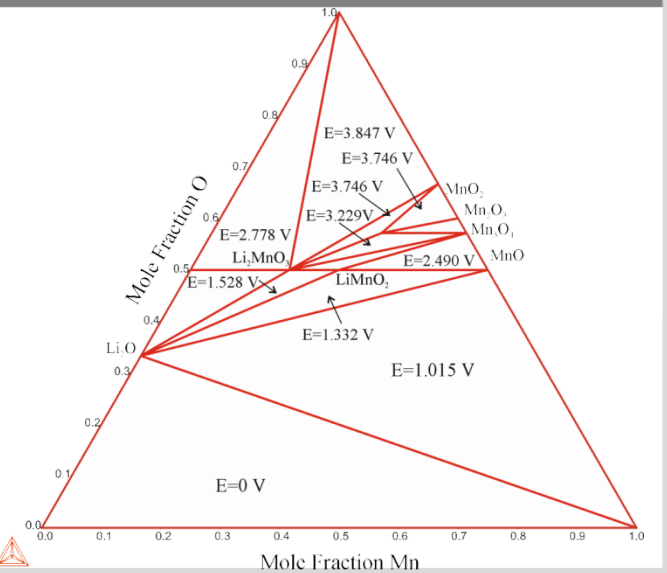
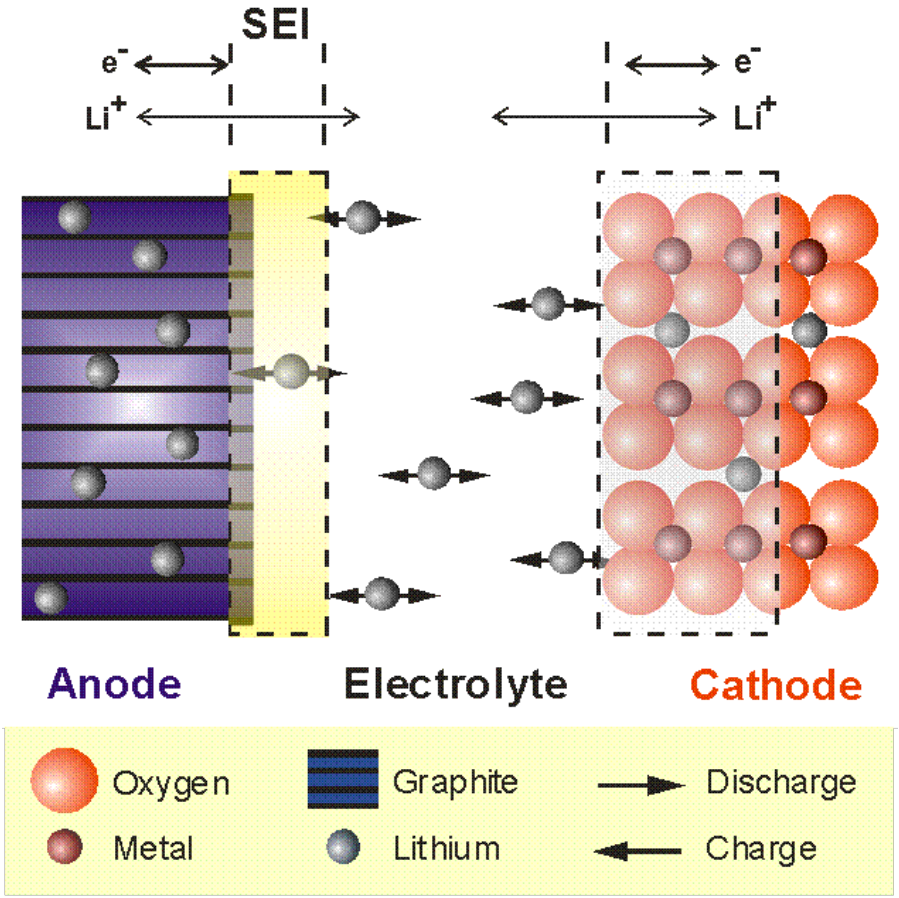
Institute for Applied Materials – Applied Materials Physics (IAM-AWP)







Lithium ion cell; Intercalation mechanisms



$$Li_x AN + CA \xrightarrow{\text{discharge}} AN + Li_x CA$$

Thermodynamics and Electrochemistry

Full lithium ion cell discharge reaction

$$Li_x AN + CA \xrightarrow{\text{discharge}} AN + Li_x CA$$

Free energy of the full reaction is:

$$\Delta G(x,T) = -n \cdot F \cdot E_0(x,T)$$

Free energy of the full reaction can be written:

$$\Delta G(x,T) = \Delta H(x,T) - T\Delta S(x,T)$$

Neglecting T-dependence:

$$\Delta G_0(x,T) = \Delta H(x) - T\Delta S(x)$$

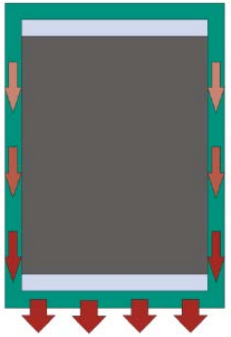
Combining equations:

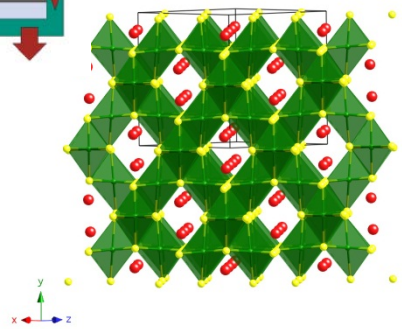
$$\Delta S(x) = F\left(\left.\frac{\partial E_0(x,T)}{\partial T}\right|_x\right) \qquad \Delta H(x) = F\left(-E_0(x,T) + T\left.\frac{\partial E_0(x,T)}{\partial T}\right|_x\right)$$

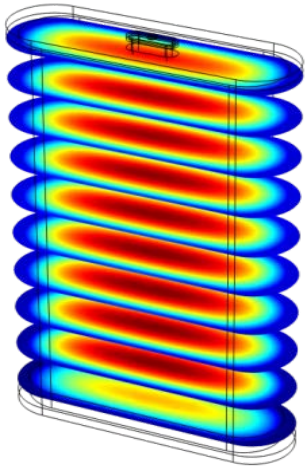
$E_0(x,T)$	**Open circuit voltage**
n	**Charge number (n=1 for Li^+)**
F	**Faraday constant**
ΔH, ΔS	**Heat and entropy of reaction**
$\left.\frac{\partial E_0(x,T)}{\partial T}\right\|_x$	**Temperature slope of $E_0(x,T)$**

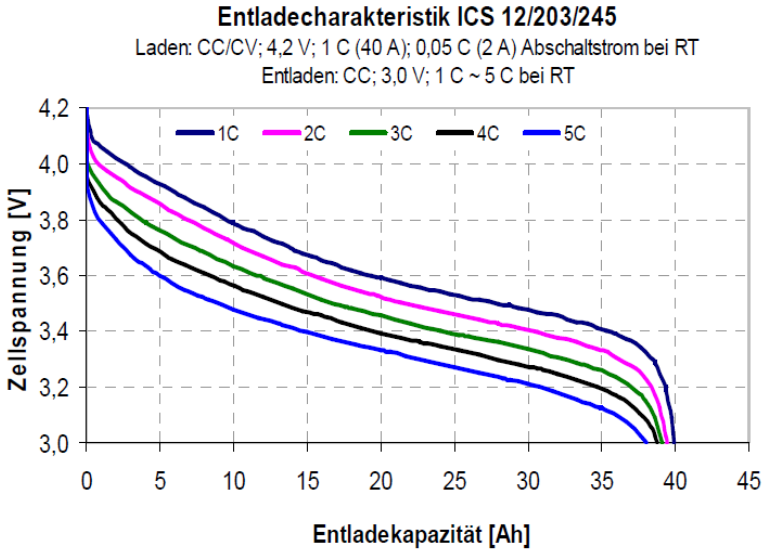
Focus Themes of WeNDeLIB

- Thermodynamics and phase diagrams govern battery performance
- Thermal management of batteries
- Battery safety (thermal runaway)
- Structural stabilities of active materials
- Synthesis of active materials

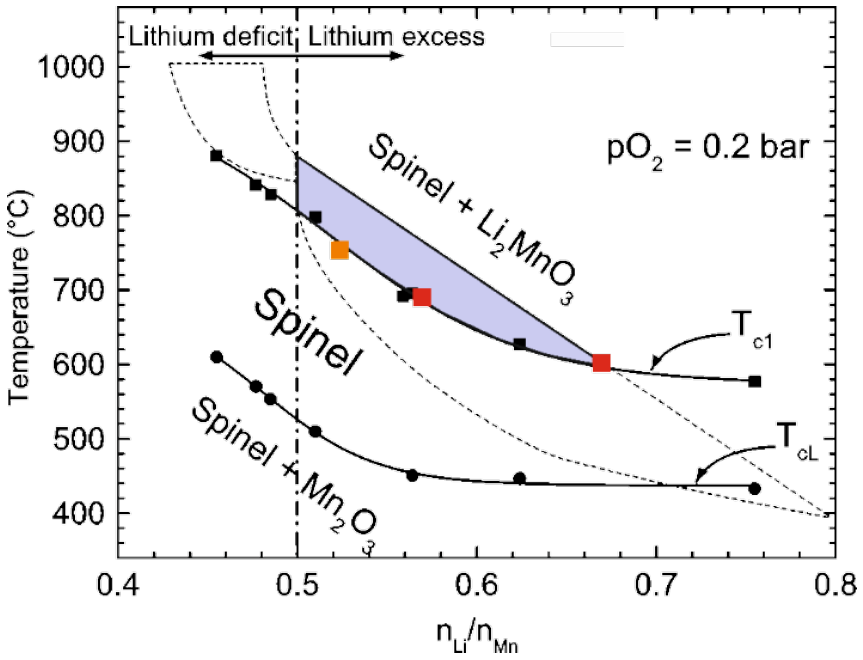




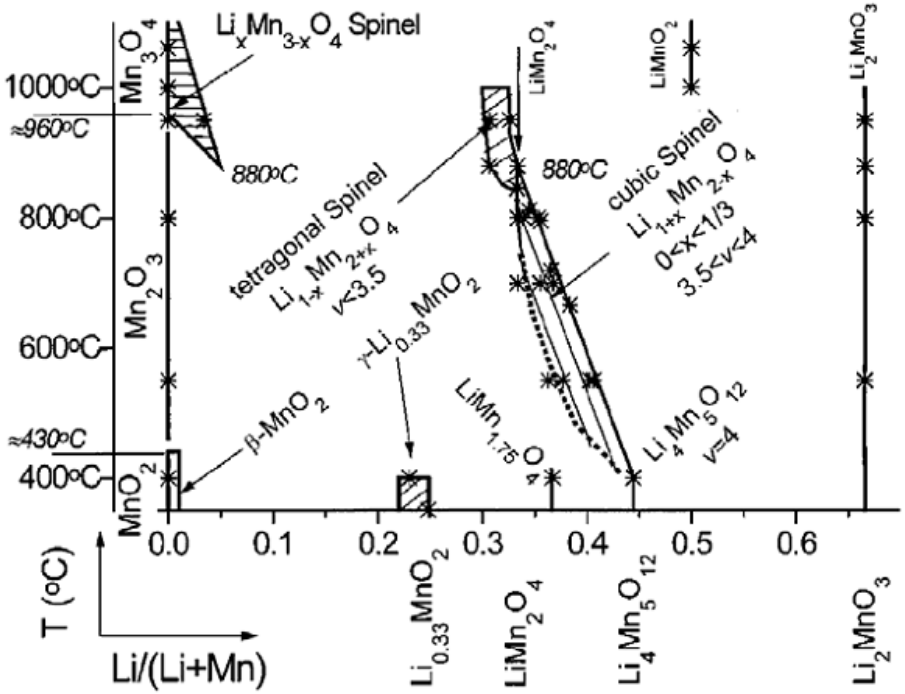




$Li_{1+x}Mn_{2-x}O_4$ Spinel - Phase Boundaries



[2007Luo] Luo and Martin, J. Mater. Sci., 42, 2007, 1955-1964



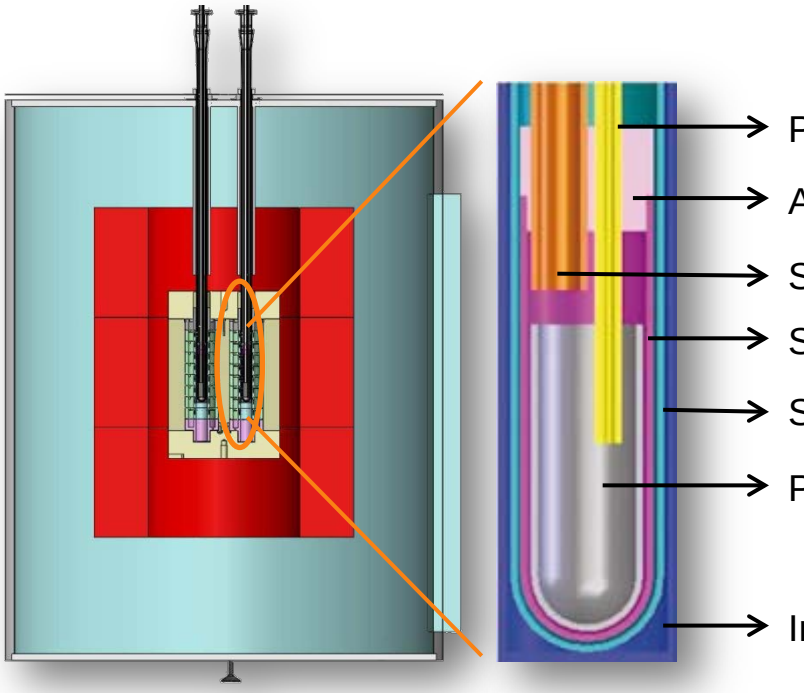
[1999Pau] Paulsen and Dahn, Chem. Mater., 11, 1999, 3065-3079

Commercial powder from MTI Sol-gel prepared samples

- Samples prepared using sol-gel synthesis
- The Li-rich boundary of the $Li_{1+x}Mn_{2-x}O_4$ phase determined using thermogravimetric analysis

High Temperature Oxide Solution Calorimetry

- Drop Solution Calorimeter (Alexsys 1000, Setaram)
  - Twin-Calvet-Type
  - Sodium molybdate ($3Na_2O{\cdot}4MoO_3$) solvent
  - Solution calorimetry performed at 700°C



Platinum tube for bubbling gas

Al_2O_3 lid

SiO_2 glass dropping tube

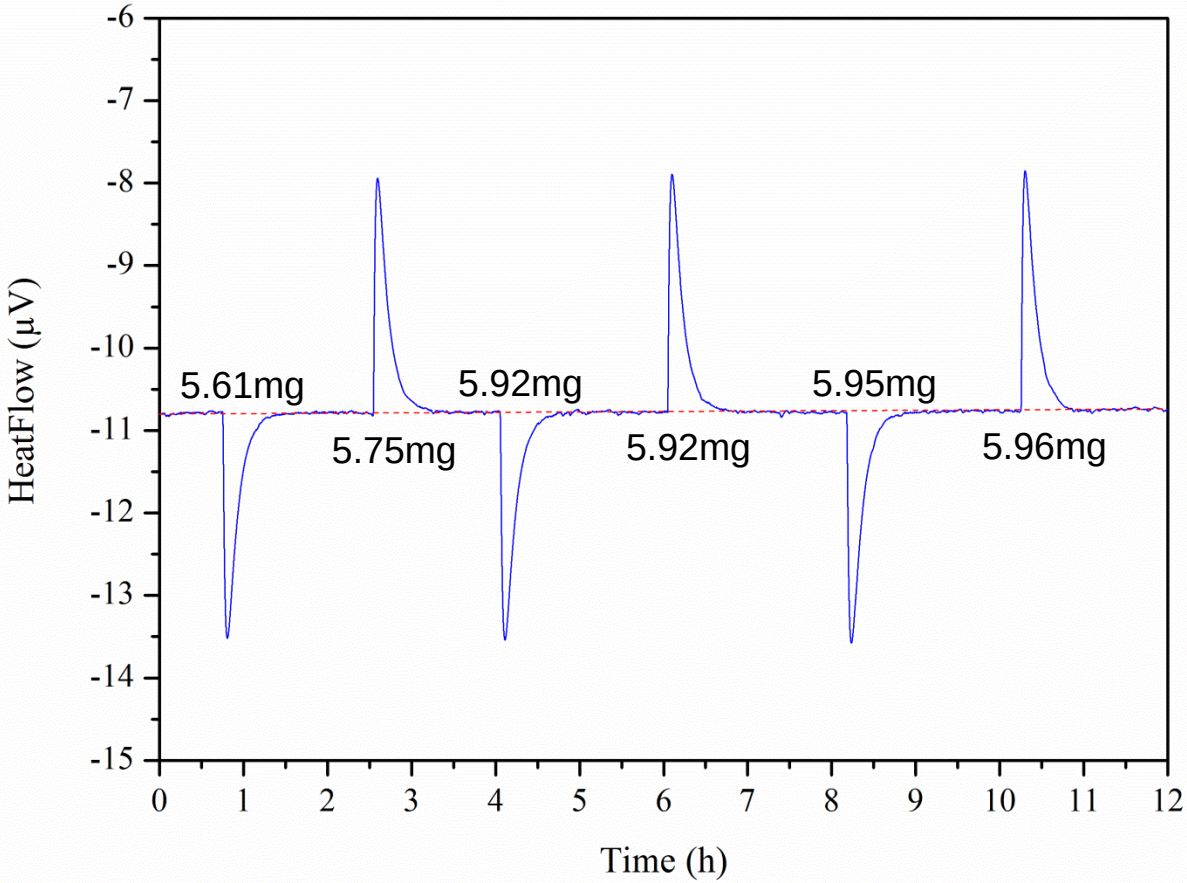
SiO_2 crucible

SiO_2 glass liner

Platinum crucible

Inconel protection tube

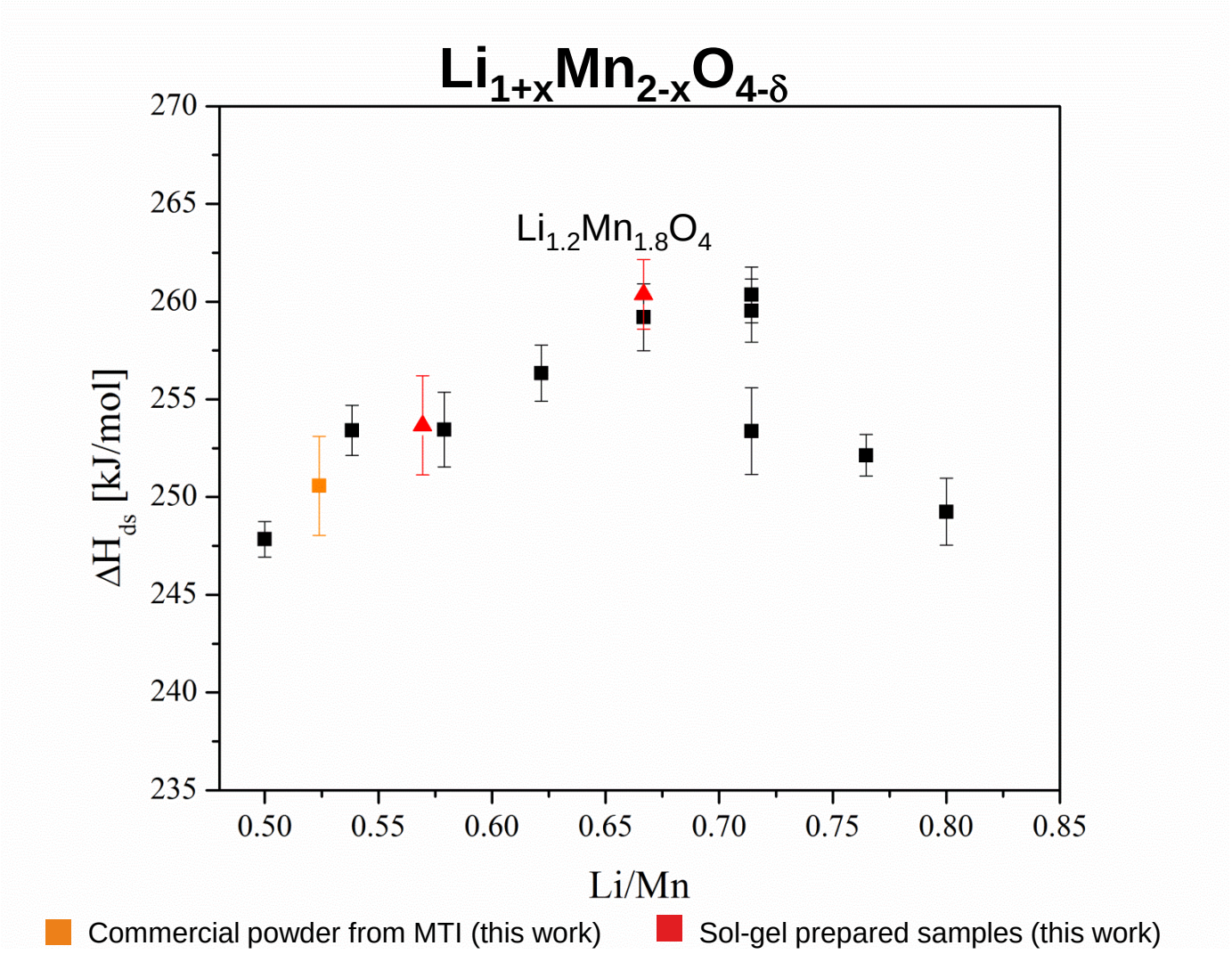
$Li_{1.2}Mn_{1.8}O_4$: Drop Solution Measurements



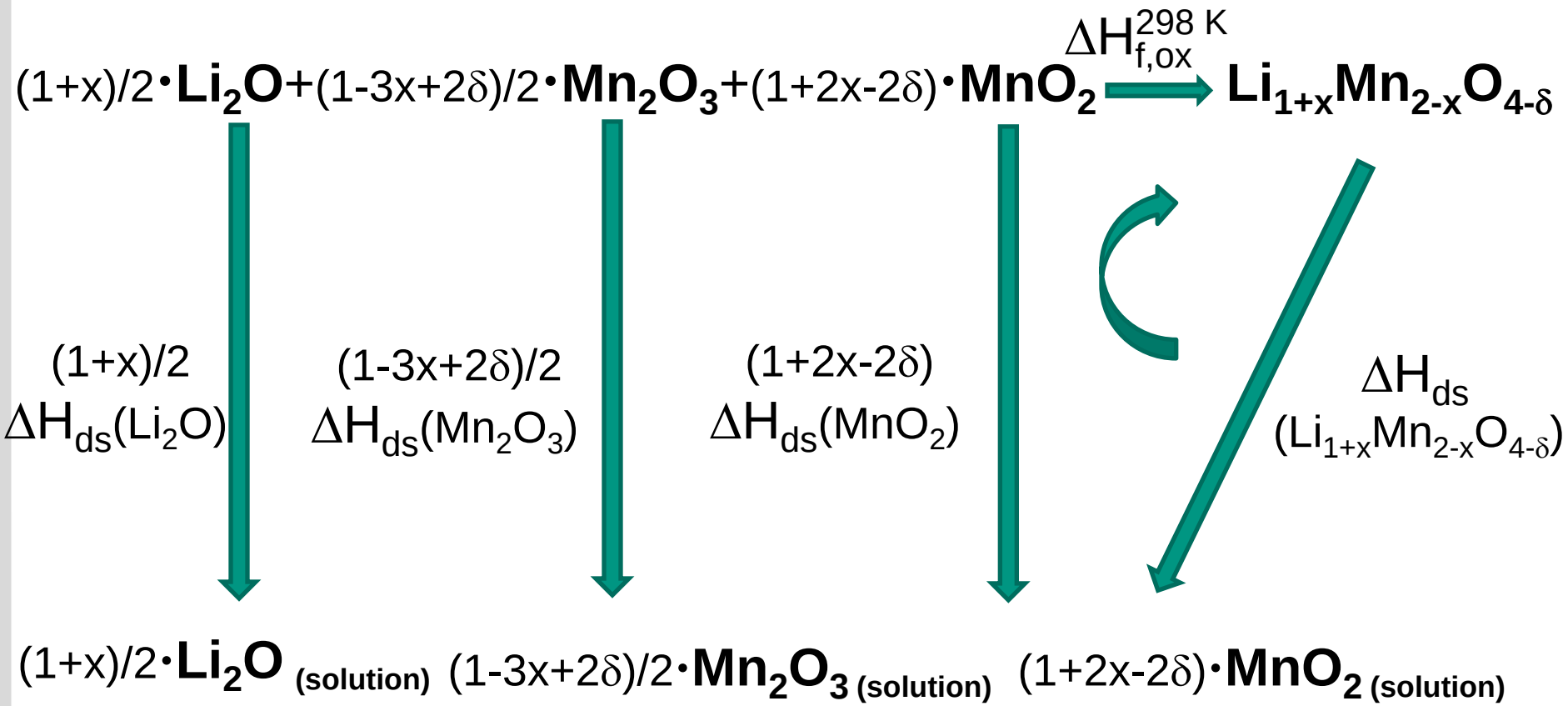
Right Side (6): ΔH_{ds}=260.64±1.90 kJ/mol Left Side (6): ΔH_{ds}=260.11±3.18 kJ/mol

All Measurements (12): ΔH_{ds}=260.37±1.77 kJ/mol

Measured Enthalpy of Drop Solution

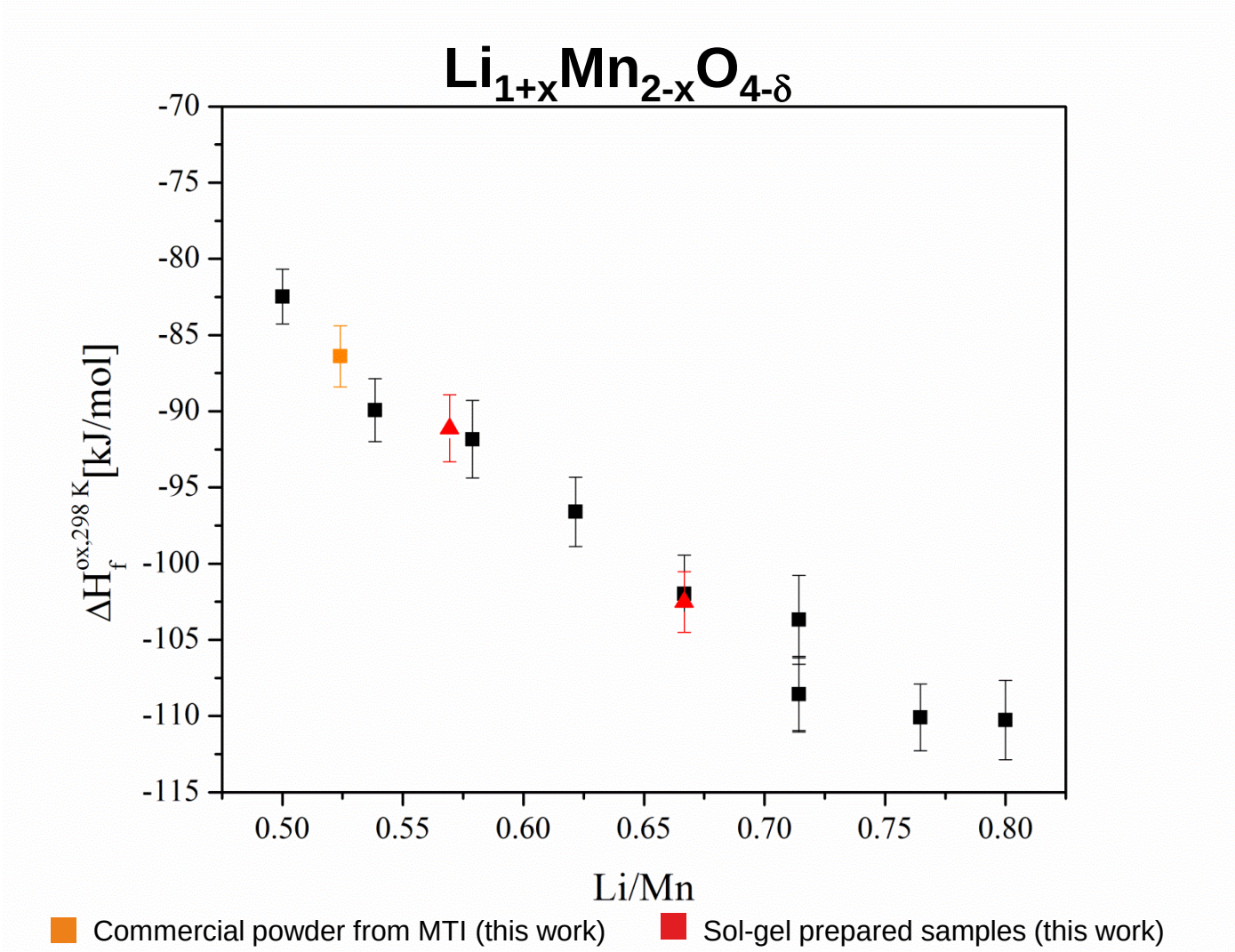


Thermodynamic Cycle: Enthalpy of Formation from the Oxides

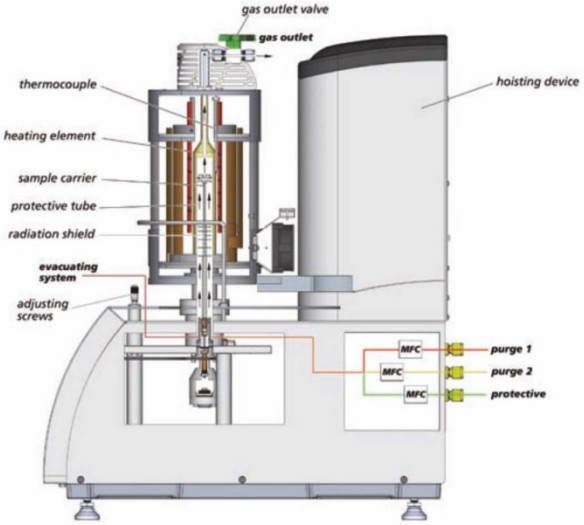


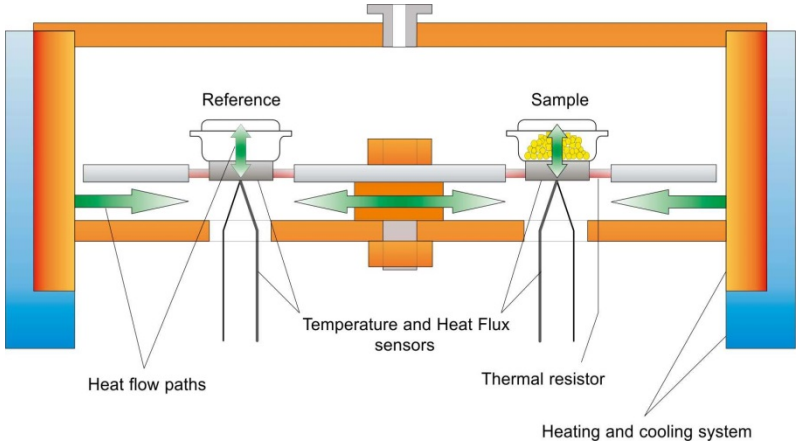
$$\Delta H_{f,ox}^{298\ K} = (1+x)/2 \cdot \Delta H_{ds}(Li_2O) + (1-3x+2\delta)/2 \cdot \Delta H_{ds}(Mn_2O_3) + (1+2x-2\delta) \cdot \Delta H_{ds}(MnO_2) - \Delta H_{ds}(Li_{1+x}Mn_{2-x}O_{4-\delta})$$

Enthalpy of Formation from the Oxides

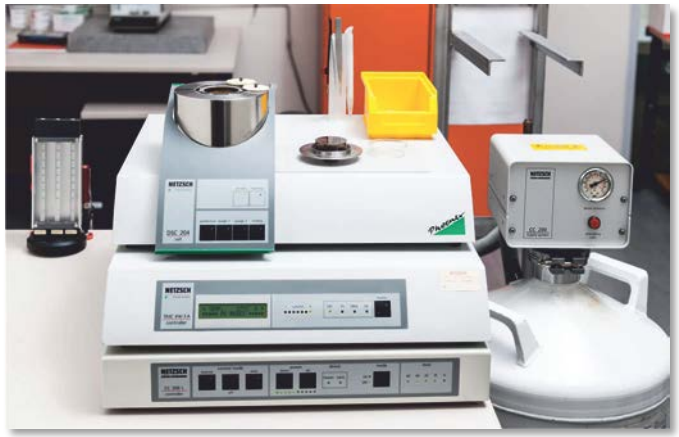


Differential Scanning Calorimetery



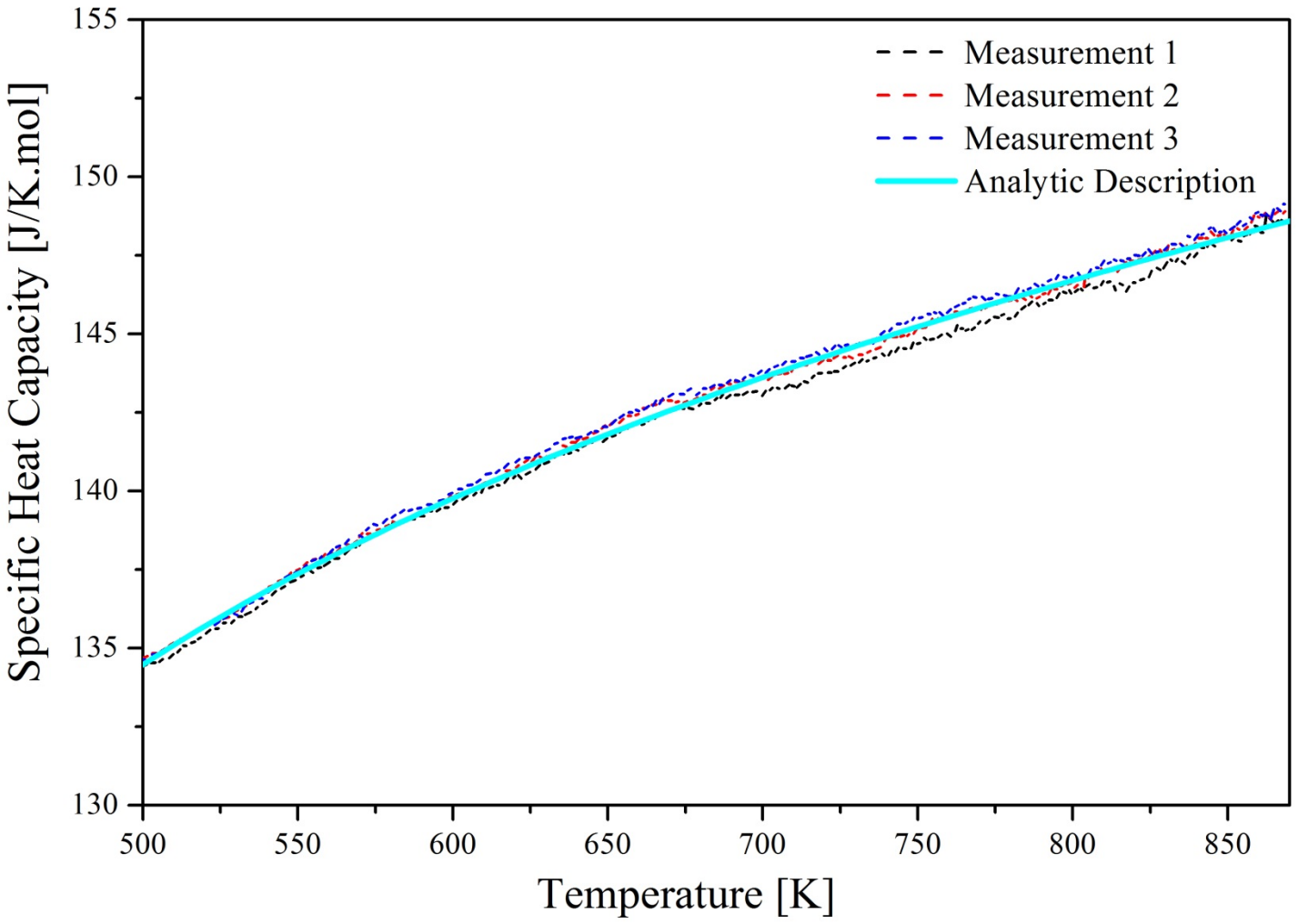


Netzsch 404 F 1



Netzsch 204C

Measured Specific Heat Capacity of Li_2MnO_3



$$C_p=(137.97\pm0.11) + (16.71\pm0.11)\bullet10^{-3}\bullet T+(-2.96\pm0.02)\bullet 10^{6}\bullet T^{-2}$$

Thermodynamic Desciptions in the Li-Mn-O System

Modeling of $LiMnO_2$ and $LiMn_2O_4$ as stoichiometric phases

$$^0G_m^{LiMnO_2} = 0.5 \cdot {}^0G_m^{Li_2O} + 0.5 \cdot {}^0G_m^{Mn_2O_3} + A + B \cdot T$$

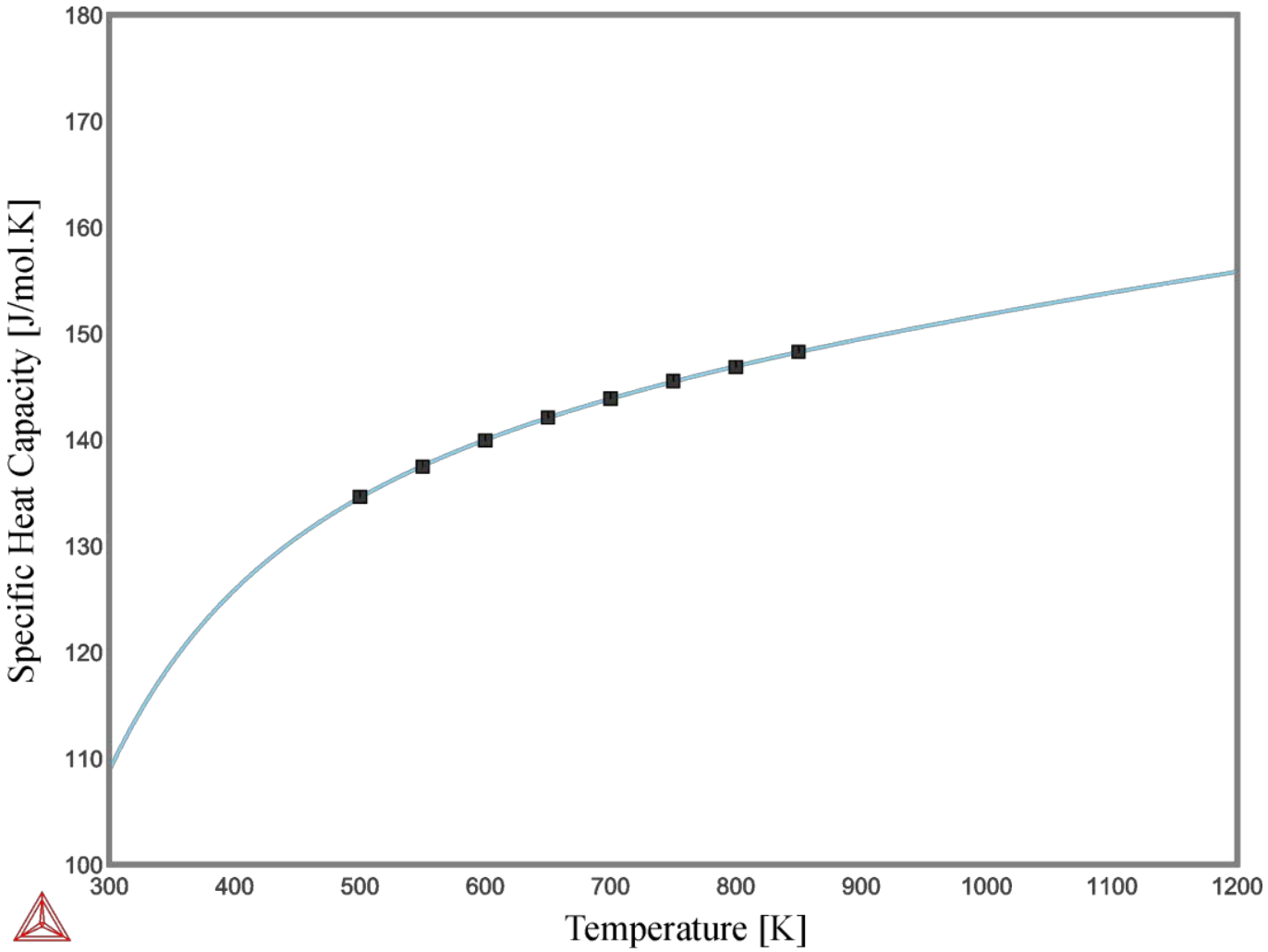
$$^0G_m^{LiMn_2O_4} = 0.5 \cdot {}^0G_m^{Li_2O} + 0.5 \cdot {}^0G_m^{Mn_2O_3} + 0.5 \cdot {}^0G_m^{MnO_2} + A + B \cdot T$$

A: Enthalpy of Formation from the oxides. Determined by solution calorimetry

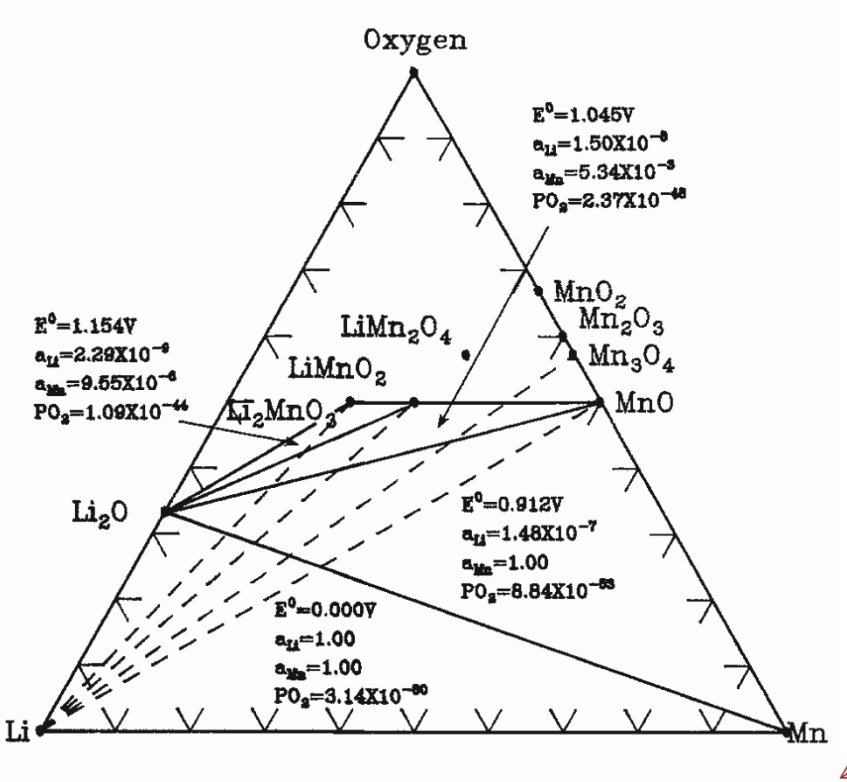
Calculation of cell potentials

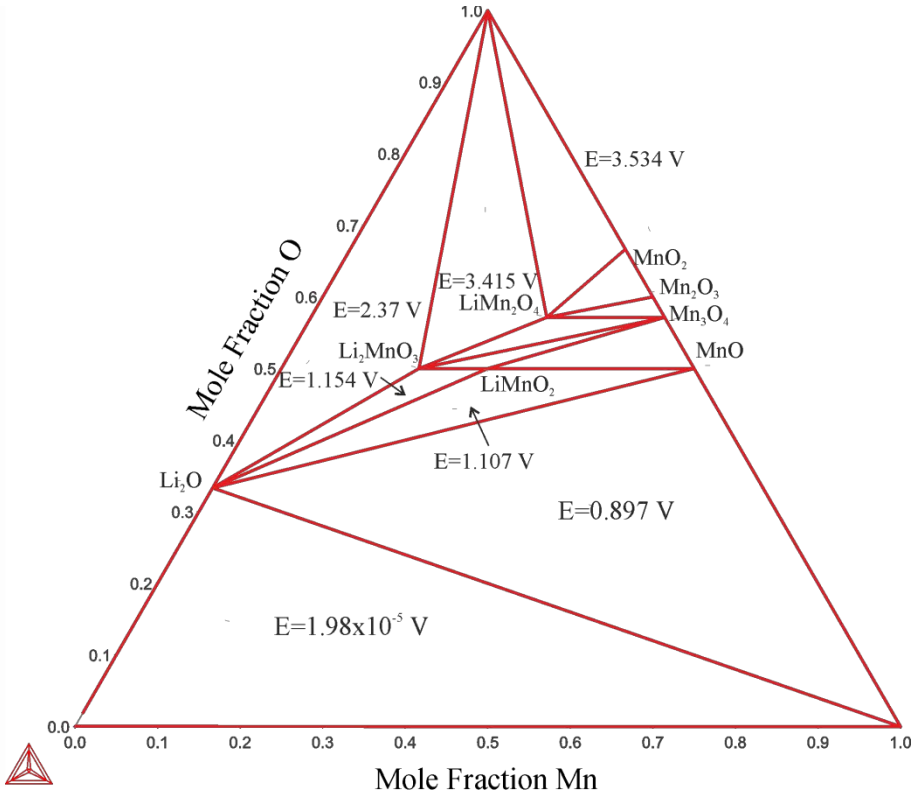
$$V = -\frac{\mu_{Li}^{Cathode} - \mu_{Li}^{Anode}}{F} = -\frac{\mu_{Li}^{Cathode}}{F}$$

Calculated Specific Heat Capacity of Li_2MnO_3



Calculated Isothermal Section at 400°C





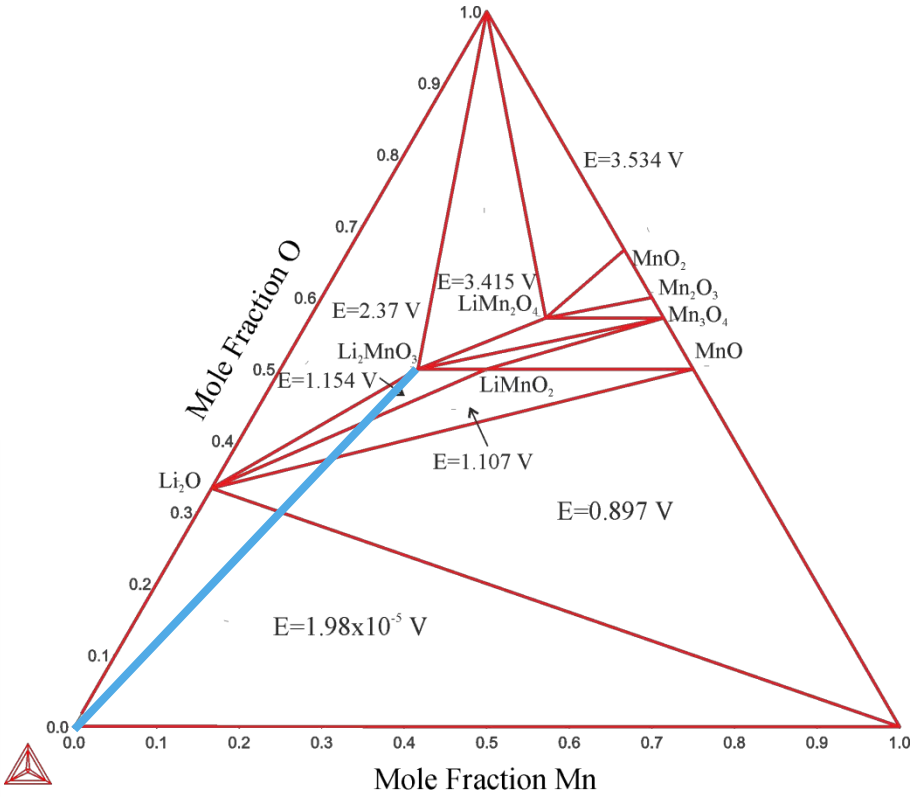
$^{0}G_m^{LiMnO_2}$ and $^{0}G_m^{LiMn_2O_4}$ at 680, 740 and 800 K taken from Rog et al. [1]

$\Delta H_{f,ox}^{LiMn_2O_4}$ taken from Wang and Navrotsky [2]

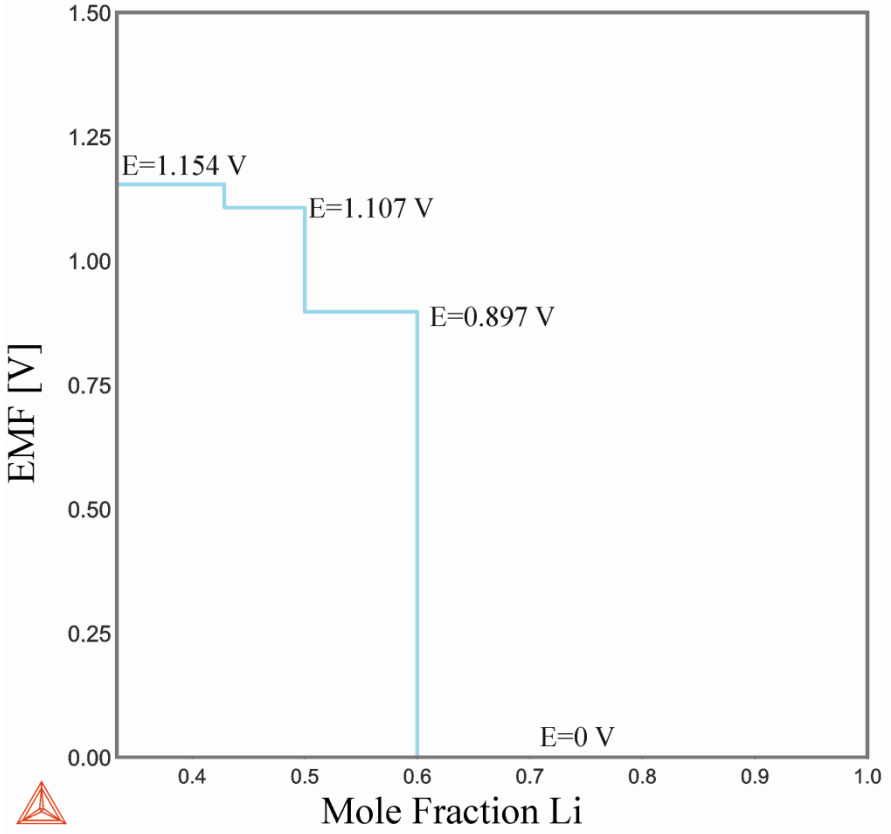
$\Delta H_{f,ox}^{LiMnO_2}$ taken from Wang and Navrotsky [3]

[1] Rog et al. J. Chem. Thermodynamics., 364, (2003) 473-476
[2] Wang and Navrotsky, J. Solid State Chem. 178 (2005) 1182-1189
[3] Wang and Navrotsky, J. Solid State Chem. 178 (2005) 1230-1240

Calculated Coulometric Titration Curve at 400°C

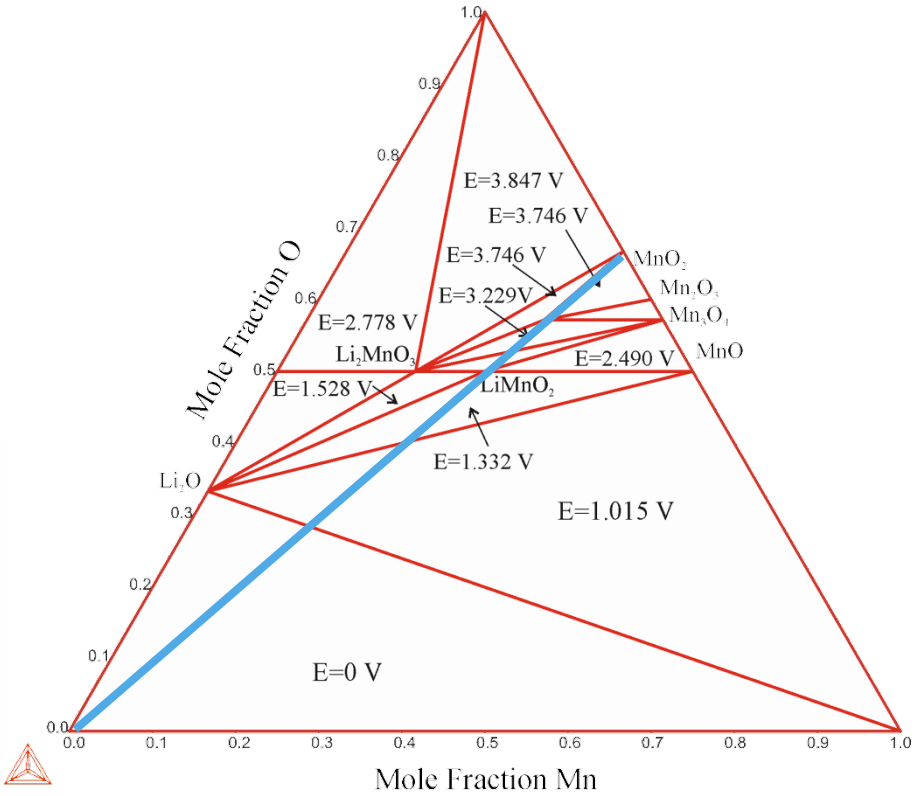


Calculated phase diagram at 400°C

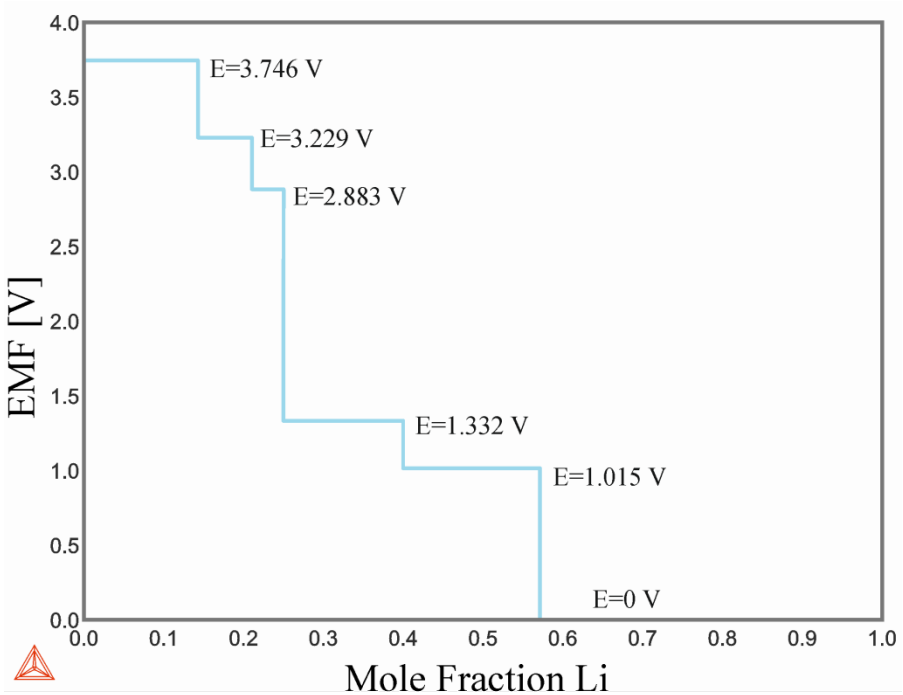


Calculated coulometric titration curve at 400°C

Calculated Coulometric Titration Curve at R. T.



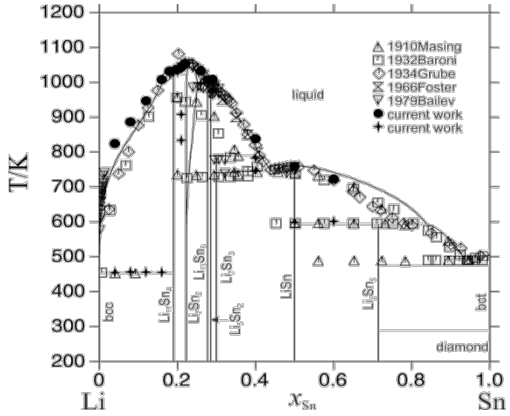
Calculated phase diagram at 25°C



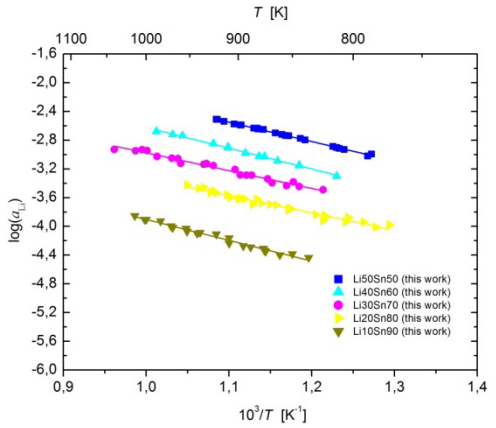
Calculated coulometric titration curve at 25°C

Li-Sn: Collaboration Map

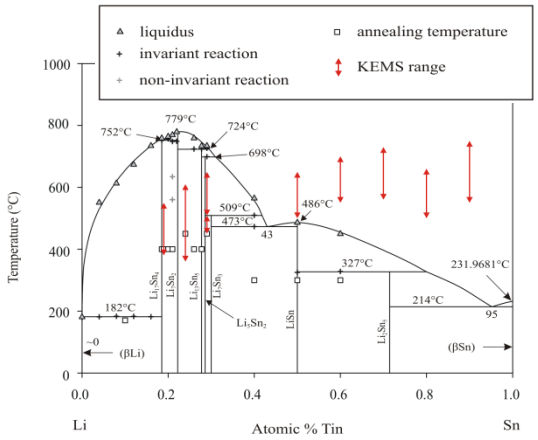
Sample preparation



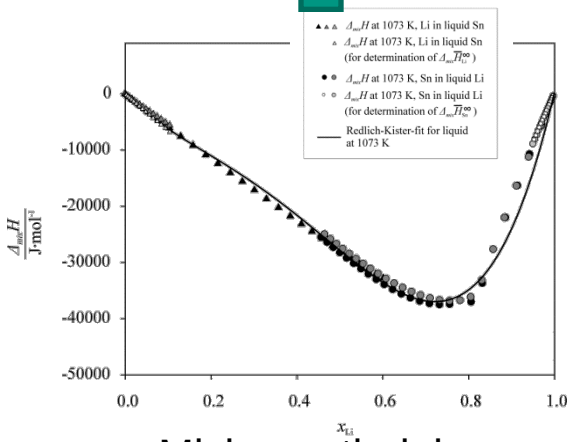
Optimized phase diagram



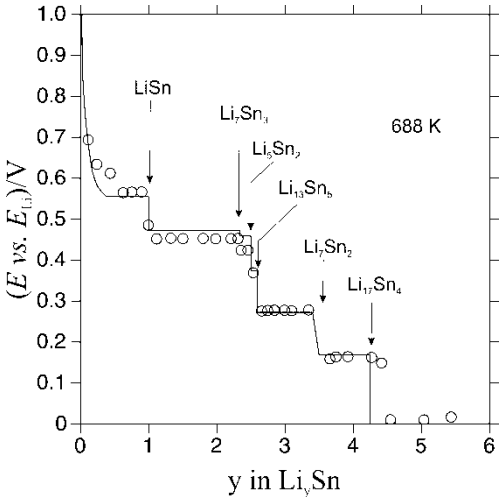
Temperature dependencies of Li activity (KEMS)



Experimental phase diagram

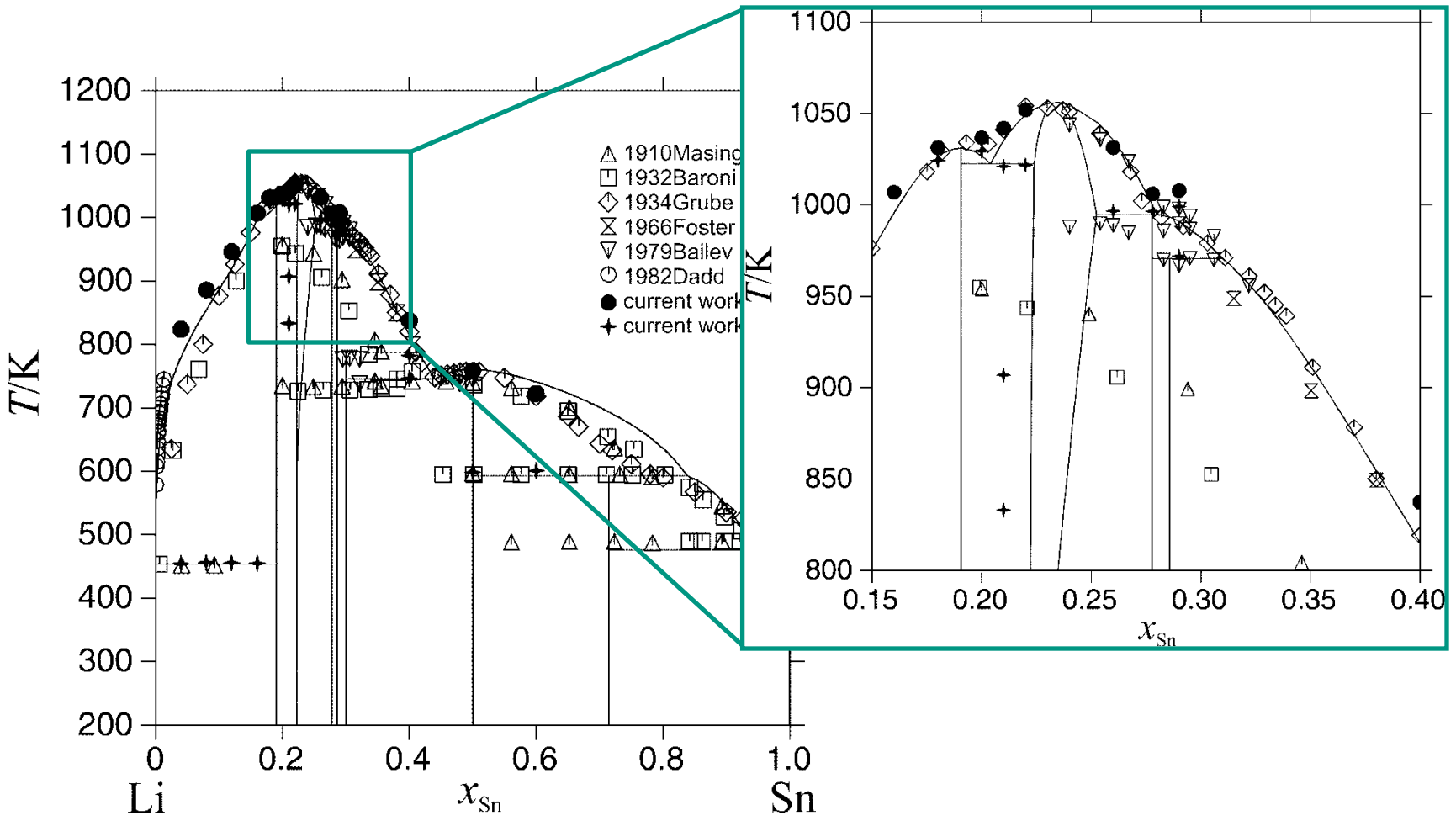


Mixing enthalpies (drop calorimetry)

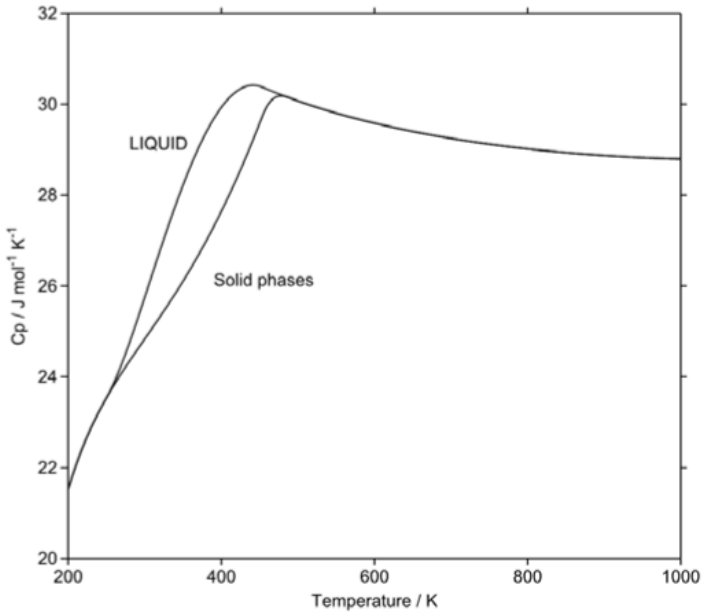


Calculated EMF

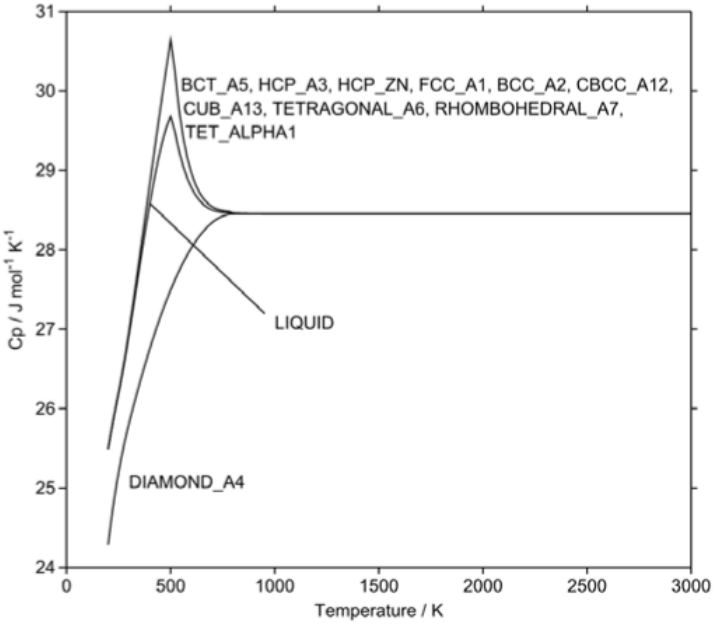
Li-Sn: Calculated Phase Diagram



Heat Capacity of Li-Sn Intermetallics



Heat capacity of Li

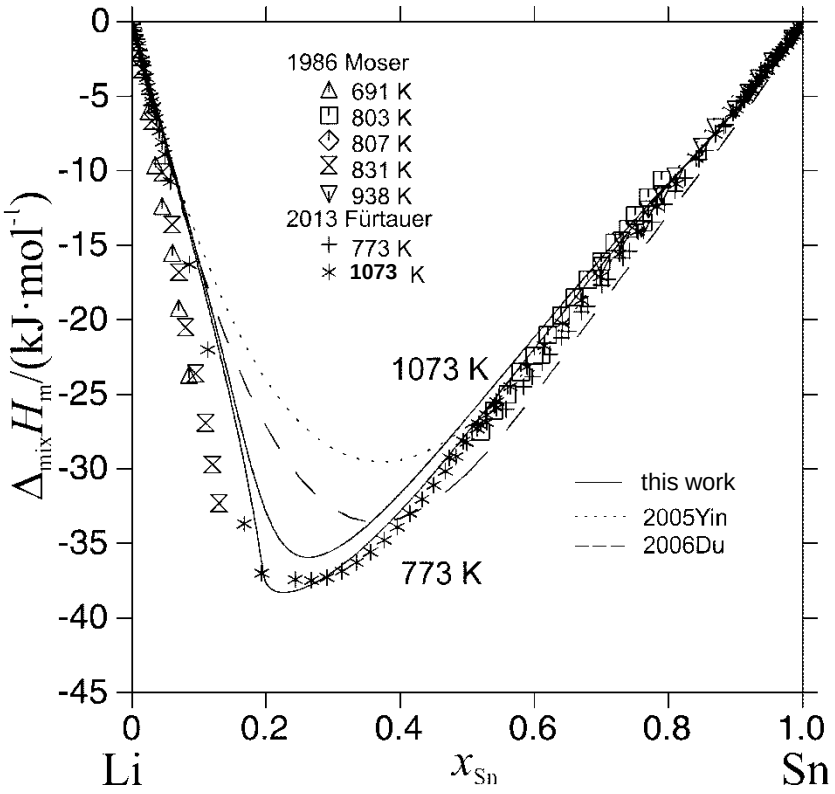


Heat capacity of Sn

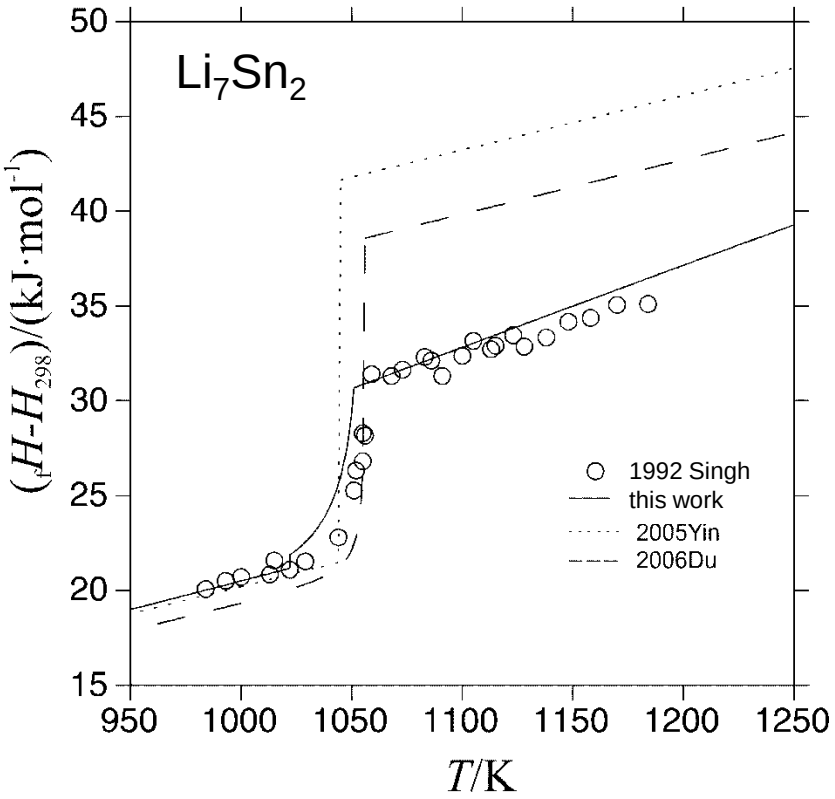
Li_5Sn_2: Model $(Li)_{0.714}(Sn)_{0.286}$

$$ {}^{0}G^{Li_5Sn_2}_{Li:Sn} - 0.714H^{SER}_{Li} - 0.286H^{SER}_{Sn} = -50890 + 165.654838T - 29T\ln T $$

Li-Sn: Thermochemical Data

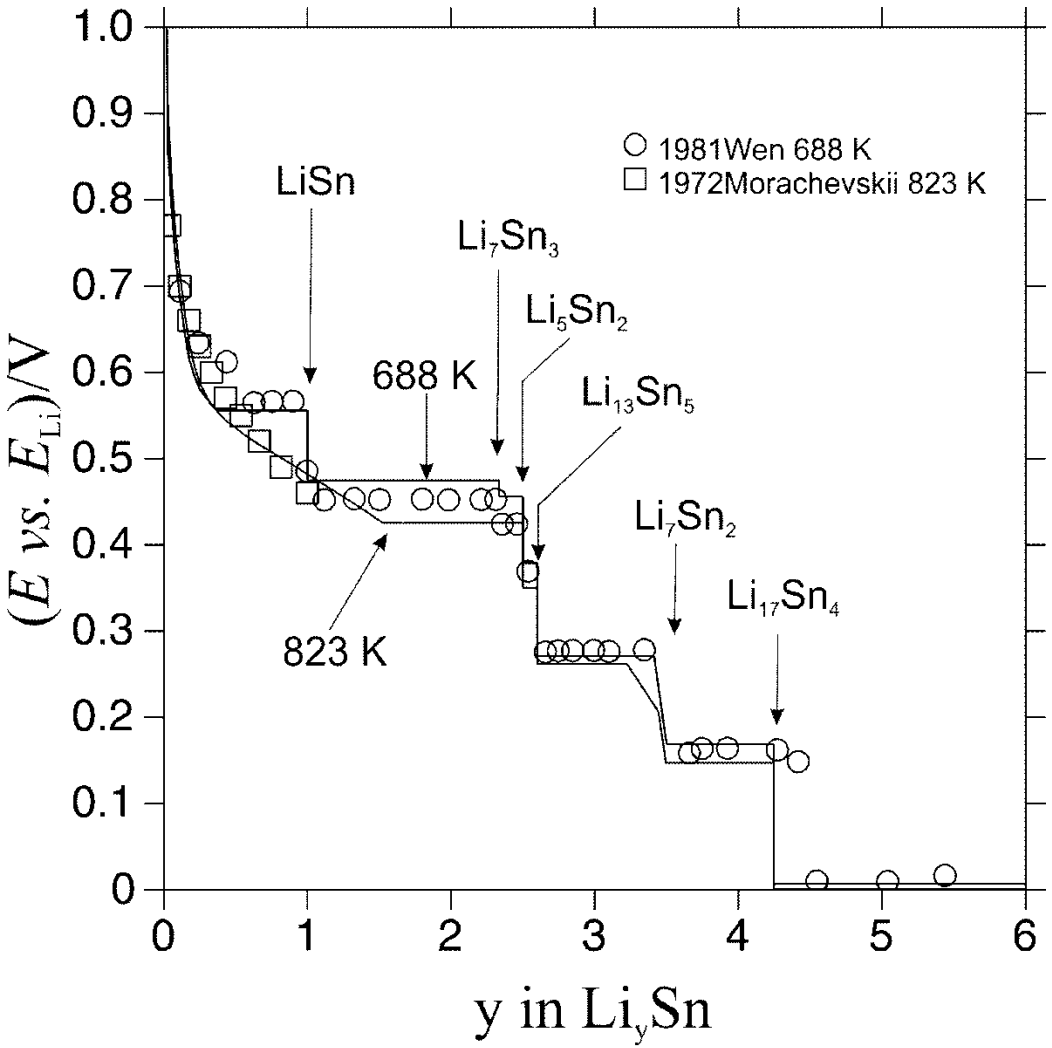


S. Fürtauer et al., J. Chem. Thermodyn., 61 (2013), 105

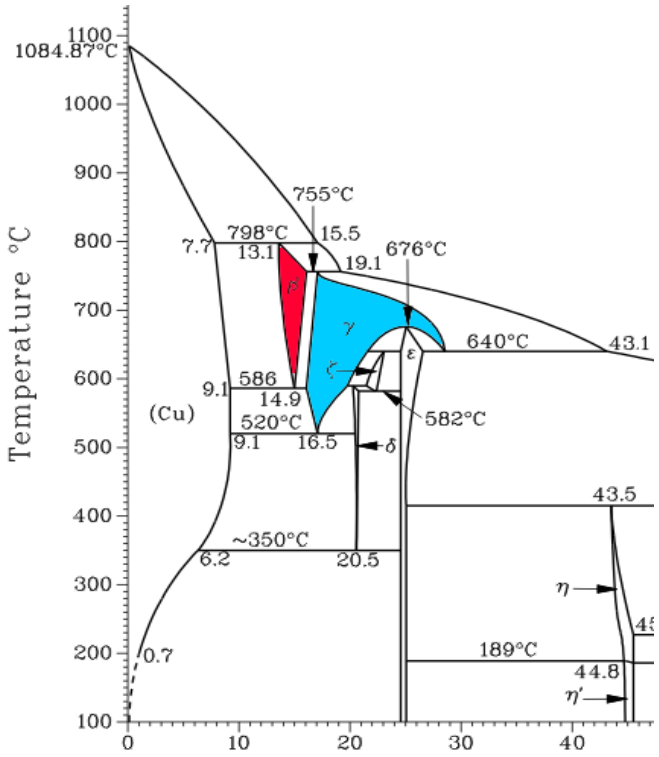


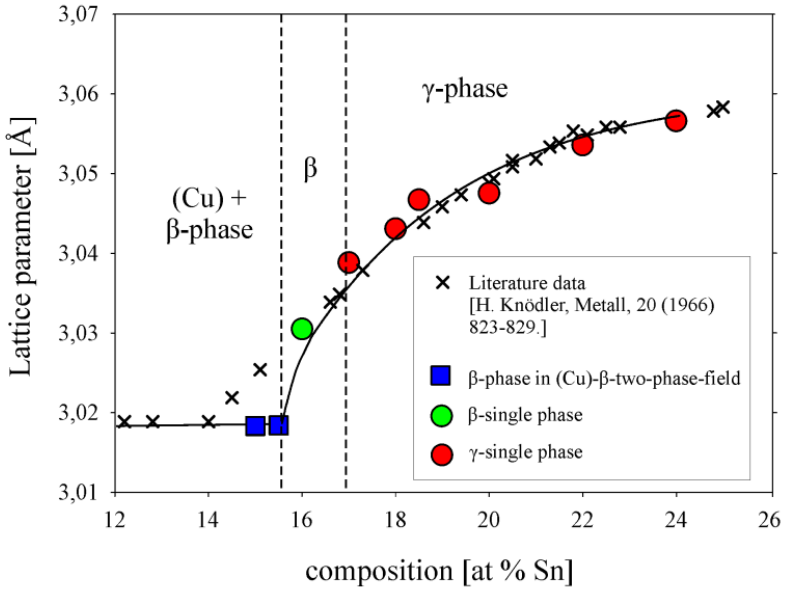
R.N. Singh et al., J. Phys.-Condens. Mat. 4 (1992), 5345

Li-Sn: Coulometric Titration Curve



Cu-Sn: Order-Disorder Transformation



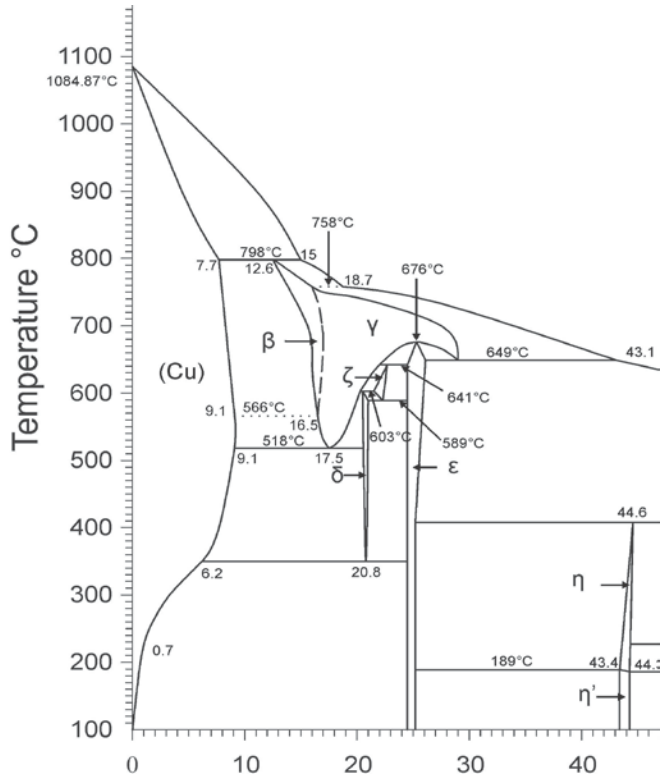


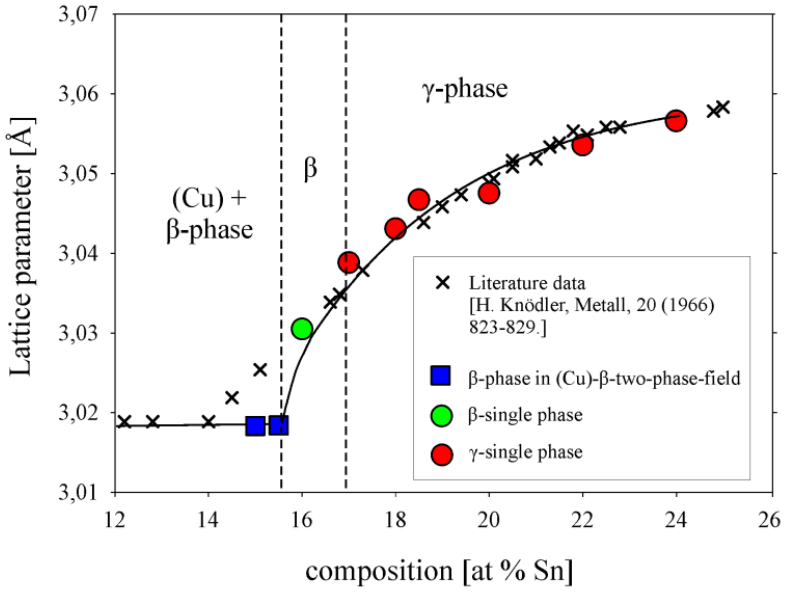
HT-XRD, 973 K

T.B. Massalski, H. Okamoto, Binary alloy phase diagrams, ASM International, Materials Park, Ohio, 2001.

S. Fürtauer et al., Intermetallics 34 (2013) 142-147.

Cu-Sn: New Experimental Phase Diagram



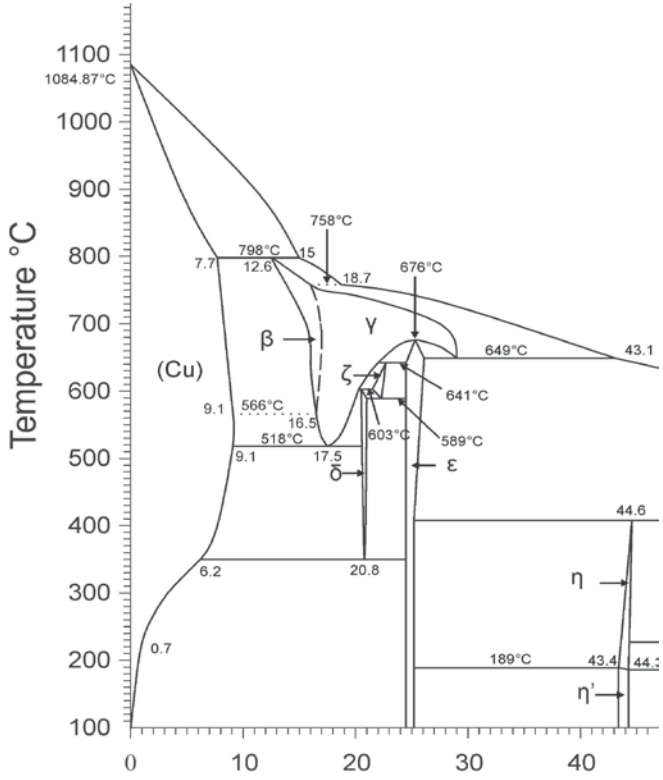


HT-XRD, 973 K

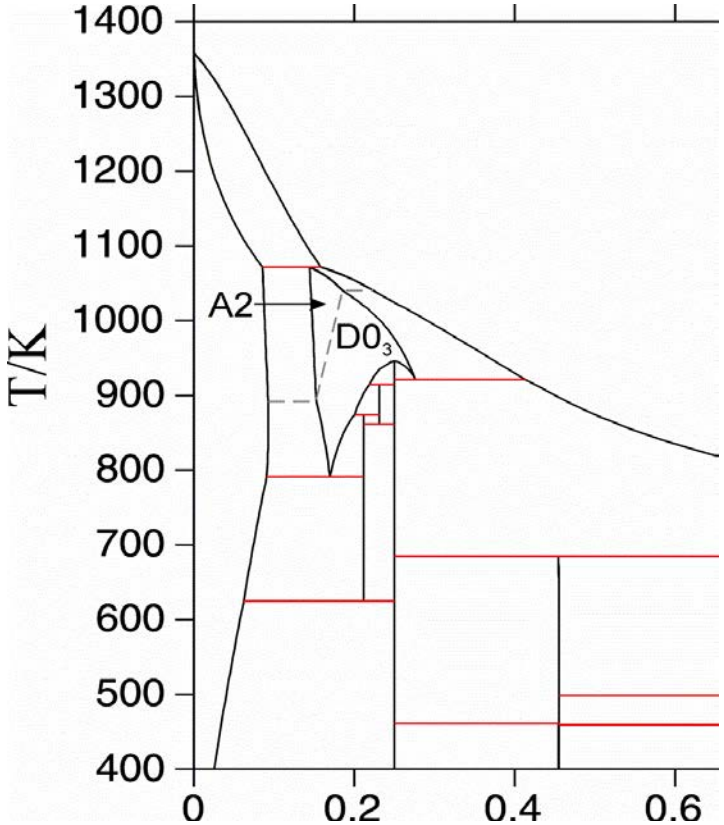
S. Fürtauer et al., Intermetallics 34 (2013) 142-147.

S. Fürtauer et al., Intermetallics 34 (2013) 142-147.

Cu-Sn: Calculated Phase Diagram



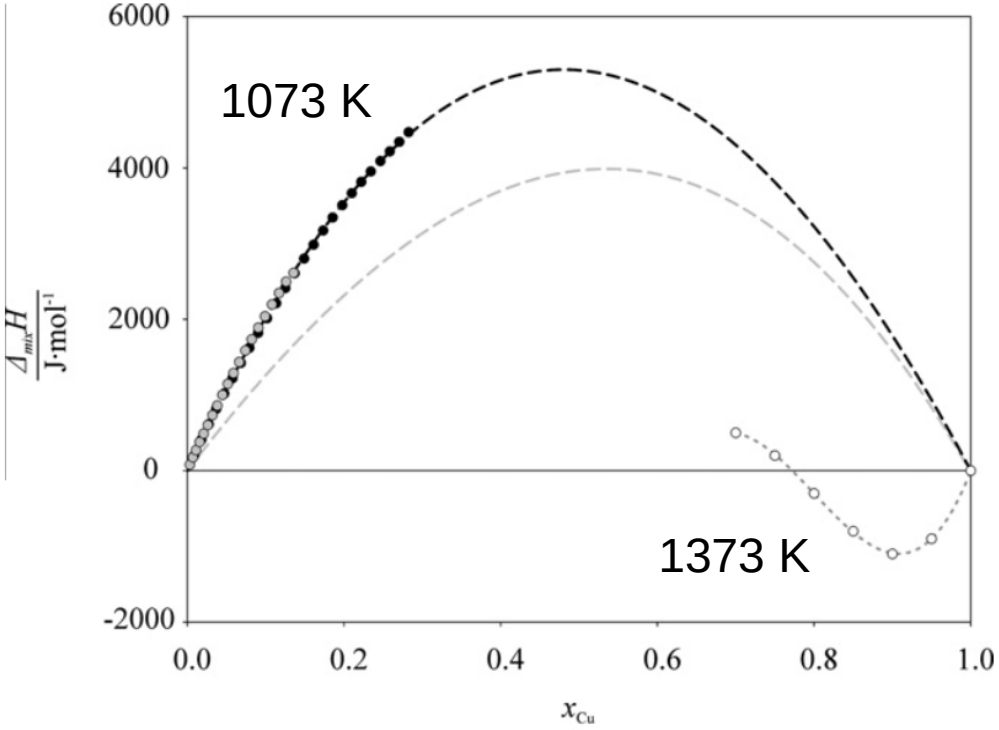
S. Fürtauer et al. , Intermetallics 34 (2013) 142-147.



D. Li et al. , Intermetallics 34 (2013) 148-158.

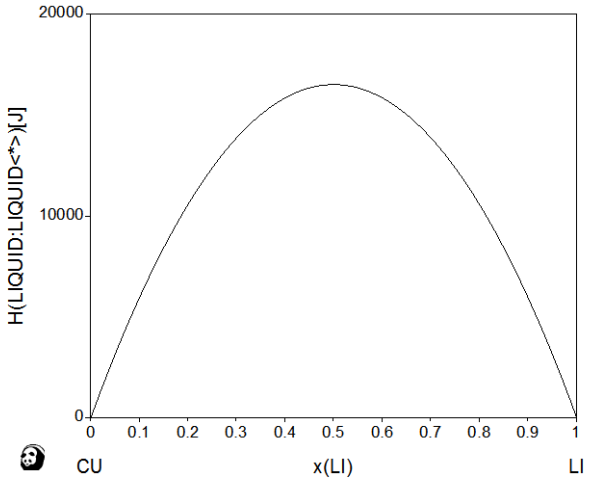
A2/D0$_3$ model: $(Cu,Sn)^{I}_{0.25}(Cu,Sn)^{II}_{0.25}(Cu,Sn)^{III}_{0.25}(Cu,Sn)^{IV}_{0.25}$

Cu-Li: Motivation



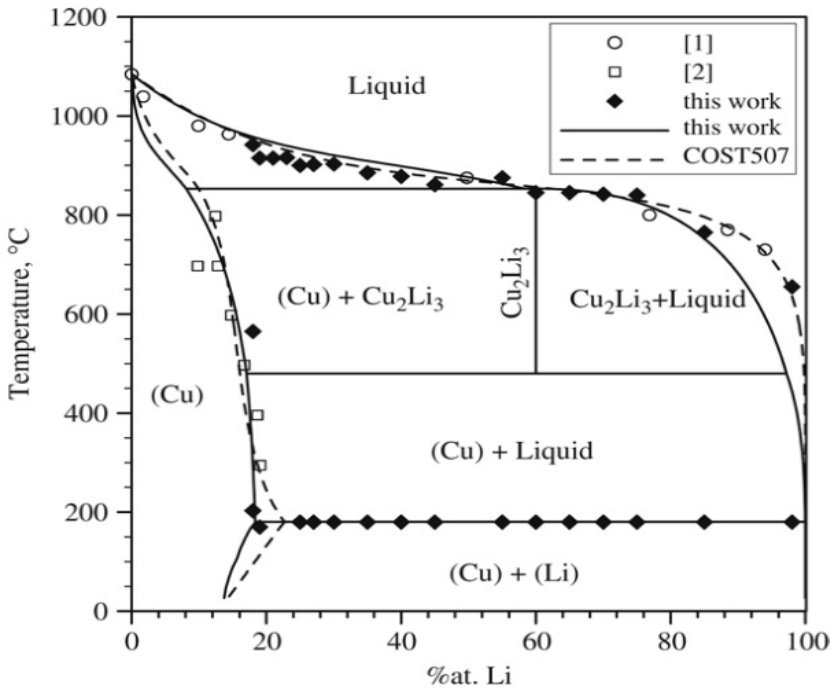
Drop calorimetric measurement at 1073/1373 K

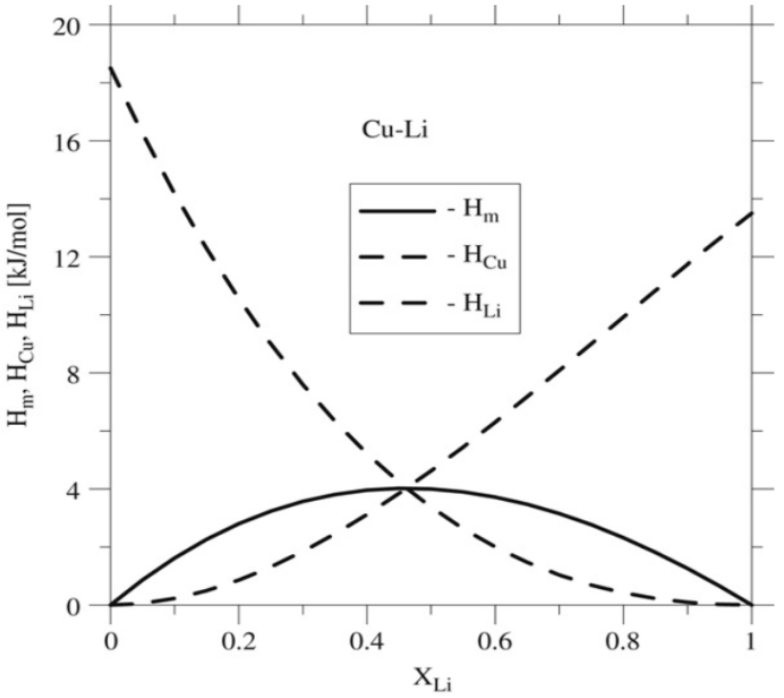
S. Fürtauer et al., J. Chem. Thermodyn., 61 (2013), 105



Calculated from COST 507 Database

Cu-Li: Motivation

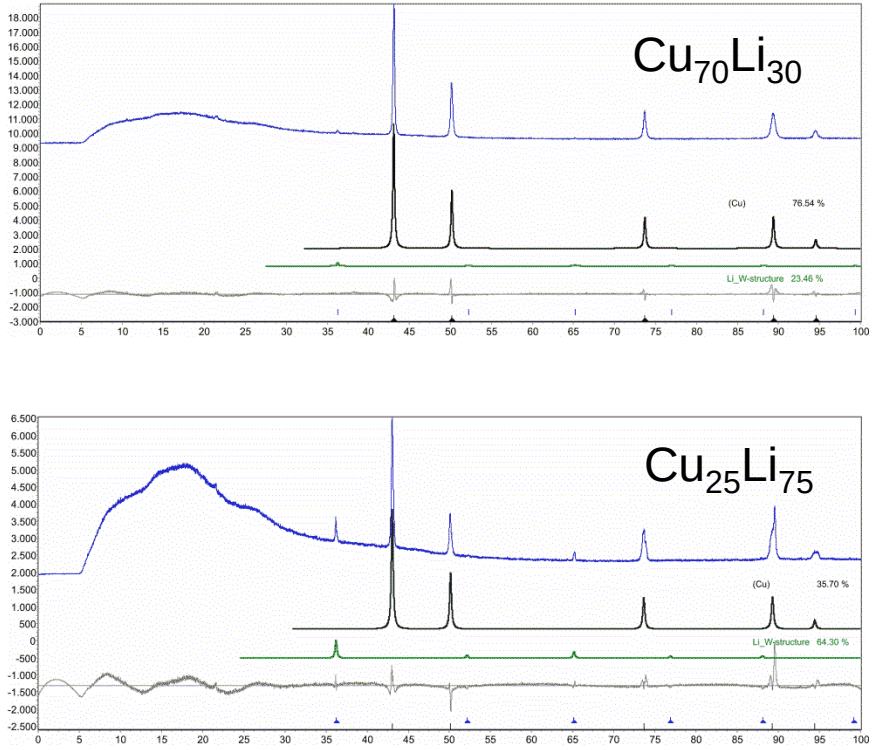


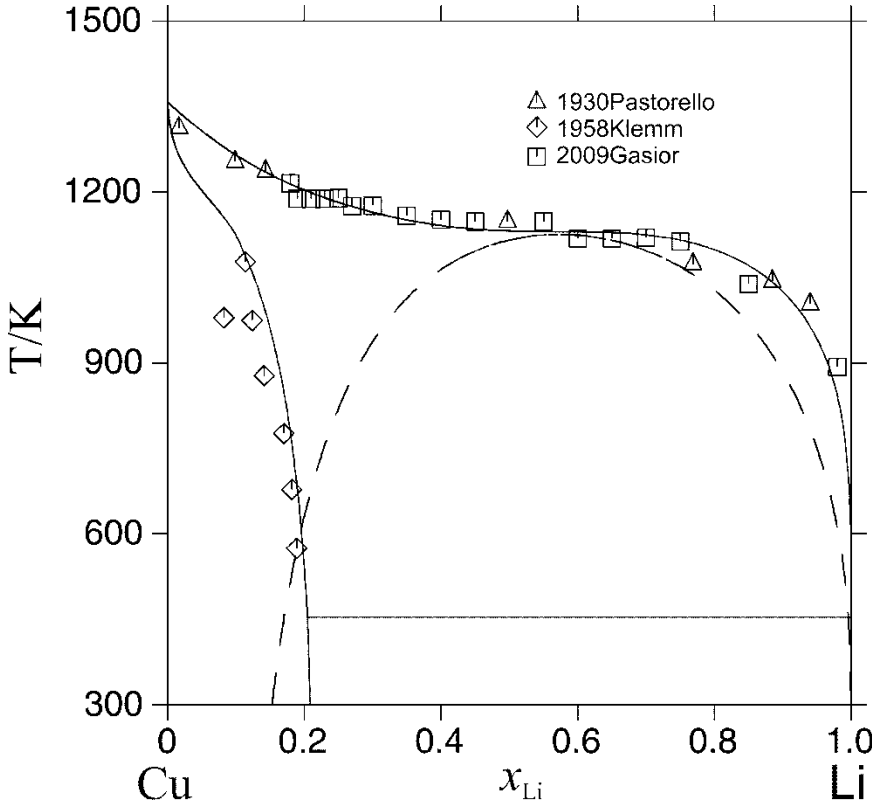


Derived from emf data

W. Gasior et al., CALPHAD 33 (2009) 215

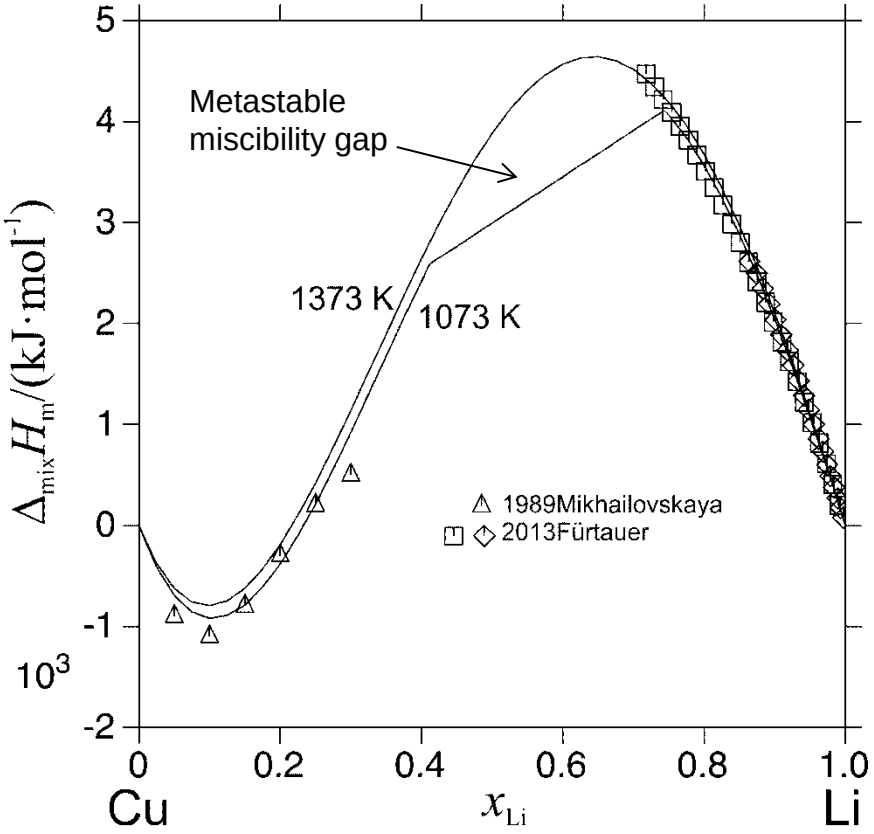
Cu-Li: Calculated Phase Diagram



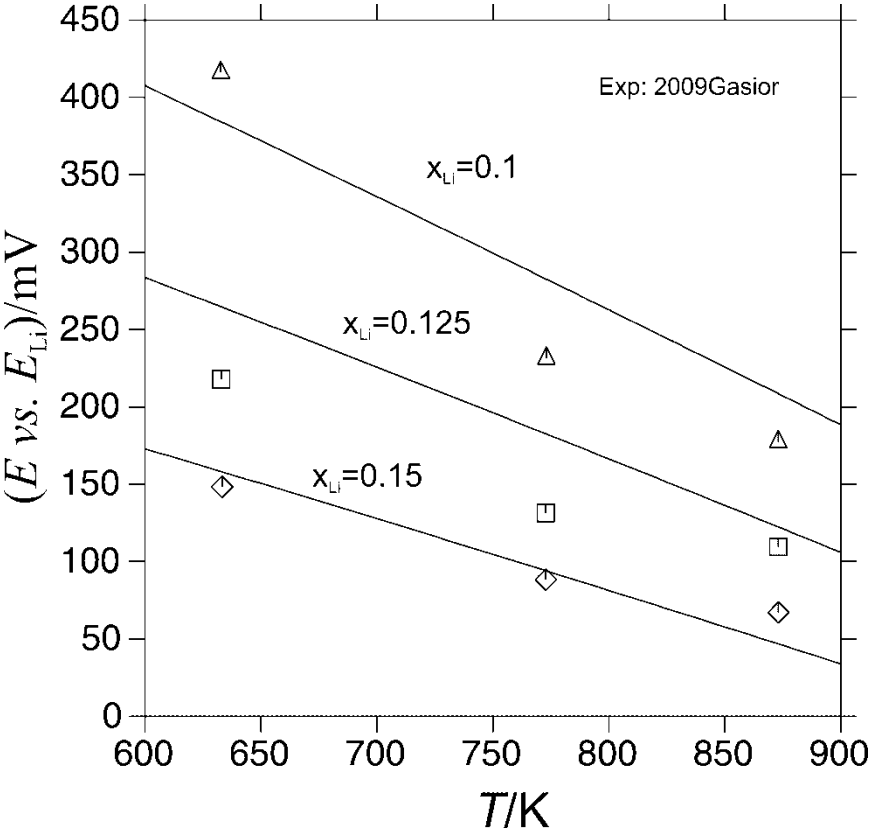


Quench experiments (973 K, 14 days) on $Cu_{70}Li_{30}$ and $Cu_{25}Li_{75}$ performed (University of Vienna), Cu_2Li_3 phase not detected

Cu-Li: Enthalpy of Mixing and EMF Data

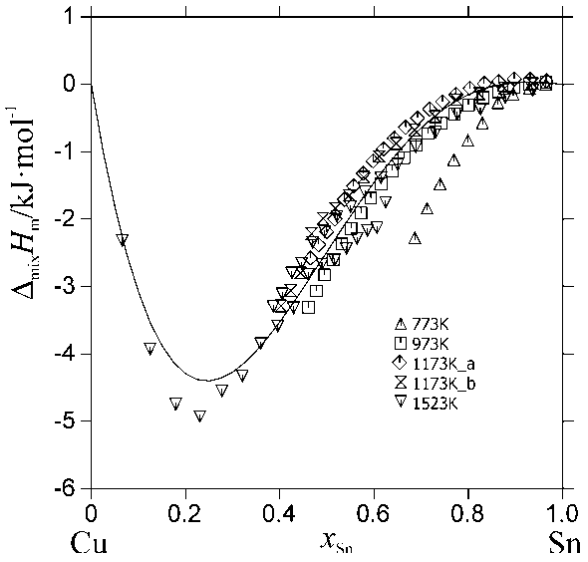


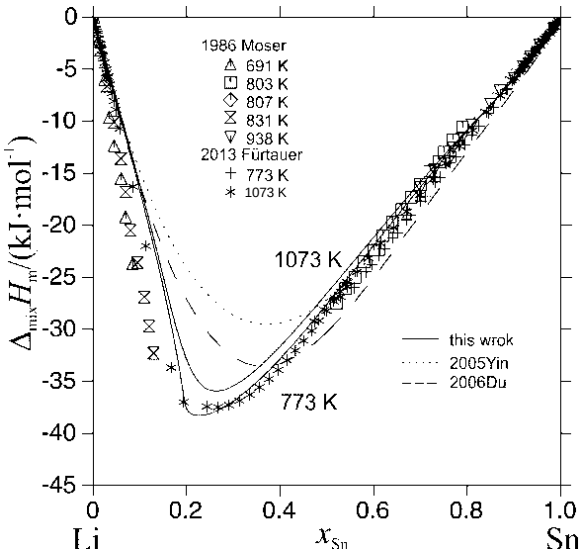
Liquid Phase

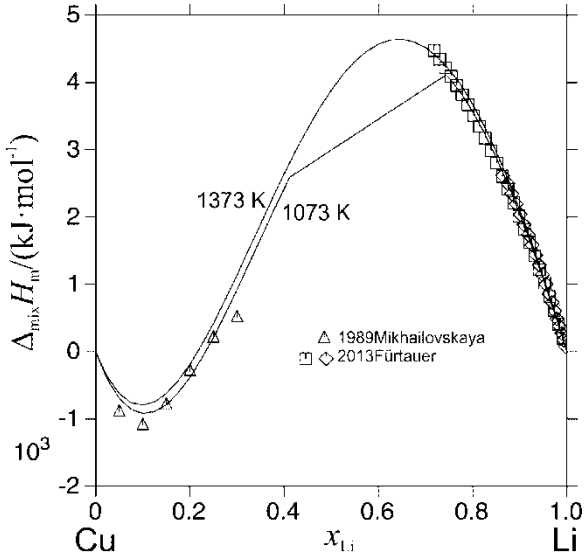


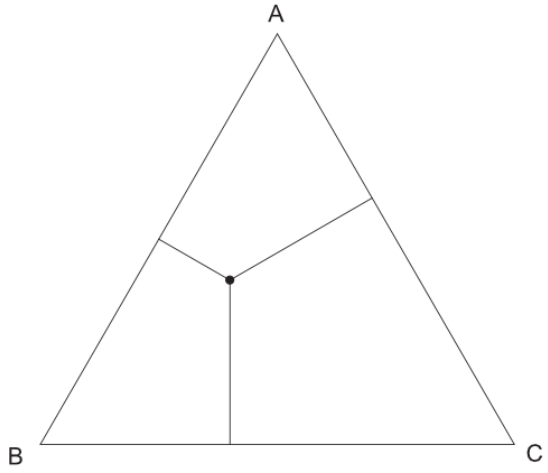
fcc(Cu)

Cu-Li-Sn: Extrapolation of Enthalpies of Mixing



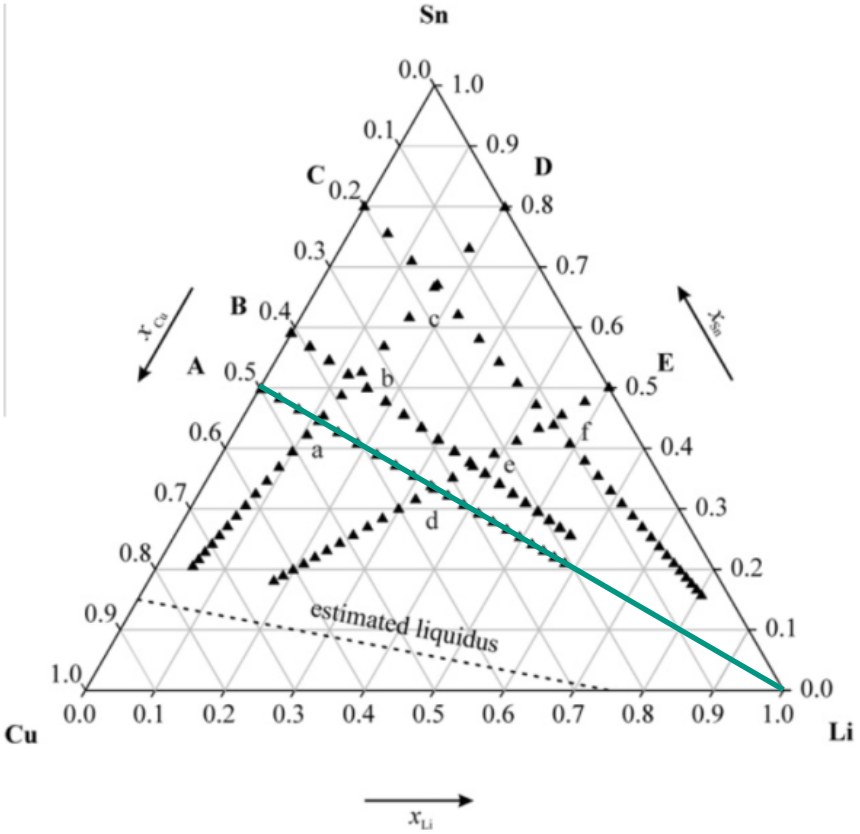


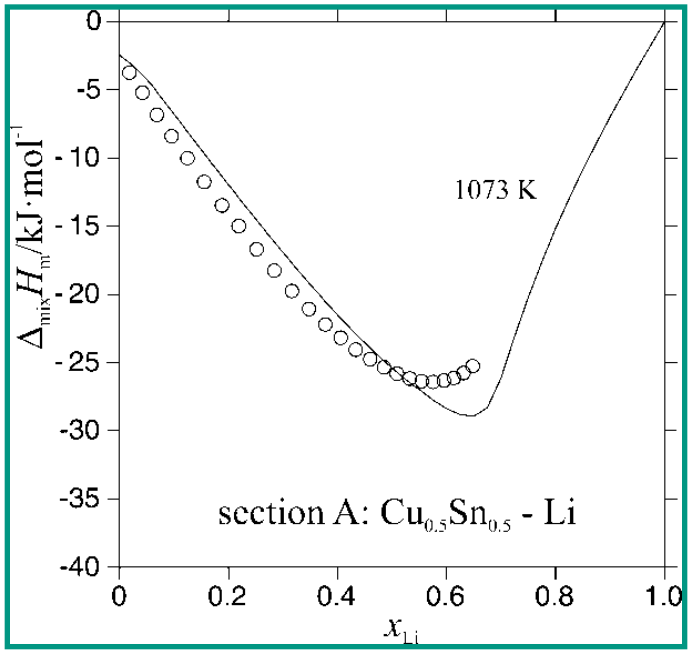




Y. Muggianu et al., Journal de Chimie Physique, 1 (1975), 83

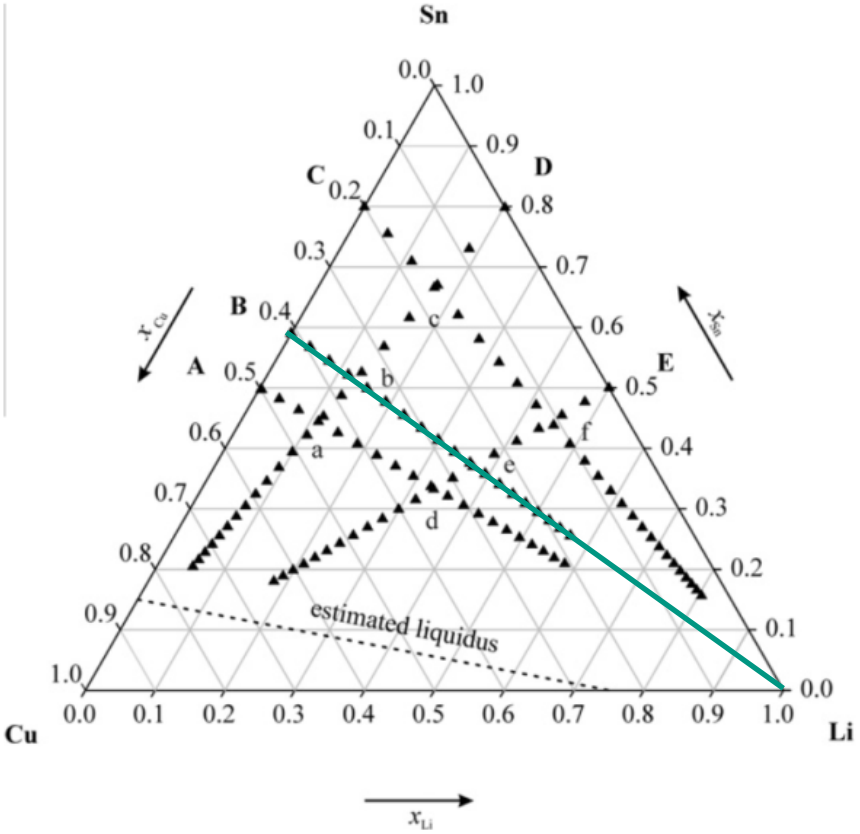
Cu-Li-Sn: Enthalpies of Mixing

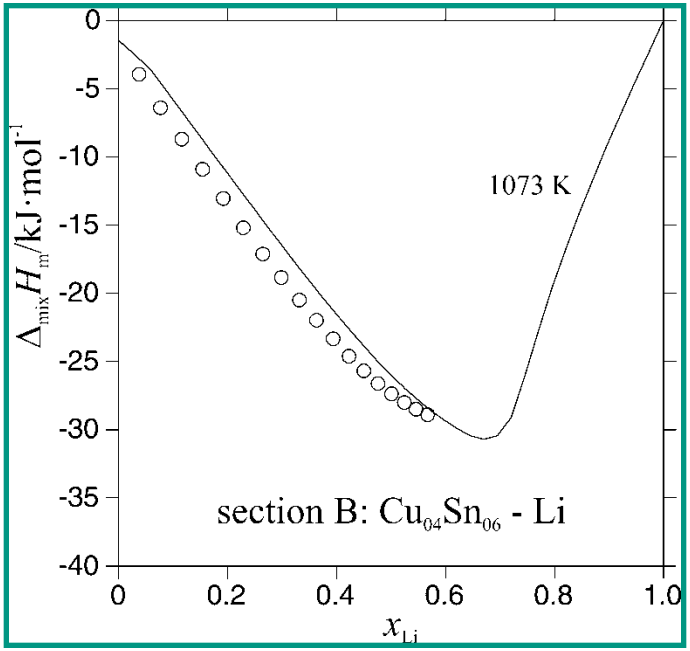




S. Fürtauer et al. , J. Chem. Thermodyn., 61 (2013), 105.

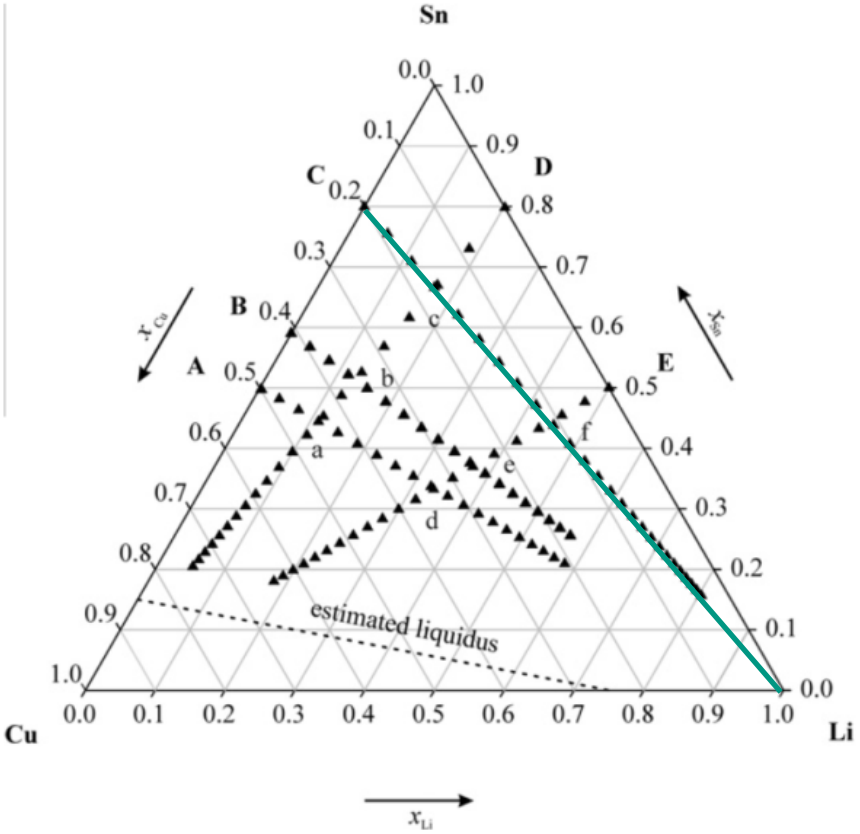
Cu-Li-Sn: Enthalpies of Mixing

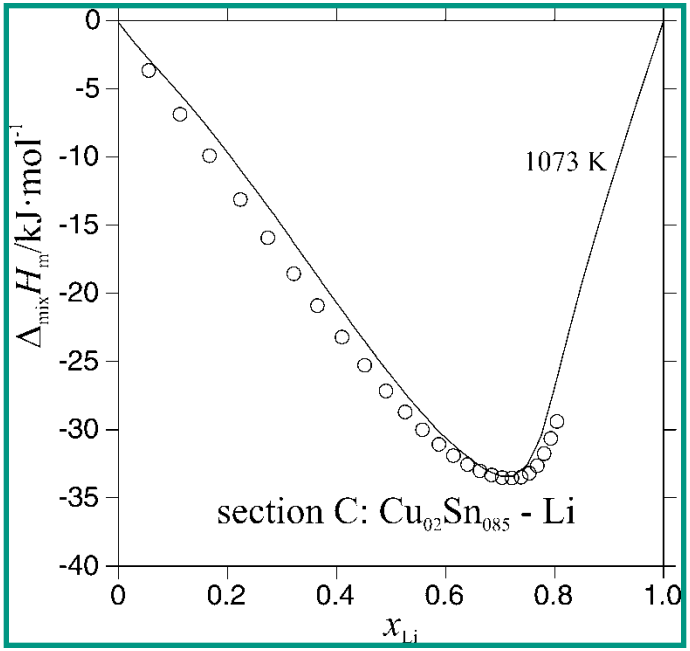




S. Fürtauer et al. , J. Chem. Thermodyn., 61 (2013), 105.

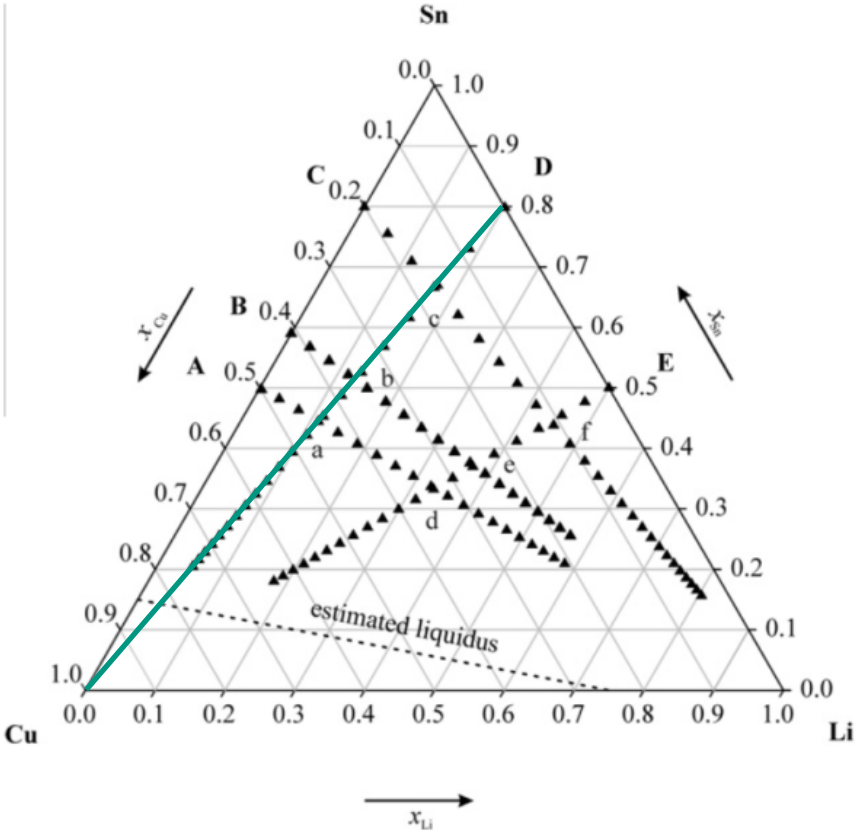
Cu-Li-Sn: Enthalpies of Mixing

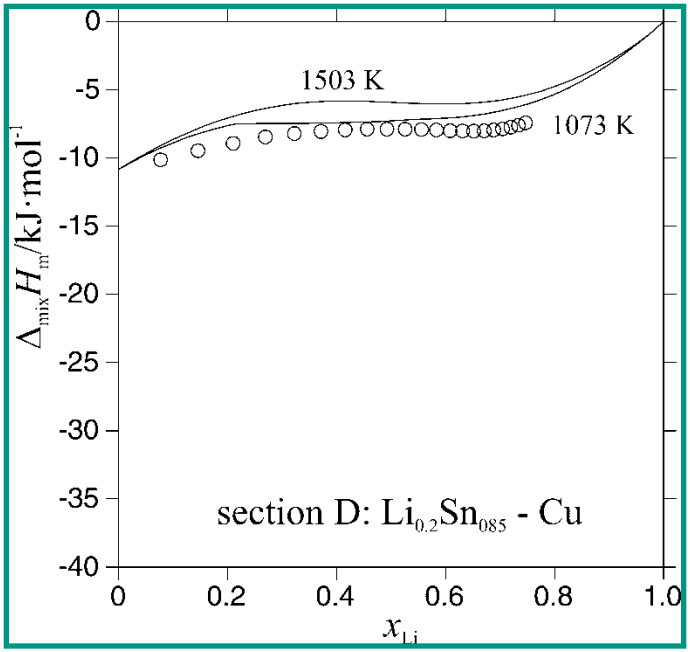




S. Fürtauer et al. , J. Chem. Thermodyn., 61 (2013), 105.

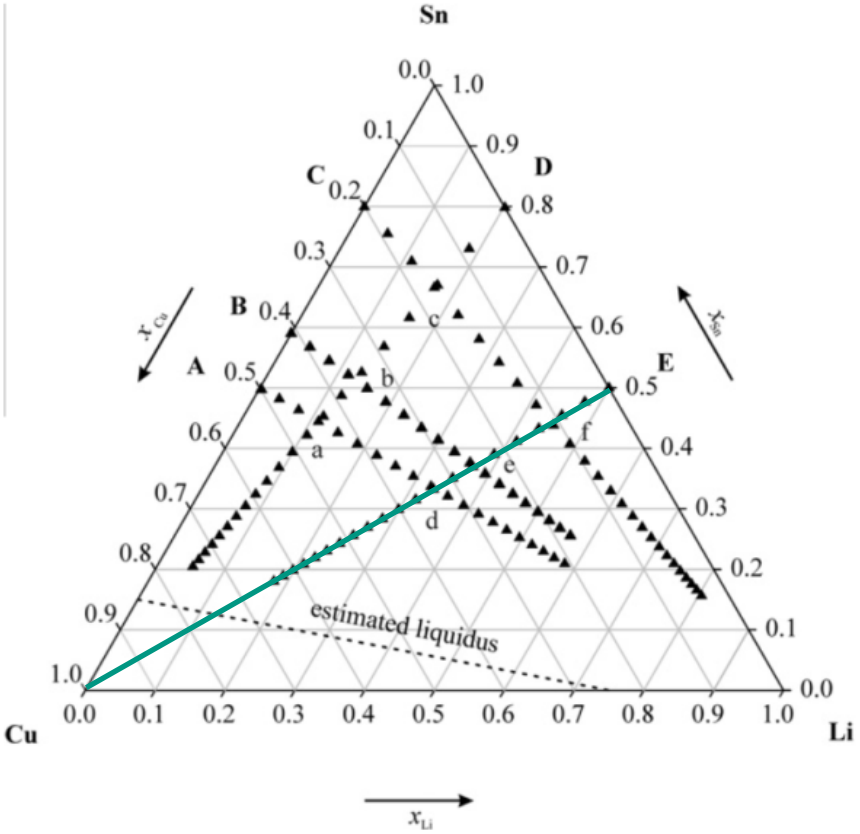
Cu-Li-Sn: Enthalpies of Mixing

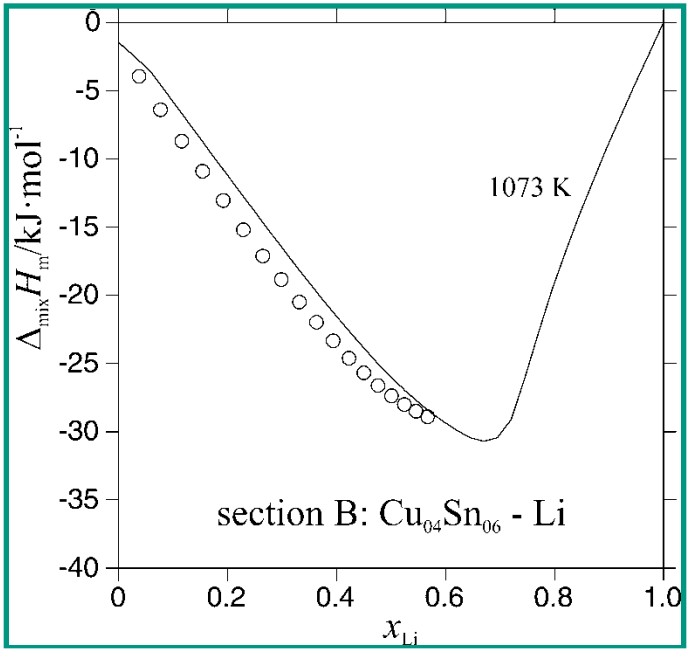




S. Fürtauer et al. , J. Chem. Thermodyn., 61 (2013), 105.

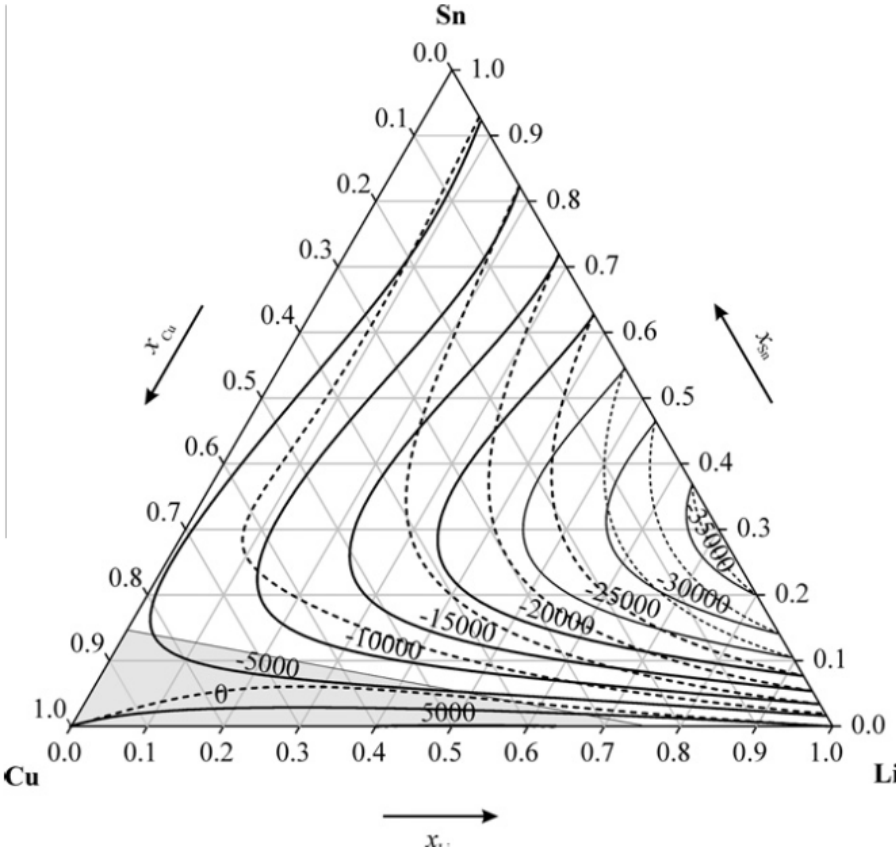
Cu-Li-Sn: Enthalpies of Mixing

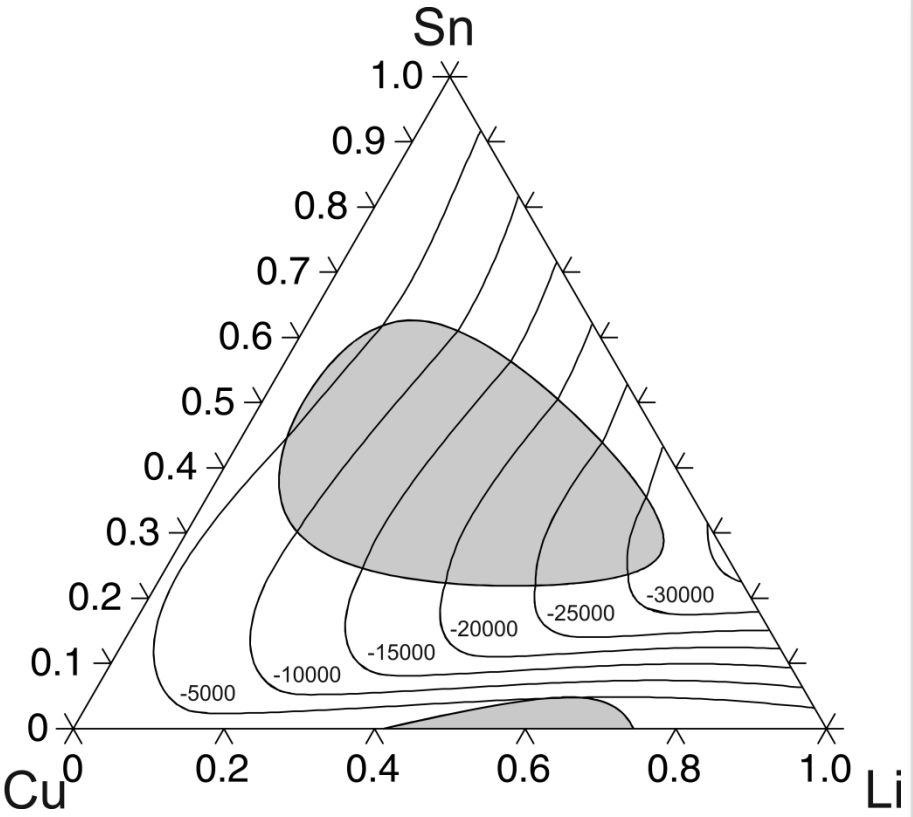




S. Fürtauer et al. , J. Chem. Thermodyn., 61 (2013), 105.

Cu-Li-Sn: Isoenthalpy Curves of the Liquid



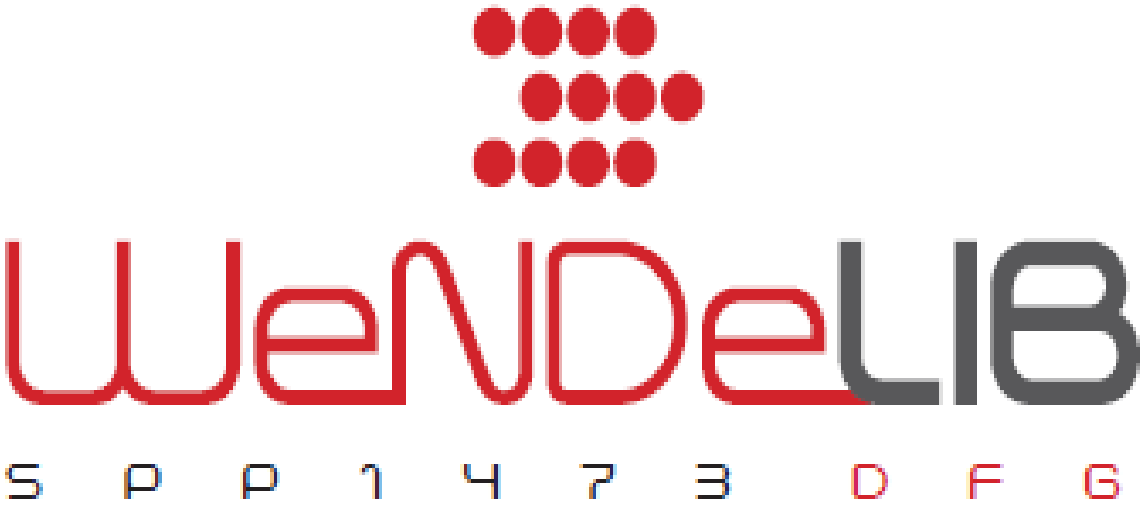


S. Fürtauer et al. , J. Chem. Thermodyn., 61 (2013), 105.

Calculation

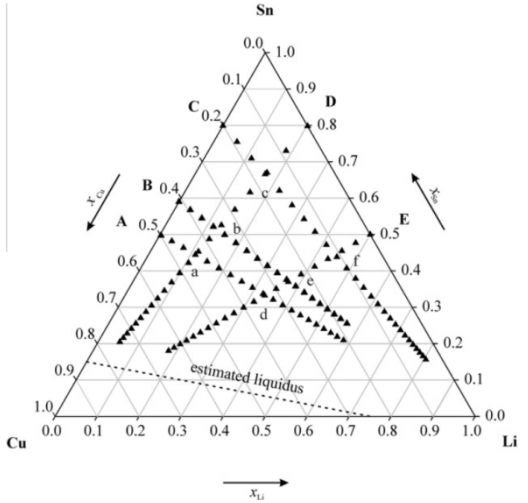
No ternary interaction parameter used!

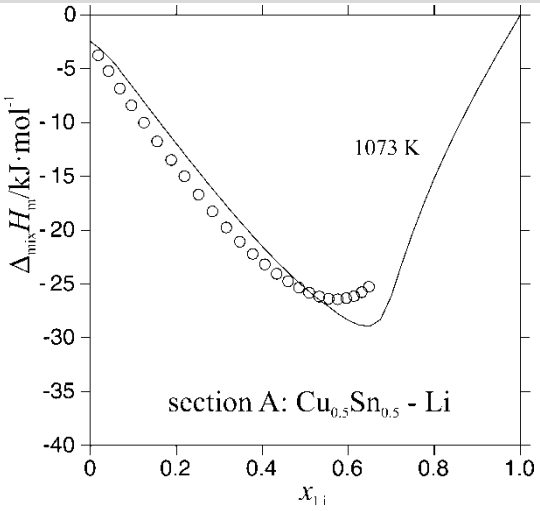
Conclusions

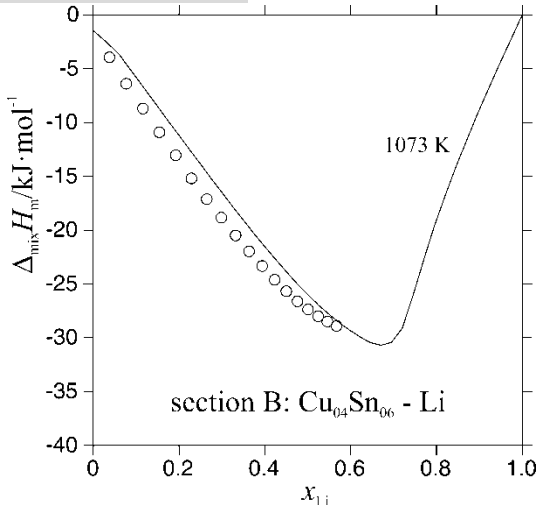


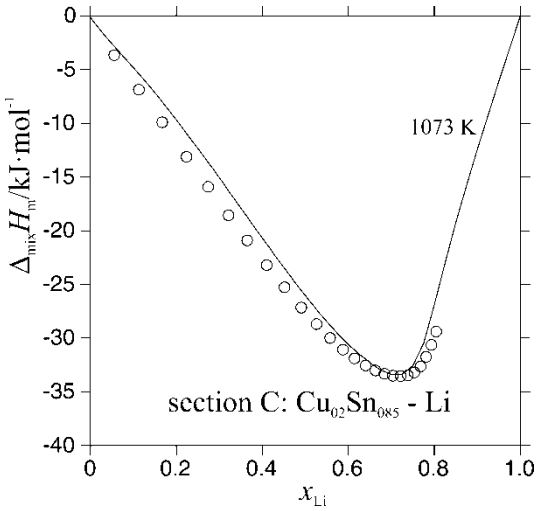
Lots of work still needs to be done!

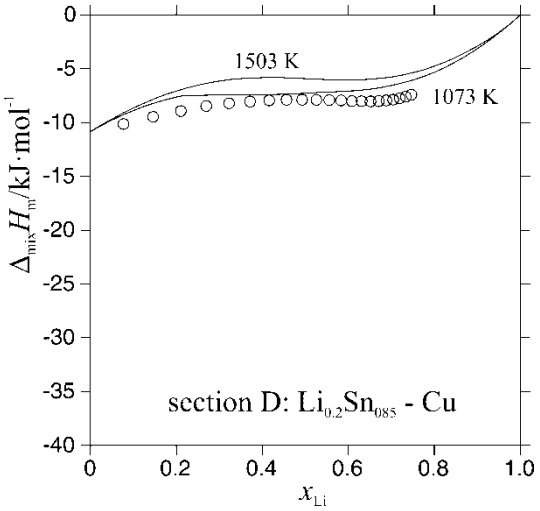
Cu-Li-Sn: Extrapolated Enthalpies of Mixing

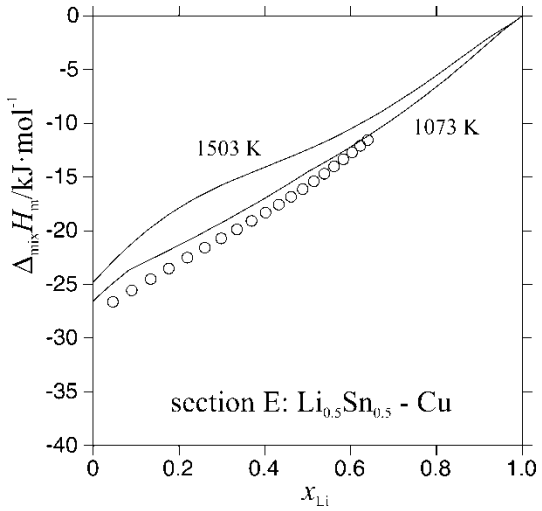












No ternary interaction parameter used!