Home assignment

Computational Thermodynamics

Your assignment is to investigate the silver – copper systems and obtain a simple thermodynamic description of the system. You do not need to use any optimiser; you are supposed to obtain the necessary parameters from mathematical descriptions of the thermodynamic properties. You may use Maple, Matlab or any other software you like. Put your expressions in a database-file (name.TDB) and test your result by plotting the diagram using Thermo-Calc.

Ag-Cu is a simple eutectic system with the eutectic point at 1053 K and 40 at% Cu.

The solid structure of both Ag and Cu is fcc and the melting temperature of Ag is 1235 K and that of Cu is 1358 K. The enthalpy of melting is 11 300 J/mol for silver and 13 300 J/mol for copper. There is a miscibility gap between the two fcc phases and its (metastable) critical point (top of the miscibility gap) is at around 1388 K and 63 at% Cu.

At the eutectic temperature the compositions of Ag-fcc and Cu-fcc is 13 and 95.5 at% Cu respectively.

In the Fig. below the measured activity at 1400 K in the liquid is plotted (S M Howard, Metallurgical Transactions B, **20B** (1989) 845-852). The reference state is liquid.

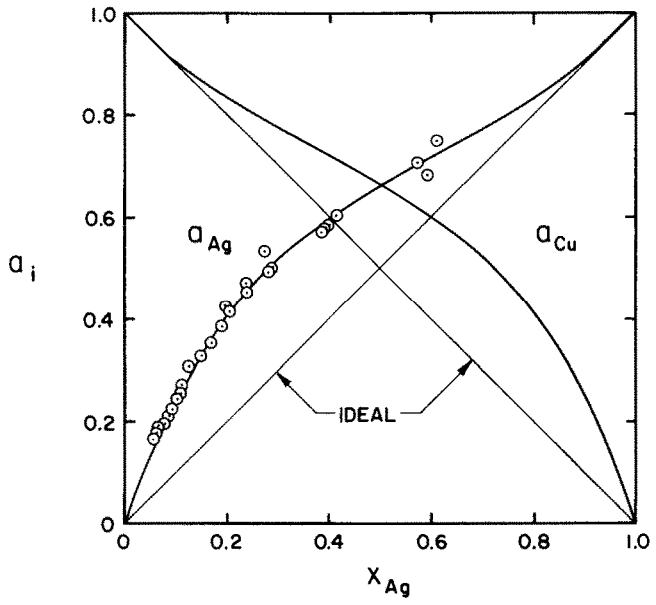

Fig. 4—Activities for the liquid Ag-Cu system at 1400 K.

Use the substitutional solution model for both phases. The molar Gibbs energy expression is given below

$$G_m = x_{Ag}{}^\circ G_{Ag} + x_{Cu}{}^\circ G_{Cu} + RT(x_{Ag} ln x_{Ag} + x_{Cu} ln x_{Cu}) + {}^E G_m$$

where

$^{E}G_m = x_{Ag}x_{Cu}I$

and the interaction parameter is given by a Redlich-Kister polynomial restricted to two terms

$I = {}^{0}L + (x_{Ag} - x_{Cu})\ {}^{1}L.$

In the database you are supposed to enter $^{\circ}G_{Ag}$, $^{\circ}G_{Cu}$, ^{0}L and ^{1}L for fcc and liquid.

1. Use fcc as the reference phase i.e. set $^{\circ}G_{Ag} = {}^{\circ}G_{Cu} = 0$ for fcc.
2. The information on the pure elements gives you the $^{\circ}G$-parameters for the liquid phase.
3. The activity data gives you the interaction parameters for the liquid. Remember that $^{E}G_i = RTln\gamma_i = RTln(a_i/x_i)$ and that you can obtain $^{E}G_i$ from $^{E}G_m$.
4. Use the information about the top of the miscibility gap (T and x) to obtain the interaction parameters for the fcc phase. Use the criteria of the $^{O}G_m$-derivatives for the top of the miscibility gap.
5. Plot the diagram – how does the eutectic temperature and the compositions of the three phases compare to the experimental information given above? What could be done to improve the fit?
6. Calculate the spinodal for the fcc phase using Matlab, Thermo-Calc or any other software (or by hand).

Show clearly how you solve the problem i.e. what equations and relations you use.

The embryo to the database and instructions how to perform a phase diagram calculation will be emailed out to those who plan to do the home assignment.

Questions about the home assignment May 24, 10-11.