Calculation of Phase Diagrams – modern software

Przemysław Fima

1. Introduction

A phase diagram is a graphic presentation of the state of a materials system in thermodynamic equilibrium as a function of temperature, pressure and composition. In other words phase diagrams are maps of the phases in equilibrium associated with various combinations of temperature, pressure, and composition. Phase diagrams are of great importance in materials science, as well as metallurgy and chemistry. The information contained in phase diagrams can be useful to understand/analyze solidification processes (which affect microstructure and, further, properties of materials) and reactions, such as those occurring during soldering or formation of surface layers. Until the 1960s phase diagrams were constructed only experimentally based on the data from such techniques as: thermal analysis (simple thermal analysis, differential thermal analysis, and more recently differential scanning calorimetry), metallography combined with optical microscopy and more recently scanning electron microscopy, electron probe microanalysis, x-ray diffraction, and diffusion couples [1].

Assuming there is 80 metals in periodic table of elements they can form over 3500 binary systems – a significant portion of which is known in a greater or smaller detail [2]. The number of possible ternary and higher order systems is much larger, but for higher-order systems only a small percentage of systems are known. The experimental work is still crucial in providing data for phase diagram construction. It is easy to imagine that the complexity of experimental work (as well as cost and time required) significantly increases with number of elements in the system. On the other hand, in modern applications often multicomponent systems are used, and they need to be well understood. The collections of assessed phase diagrams can be found in books such as "Binary alloy phase diagrams" edited by T.B. Massalski [3]. Phase diagrams are also published in journals devoted to this subject: "Journal of Phase Equilibria and Diffusion" and "CALPHAD - Computer Coupling of Phase Diagrams and Thermochemistry".

With the first computers available the idea of computer aided Calculation of Phase Diagrams (CALPHAD) could be realized. This was important from the point of view of binary systems but is even more important in the case of higher order systems. Starting in the 1970s, over the years a number of groups worldwide developed their programs, some of which later turned into complex software packages. Two of the software packages that are currently in use at the Institute of Metallurgy and Materials Science are: Thermo-calc® S by Thermo-calc Software [4] and Pandat® 2012 by CompuTherm LLC [5,6]. On following pages some examples of calculations performed in Pandat are presented.

2. The basics

In order to perform phase diagram calculations input data are needed. The process of preparing such data is briefly described below. The base of the CALPHAD is that a phase diagram is graphic representation of thermodynamic equilibrium in a system, and the system is in equilibrium when its free energy is at minimum value. This is equivalent to the equality of potentials i.e. chemical

potentials of components of phases in equilibrium are equal [1]. Since free energy of a system is arithmetic, weighted sum of free energy of its phases, one has to determine energy of each phase, and find minimum of the sum of energies. As a result mathematic formulae are obtained, expressing this minimum as a function of composition, temperature and pressure (in the case of condensed phases pressure is typically set to 1 bar). Using such formulae it is possible to determine composition of neighboring phases at specific temperature (coordinates of phase boundaries). This idea is quite complicated in practice and is splitted into a number of stages. The whole process starts with finding the phases existing in the system and collecting the available experimental data. These experimental data are next critically assessed (it has to be checked if they are consistent internally and externally) - this may lead to some data being rejected. This is followed by mathematical modeling with different models and optimization of the parameters (a set of parameters per each phase), which are collected in thermodynamic parameters database. This database of thermodynamic parameters is mathematical description of existing phases and their equilibrium. An interested reader will find more details on this subject in books [7,8]. The database is further used to calculate phase equilibria based on which phase diagram is drawn. It has to be noted that calculations performed with the same database and with the same set of parameters (selected phases, compositions, temperature, etc.) always give the same output (for example phase diagram) regardless the software used.

Several, different databases were developed over the years including databases for different groups of alloys such as aluminum alloys, nickel-based alloys, titanium-based alloys, steels, etc. These are often sold by the producers of software packages, yet such databases are typically encrypted and cannot be used in different software package than then the one they were sold for. Free of charge database files are sometimes published as attachments to the articles published in journals such as for example CALPHAD, or can be downloaded from dedicated websites like NIST Database for Solder systems [9] and NIMS Thermodynamic Database [10].

3. Examples of calculations performed in Pandat

The database file, as displayed in the window of the Pandat in Fig. 1 software starts with definition of elements and all existing phases followed by property parameters of respective phases. This and the following examples of calculations are based on the data for Cu-Sn-Zn system published by Huang et al. [11]. Parameters of calculations such as range of temperature and compositions are set in window shown in Fig.2.

Elements (3)

Name	Structure	Atomic Number	Atomic Weight	H298	S298
CU	FCC_A1	29	63.546	5004.1	33.15
SN	BCT_A5	50	118.71	6322	51.195
ZN	HCP_ZN	30	65.39	5656.8	41.631

Type Definition (2)

Type Code	Function	Phase	Property	Parameter
&	AMEND_PHASE_DESCRIPTION	BCC_A2	MAGNETIC	(-1) (0.4)
'	AMEND_PHASE_DESCRIPTION	FCC_A1	MAGNETIC	(-3) (0.28)

Phases (17)

Name	Model	Type_Def Code	Lattice Size	Constituent
BCC_A2	CEF (SLN)	&	(1)(3)	(CU,SN,ZN)(VA)
BCT_A5	CEF (SLN)		(1)	(SN,ZN)
CU10SN3	CEF (ST2)		(0.769)(0.231)	(CU)(SN)
CU3SN	CEF (SLN)		(0.75)(0.25)	(CU,SN)(CU,SN,ZN)
CU41SN11	CEF (ST2)		(0.788)(0.212)	(CU)(SN)
CU6SN5	CEF (SLN)		(0.3333)(0.3334)(0.3333)	(CU)(CU,SN,ZN)(SN,ZN)

Phase Parameters

Name	Property	x-Term	x-order	Parameter	T-limit (K)
	L0	(CU)(VA)	0	-3753.458+129.230235*T -24.112392*T*LN(T)-.00265684*T**2+1.29223E-07*T**3+52478*T**(-1)	1357.77
				-9525.026+182.548828*T-31.38*T*LN(T)+3.64167E+29*T**(-9)	3200
	L0	(SN)(VA)	0	-3558.517+116.765451*T -25.858*T*LN(T)+5.1185E-04*T**2-3.192767E-06*T**3+18440*T**(-1)	250
				-1455.135+59.443315*T-15.961*T*LN(T)-.0188702*T**2+3.121167E-06*T**3 -61960*T**(-1)	505.08
				+6924.724-1.994731*T-8.2590486*T*LN(T)-.016814429*T**2+2.623131E-06*T**3 -1081244*T**(-1)-1.2307E+25*T**(-9)	800
				-3856.959+132.99688*T-28.4512*T*LN(T)-1.2307E+25*T**(-9)	3000
	L0	(ZN)(VA)	0	-4398.827+115.959669*T -23.701314*T*LN(T)- .001712034*T**2-1.264963E-06*T**3	692.68
				-8183.599+169.83526*T-31.38*T*LN(T)+4.70514E+26*T**(-9)	1700
BCC_A2	L	(CU,SN)(VA)	0	-41774.195+47.877361*T	3000
	L	(CU,SN)(VA)	1	-12316.502-50.445819*T	3000
	L	(CU,SN,ZN)(VA)	0	-3.70216293E+05 +2.44585559E+02*T	3000

Fig. 1. A view of the TDB viewer window: definition of elements and phases (left) and phase parameters (right).
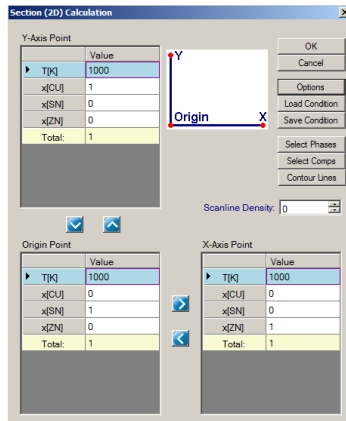
2

Fig. 2. A window, in which parameters of calculations (compositions and temperature) are set.
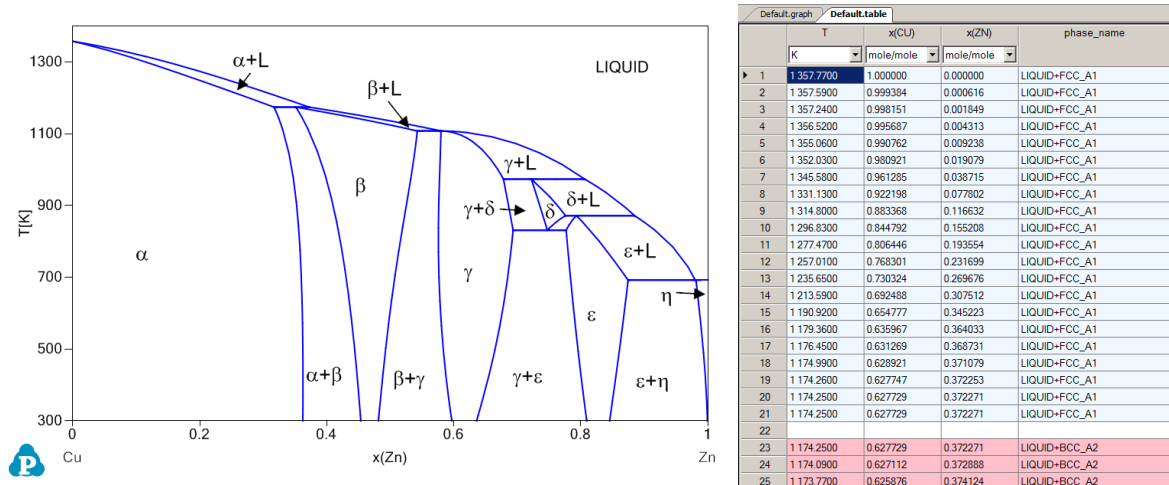

Fig. 3. The Cu-Zn phase diagram calculated based on Huang et al. data [8] (left) and the coordinates of lines drawn in the phase diagram (right).

The output of phase diagram calculation software is typically a phase diagram such as shown in Fig. 3. Pandat allows user to modify the looks of phase diagram i.e. color and thickness of lines can be changed, as well as size and style of labels. Since phase diagram is graphic presentation of phase equilibria the coordinates of calculated equilibria are saved in a file and can be displayed such as the coordinates of liquidus line in Fig. 3. The software allows extracting additional information from calculated phase equilibria such as proportion (fraction) of existing phases at specific temperature. Figure 4 shows phase fractions of phases existing in the range 600-1100 K calculated for Cu-Zn alloy containing 70 at.% of Zn. Thermodynamic property data can be calculated as well, as can be seen in Fig. 5 showing the change of enthalpy of a system vs. temperature calculated for the same alloy composition. Solidification simulation (calculation of solidification path) is another useful feature. These calculations can be performed either with the use of lever rule (equilibrium) or with Scheil model (non-equilibrium), as illustrated in Fig. 6.
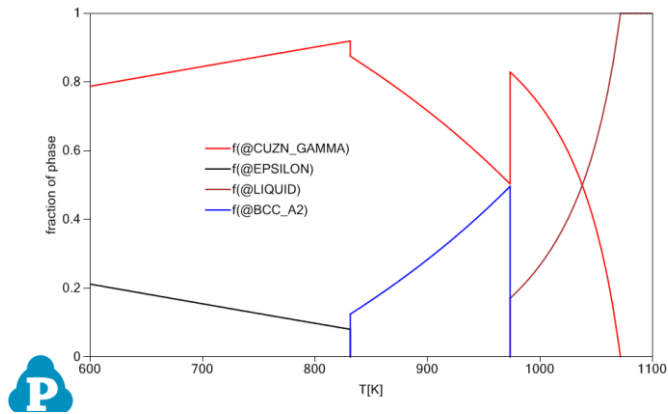
3

Fig. 4. Fraction of phases for 30Cu70Zn alloy (at.%).
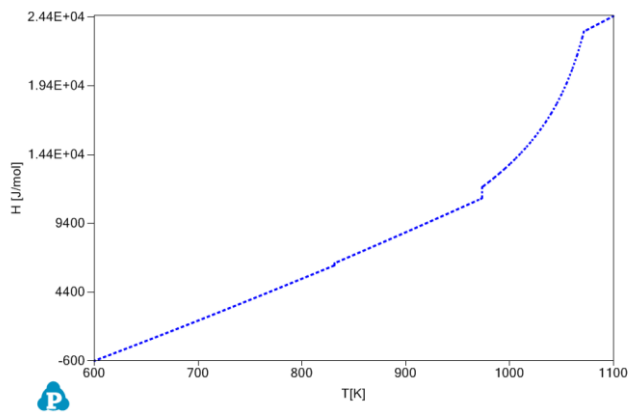

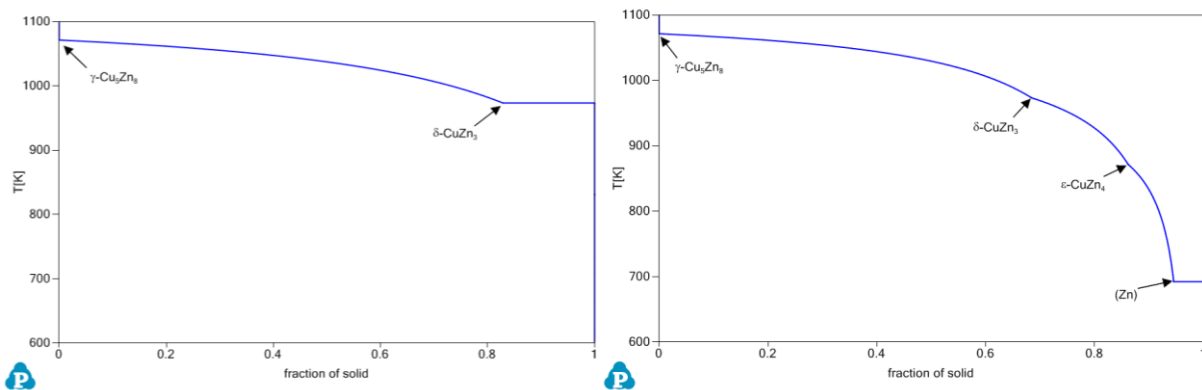Fig. 5. Total enthalpy of system vs. temperature for 30Cu70Zn alloy (at.%).

Fig. 6. Solidification simulation for 30Cu70Zn alloy (at.%) with lever rule (left) and Scheil model (right). Blue line denotes fraction of solid; arrows mark the beginning of solidification of phases.

Another option is the calculation of ternary phase diagrams. In this case vertical (temperature vs. composition) sections can be calculated as well as horizontal (isothermal) sections presented in Gibbs triangle. Figure 7 shows tin-rich corner of isothermal section (523 K) of Cu-Sn-Zn system. In the case of higher order systems equlibria can be drawn as pseudo-binary vertical sections with remaining components set constant. In addition to calculating sections liquidus surface can be easily calculated as shown in Fig. 8, together with a part of output table with coordinates of the isotherms (green lines in Fig. 8).
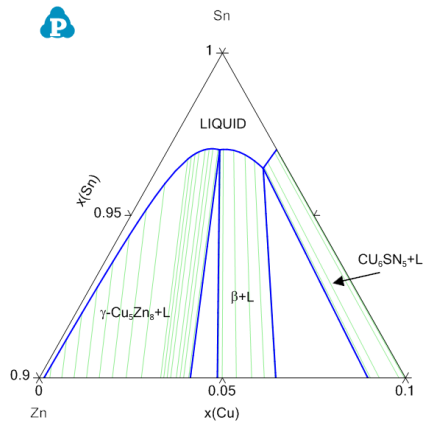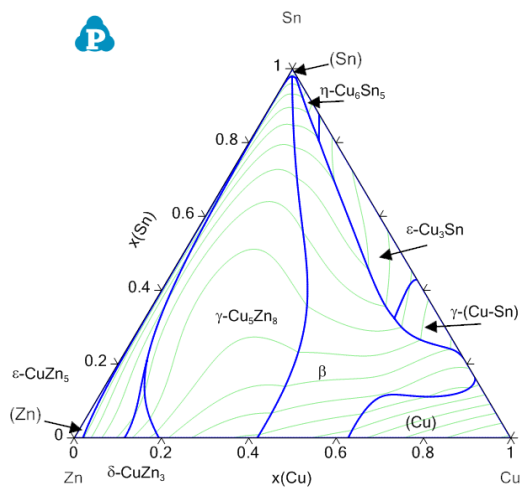
Fig. 7. Isothermal (523 K) section of the Sn-rich corner of Cu-Sn-Zn system.

	T	phase_name	x(CU)	x(SN)	x(ZN)
	K		mole/mole	mole/mole	mole/mole
1	1 350.0000	LIQUID+FCC_A1	0.993273	0.006727	0.000000
2	1 350.0000	LIQUID+FCC_A1	0.993199	0.006701	0.000100
3	1 350.0000	LIQUID+FCC_A1	0.993124	0.006676	0.000200
4	1 350.0000	LIQUID+FCC_A1	0.992974	0.006626	0.000400
5	1 350.0000	LIQUID+FCC_A1	0.992675	0.006525	0.000800
6	1 350.0000	LIQUID+FCC_A1	0.992077	0.006323	0.001600
7	1 350.0000	LIQUID+FCC_A1	0.990884	0.005916	0.003200
8	1 350.0000	LIQUID+FCC_A1	0.988506	0.005094	0.006400
9	1 350.0000	LIQUID+FCC_A1	0.983780	0.003420	0.012800
10	1 350.0000	LIQUID+FCC_A1	0.979093	0.001707	0.019200
11	1 350.0000	LIQUID+FCC_A1	0.976764	0.000836	0.022400
12	1 350.0000	LIQUID+FCC_A1	0.975602	0.000398	0.024000
13	1 350.0000	LIQUID+FCC_A1	0.975023	0.000177	0.024800
14	1 350.0000	LIQUID+FCC_A1	0.974557	0.000000	0.025443
15					
16	1 300.0000	LIQUID+FCC_A1	0.959987	0.040013	0.000000
17	1 300.0000	LIQUID+FCC_A1	0.959909	0.039991	0.000100
18	1 300.0000	LIQUID+FCC_A1	0.959830	0.039970	0.000200
19	1 300.0000	LIQUID+FCC_A1	0.959672	0.039928	0.000400
20	1 300.0000	LIQUID+FCC_A1	0.959357	0.039843	0.000800
21	1 300.0000	LIQUID+FCC_A1	0.958726	0.039674	0.001600
22	1 300.0000	LIQUID+FCC_A1	0.957468	0.039332	0.003200
23	1 300.0000	LIQUID+FCC_A1	0.954961	0.038639	0.006400
24	1 300.0000	LIQUID+FCC_A1	0.949979	0.037221	0.012800
25	1 300.0000	LIQUID+FCC_A1	0.945039	0.035761	0.019200

Fig. 8. Liquidus projection for Cu-Sn-Zn system (left) and coordinates of calculated isotherms on the liquidus surface in Cu-Sn-Zn system (right).

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