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Simple computer program used for the calculation of stable and metastable phase boundary lines for the pseudobinary edges in the BaO–CuO_x–$YO_{1.5}$ system[1]

I. Horsák[a], J. Šesták[b,*] and B. Štěpánek[b]

[a] *TORI Soft, Ježkova 3, 130 00 Prague 3 (Czech Republic)*
[b] *Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 162 00 Prague 6 (Czech Republic)*

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Abstract

A simple computer program is tested to calculate pseudobinary edges of BaO–CuO_x–$YO_{1.5}$ and the results are compared with other experimentally measured and theoretically calculated data with good success. Some discrepancies were noticed between tabulated and actually used thermochemical data for the compounds in question.

INTRODUCTION

It has been shown [1–6] that phase diagrams for the BaO–CuO_x–$YO_{1.5}$ system can be very helpful in optimizing the conditions for the preparation of single phase high T_c superconducting (HTSC) material. In order to understand the equilibria and associated metastable formation of the various phases it was found convenient to search for the restrictions of all the boundary systems. Such a user need for these diagrams is usually fourfold. (i) Growth of single crystals upon slow cooling of nonstoichiometric melts usually rich in CuO_x [4, 6]. (ii) Processing of bulk ceramics via conventional sintering [7]. (iii) Preparation of tailorable high T_c melt-textured ceramics and glass-ceramics [8]. (iv) CVD technique of thin film formation [9].

Although high T_c phases are all very complex, containing at least three basic cations, the knowledge of quasibinary phase diagrams is the first step needed to understand the equilibria. Most of them are available as the binary phase diagrams representing the result of interpretation of various experimental measurements by means of XRD, DTA, SEM etc. [1–8]. The only calculations so far accomplished are those of Lee and Lee [10, 11]

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* Corresponding author.

[1] Dedicated to Hans Georg Wiedemann.

TABLE 1

Thermochemical data for the end oxides

	Edge oxide					
	BaO	CuO_x		$YO_{1.5}$		
Crystal. mod.	—	Cu_2O	CuO	α	β	$\alpha \rightarrow \beta$
T_{melt}/K	2286	1501	1400 [a]	2676	2626 [a]	2500
ΔH_{melt}/J mol^{-1}	58568	52353	99720 [a]	58170	83100 [a]	—

[a] Hypothetical.

where the Gibbs (free) energy found for all binary compounds and interaction parameters of binary liquid phases were evaluated from phase diagram data by the tie-line-variation method [12]. Not having enough data available made them use an indirect method [10] to predict similar behaviour for known and unknown phases such as Ca_2CuO_3 for the required Ba_2CuO_3. For refined calculation of Gibbs energy they used [11] a two-sublattice "Hilbert" model of ionic solution, consisting of both the cations (Y^{3+}, Ba^{2+}, Cu^{+}, Cu^{2+}) and the anions (O^{2-}) plus vacancies (Va^{y-}) mutually maintaining neutrality. This program, however, is rather complicated and is thus difficult to use for easy understanding of phase relations. Therefore the aim of our contribution is to present a simple educational algorithm showing its applicability for the solution of such an up-to-date system and compare it with previous results.

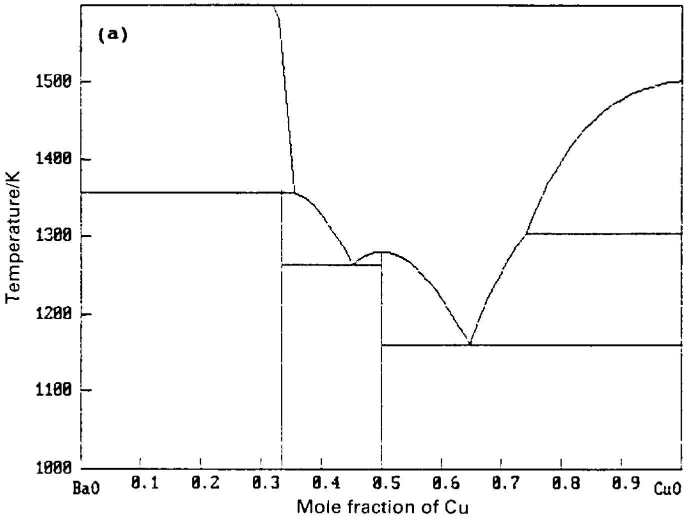
APPLICATION OF CALCULATION PROCEDURE

The simple computer program VYFADI [13] is based on the standard solution of the set of equations describing the liquidus and solidus curves

TABLE 2

Input data used for the calculation of pseudobinary phase diagrams

	System			
	$BaO–YO_{1.5}$	$BaO–CuO_x$		$YO_{1.5}–CuO_x$
Temperature range/°C	1900–2800	1000–1600		1200–1800
Calculation step	150	100		100
Oxide ratio	3:4	2:1	1:1	1:1
Equilib. constant K_T	1	6.5	4.5	1
T_{melt}/°C	2160	1280	1360	1450
ΔH_{melt}/J mol^{-1}	52250	5000	8500	28350
Interact. parameter L_0	1	−40000		−3000



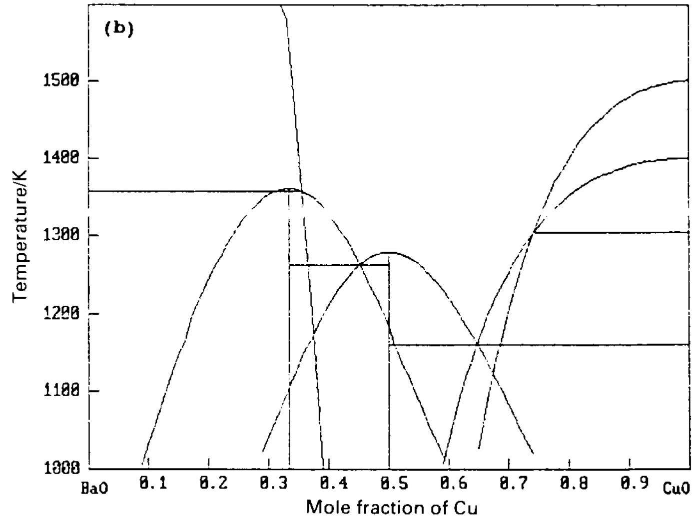


Fig. 1. Calculated phase diagrams of the BaO–CuO_x system: (a) equilibrium phase diagram; (b) complete phase diagram with liquidus curves over the whole range.

assuming non-ideality of the mixture in a most simple way, analogous to that for a regular solution [14]. The fundamental equation relating the activity a to temperature T reads in differential form as

$$\delta \ln(a) = (\Delta H_{\text{melt}}/RT^2)\delta T \tag{1}$$

and must be related to the measurable concentration x by means of the

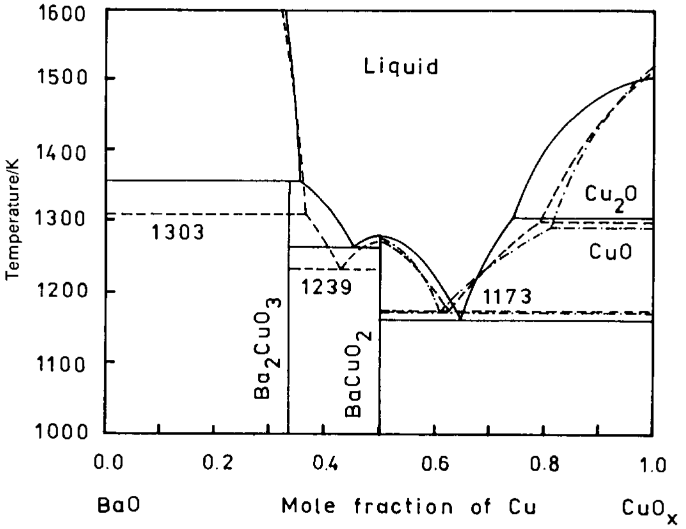


Fig. 2. Comparison of various phase diagrams for the BaO–CuO_x system: –·–·–, experimental [17]; – – –, calculated by Lee and Lee [10]; ——, calculated in this paper.

interaction parameter L_0 using

$$\ln a = \ln x + L_0(1-x)^2/RT \qquad (2)$$

where R is the standard gas constant.

Various interaction parameters for both the liquidus and solidus can be considered and their effect as well as the effect of enthalpy of melting ΔH_{melt} of edge components on the resulting shape of the phase diagram can be systematically investigated [15]. Therefore the algorithm was found to be a convenient tool for teaching graduate courses on phase diagrams as students can actively co-operate with the computer program to create various types of diagrams merely by changing input thermochemical data and interaction parameters.

For the entire calculation twofold data are required, i.e. thermochemical data of edge (pure) components and thermochemical data of possibly occurring compounds, including interaction parameters and equilibrium constants K based on the equation $\Delta G = RT \ln K$.

The program gradually calculates all the liquidus curves in question including their extrapolation to metastable regions. In the case of compounds, the program first calculates the equilibrium composition on the basis of equilibrium constants (regarded as thermodynamically "non-true") using the standard solution of a set of nonlinear equations. The liquidus temperature is solved by means of the standard LeChatelier–Schreder equation on the basis of the heat capacity data (C_p) either directly ($C_p = 0$) or by interactions ($C_p \neq 0$).

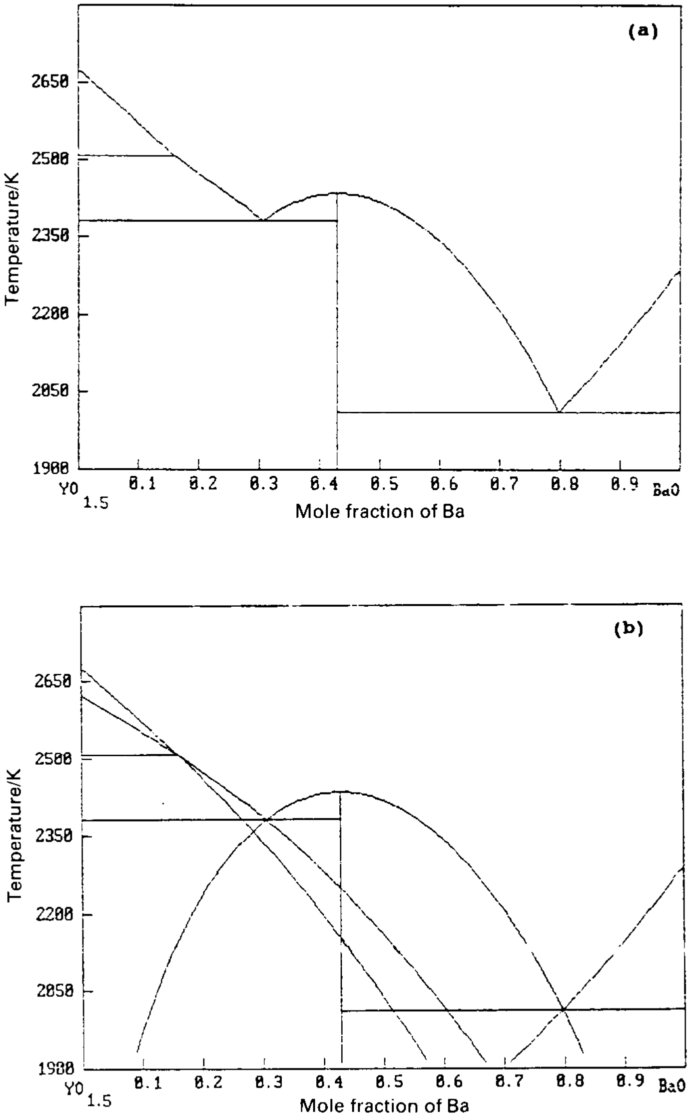


Fig. 3. Calculated phase diagram of the $YO_{1.5}$–BaO system: (a) equilibrium phase diagram; (b) complete phase diagram with liquidus curves over the whole range.

DATA USED TO CALCULATE PSEUDOBINARY EDGES OF BaO–CuO_x–$YO_{1.5}$

The data of oxide edges compiled from the literature [14] are listed in Table 1. The published value of $T_{melt} = 2286$ K for BaO proved to be too high and it was necessary to reduce it to the more suitable 2190 K.

To calculate pseudobinary edges the data for compounds were added. Again the tabulated data [14] and also the actually calculated data

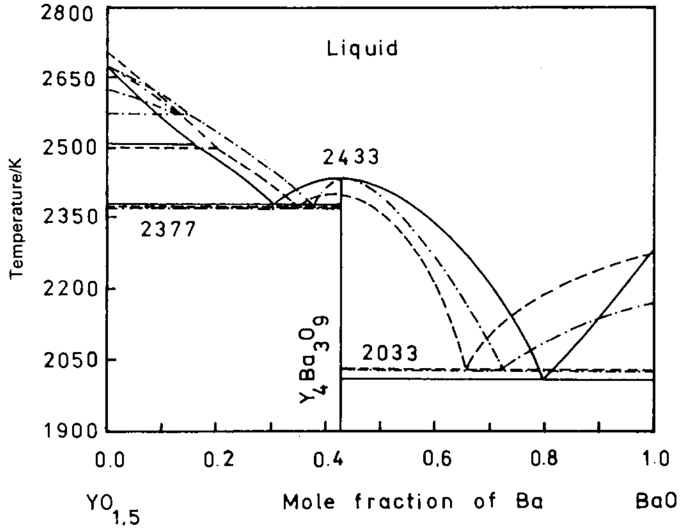


Fig. 4. Comparison of various phase diagrams for the $YO_{1.5}$–BaO system: –·–·–, experimental [17]; – – –, calculated by Lee and Lee [10]; ——, calculated in this paper.

published in ref. 18 on the basis of thermodynamic simulation were used as starting values. The data actually fitted are listed in Table 2.

The greatest difference between the predicted [16] and actually fitted data was found for $Ba_3Y_4O_9$ where the theoretically estimated value $T_{melt} = 1535$ K [18] was too low to ever get the liquidus curve into the graph and contradicted the experimentally measured value of $T_{melt} = 2433$ K. The tabulated values of ΔH_{melt} for Ba_2CuO_3 and $BaCuO_2$ yielded very shallow maxima so that it was necessary to reduce their values as much as by 50%. Similarly for the interaction parameters, it was necessary to set L_0 as high as 40 000 to get the rise of liquidus curves into the graph. It was necessary to reduce the T_{melt} for $Y_2Cu_2O_5$ to 1450 K and set the interaction parameter to $L_0 = 3000$.

RESULTS

The program has two possible outputs, printing equilibrium (upper) and full (lower) phase diagrams; the latter show liquidus and solidus curves in the whole temperature concentration region, i.e. an extension of phase lines into metastable regions.

BaO–CuO$_x$

A computer printout of a pseudobinary phase diagram is shown in Fig. 1, which illustrates both the equilibrium boundary (Fig. 1(a)) and the position

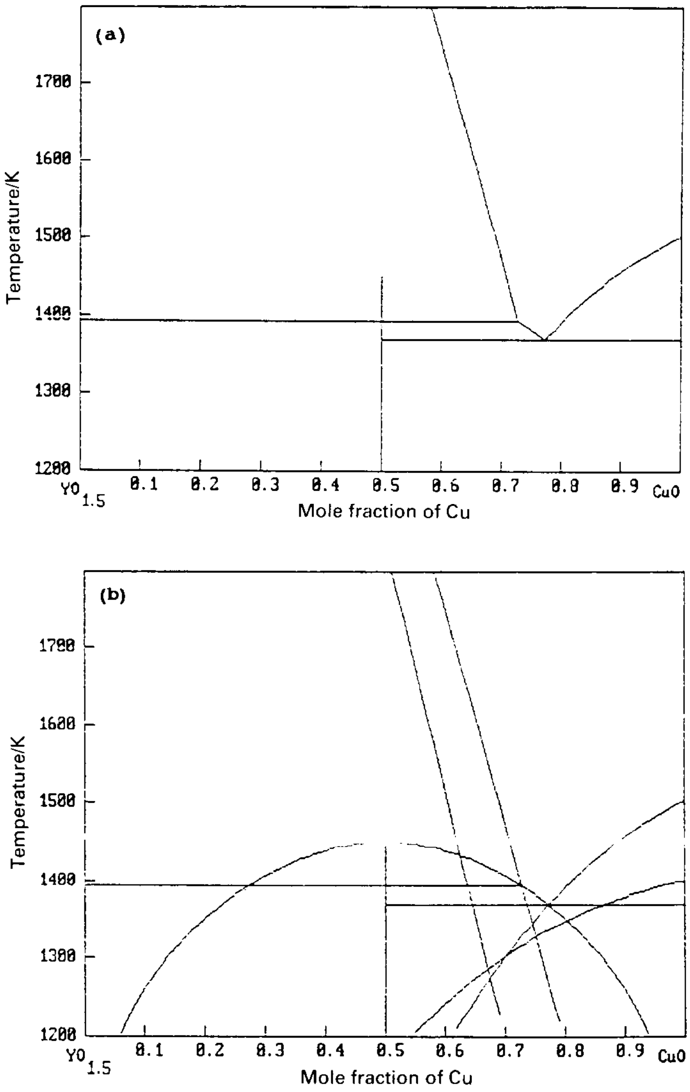


Fig. 5. Calculated phase diagram of the $YO_{1.5}$–CuO_x system: (a) equilibrium phase diagram; (b) complete phase diagram with liquidus curves over the whole range.

of boundary lines extrapolated to metastable regions (Fig. 1(b)). In Fig. 2 we compare our best version with comparable results published elsewhere [10, 17].

$YO_{1.5}$–BaO

A computer printout of a pseudobinary phase diagram is shown in Fig. 3 and compared with other results in Fig. 4.

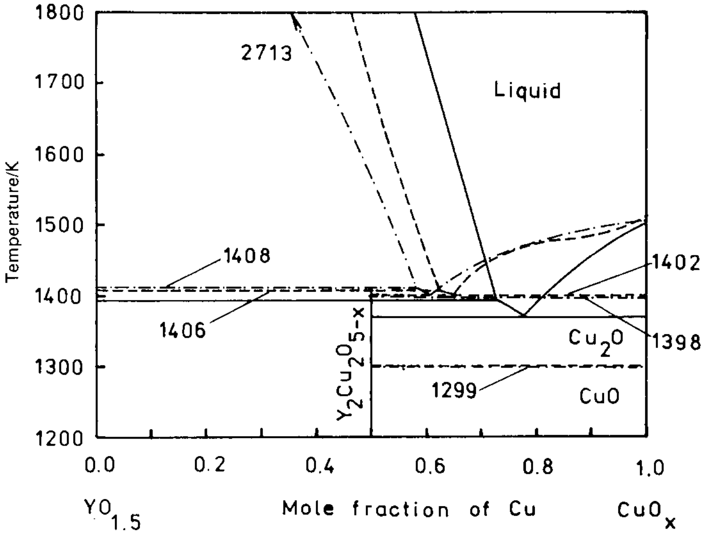


Fig. 6. Comparison of various phase diagrams for the $YO_{1.5}$–CuO_x system: –·–·–, experimental [17]; – – –, calculated by Lee and Lee [10]; —— calculated in this paper.

$YO_{1.5}$–CuO_x

A computer printout of a pseudobinary phase diagram is shown in Fig. 5 and compared with other results in Fig. 6.

DISCUSSION

The aim of calculating pseudobinary edges was not to establish the boundary lines precisely, but rather to illustrate the capability of the computer program. The algorithm [13] proved to be a useful method of picturing phase boundaries in the binary phase diagrams by gradual fitting of the known thermochemical data (T_{melt}, ΔH_{melt}) with the formally proposed interaction parameters. The example of BaO–CuO_x–$YO_{1.5}$ subsystems exhibited some discrepancies in the tabulated thermochemical data which lay outside of the fitting region and which may indicate a certain degree of error. For the system BaO–CuO_x such effects are illustrated by the change of position of the equilibrium phase boundary (Fig. 7(a)) and metastable extension lines (Fig. 7(b)) when the enthalpy of melting is reduced by 50%.

A similar example shows the shift of phase boundary lines as a result of combined change of both the enthalpy and temperature of melting in the subsystem $YO_{1.5}$–CuO_x (see Fig. 8). Other changes follow from a gradual increase of equilibrium constant as shown in Fig. 9.

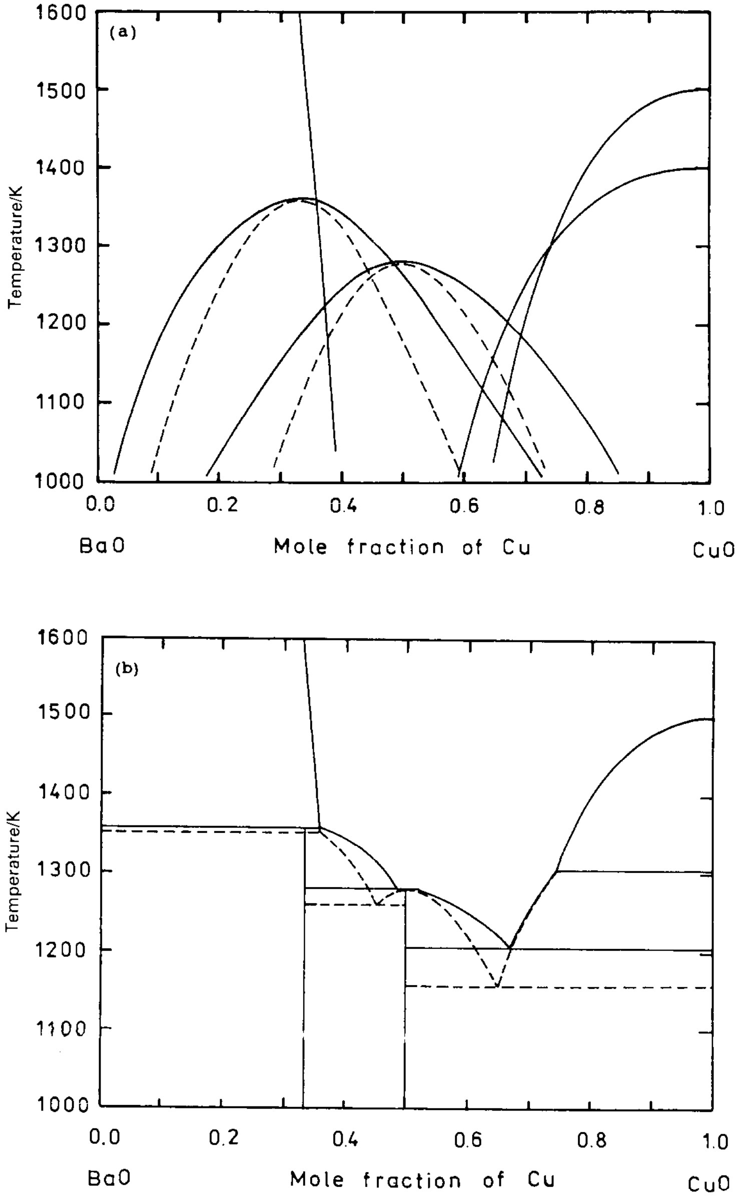


Fig. 7. Influence of ΔH_f values on equilibrium (a) and completely calculated phase diagram (b): ——, literal values [18]; – – –, literal values reduced by 50%.

In contrast the fitted data on interaction parameters L_0 for our simple regular model, where the excess Gibbs energy reads as $\Delta G^{ex} = L_0 X_A X_B$, were in fair agreement with those employed in a more complicated program by Lee and Lee [10] whose temperature dependent subregular model, where $\Delta G^{ex} = L_0 X_A X_B + L_1 X_A X_B (X_A - X_B)$ showed comparable behaviour. The $YO_{1.5}$–BaO system has a rather small deviation from ideality

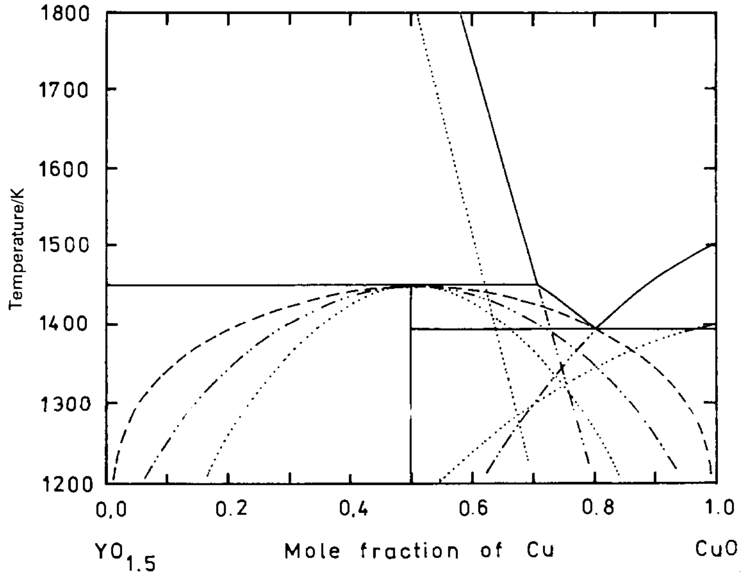


Fig. 8. Influence of ΔH_f value of compound at $T_f = 1450$ K on calculated phase diagram: – – –, 50%; –··–··–, 100%; · · · ·, 200%; ——, 100% and $T_f = 1500$ K.

($\gg L_0$) while for BaO–CuO_x the deviation from ideality is considerably larger ($\ll L_0$). It follows that even the simpler approach presented above gave phase diagrams fairly comparable with experimentally measured and theoretically calculated data.

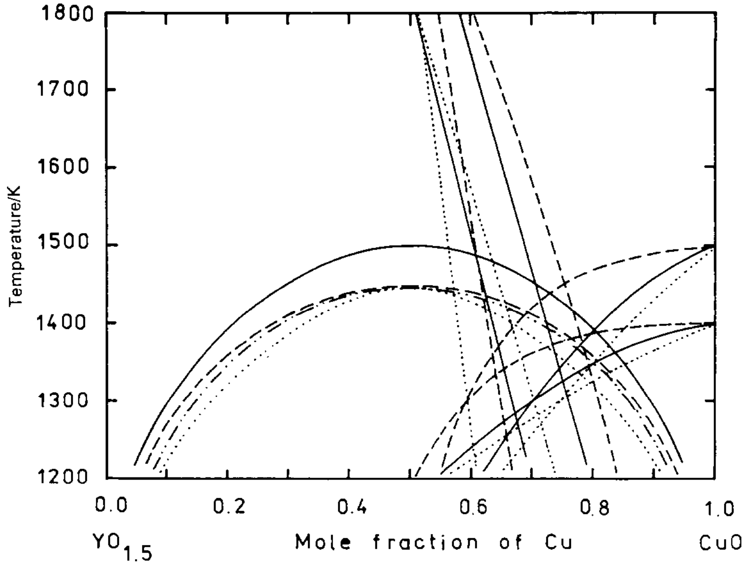


Fig. 9. Influence of equilibrium constant of compound on calculated phase diagram (at $T_f = 1450$ K): – – –, $k = 0.1$; –··–··–, $k = 1$; · · · ·, $k = 10$; ——, $k = 1$ and $T_f = 1500$ K.

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