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Thermodynamic calculation of the Ce-Te binary system

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Plan

1. Introduction
2. General information on BP
3. Thermodynamic models
4. The CALPHAD method
5. Results and discussion

1 Introduction

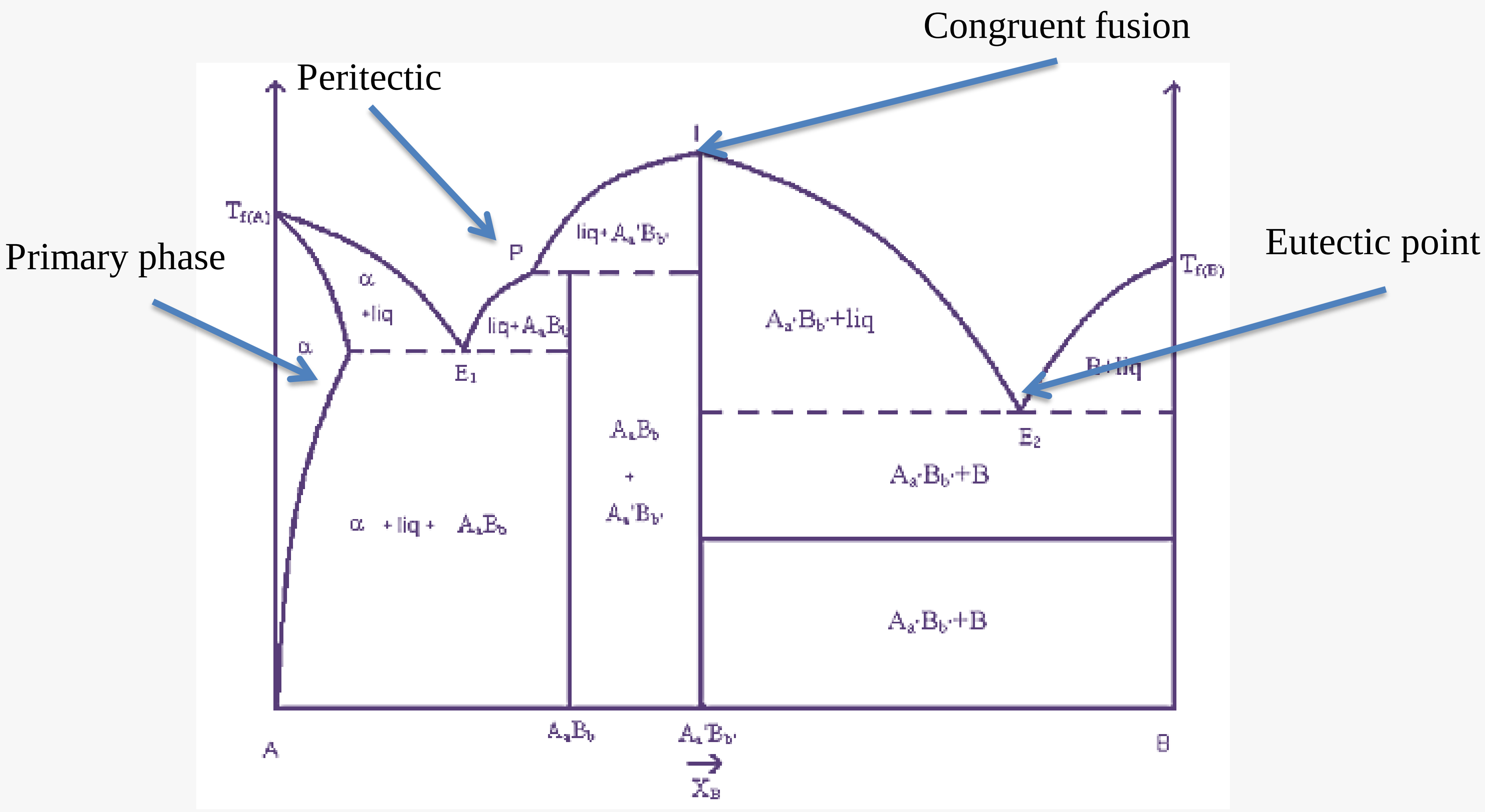
➢ Phase diagrams have always been an important source of information for the development and design of new materials.

❑ Experimental measurements of thermodynamic quantities, by different experimental methods, in a multi-phase system, are not always easy to perform and require a lot of very expensive material means.

❖ The use of numerical modeling is the approach that meets the current need to characterize complex thermodynamic systems. It was made possible by developments in computer science and by the development of thermodynamic calculation software.

General information on BP

General information on binary phase diagrams



Congruent fusion

Peritectic

Primary phase

Eutectic point

General information on BP

interests of phase diagrams

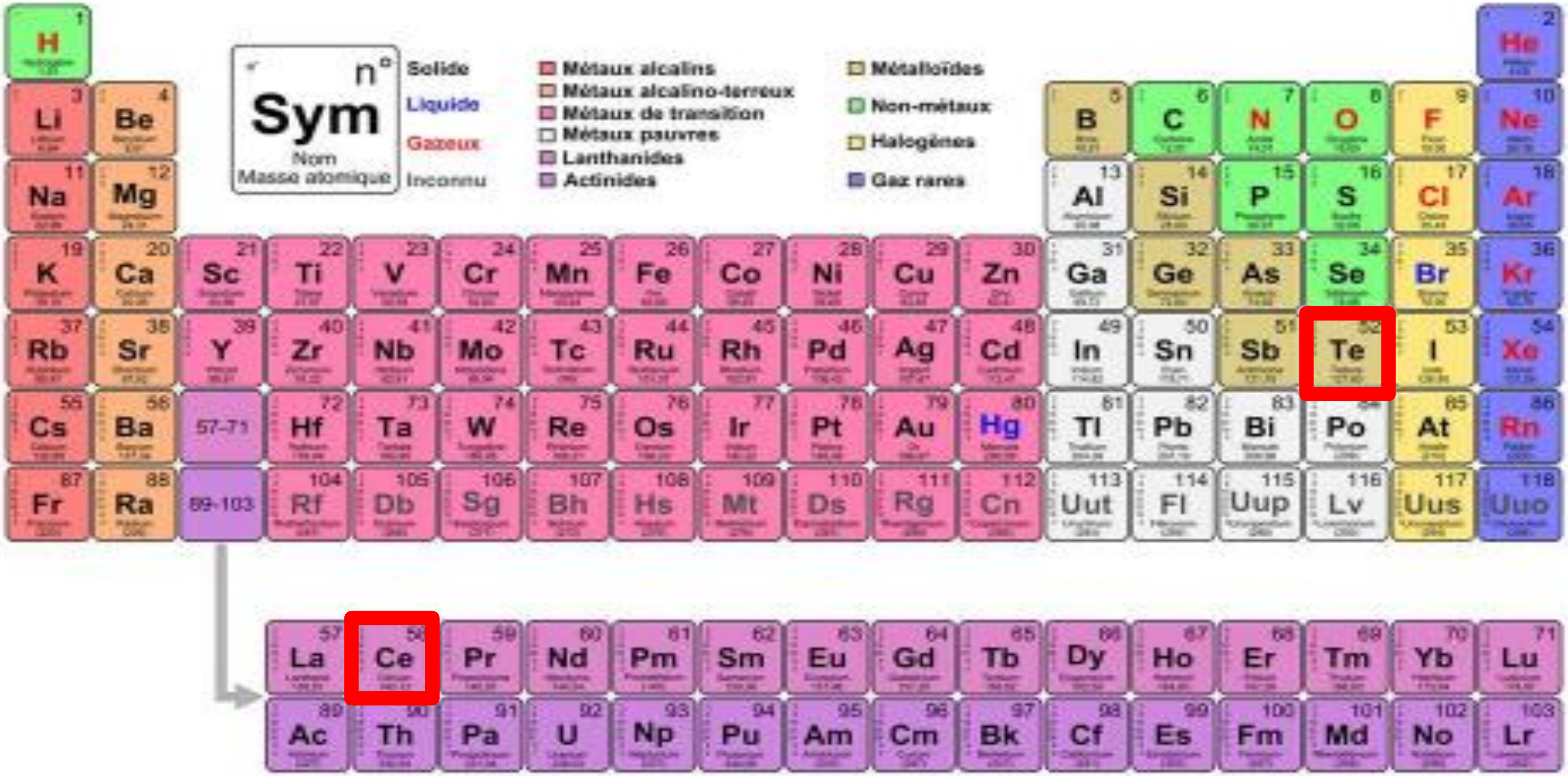
✓ Understand the relationships between chemical compounds;

○ Understand how to form intermetallic compounds from pure elements

■ Design new materials with interesting properties.

General information on BP

the choice of pure elements



n°
Sym
Nom
Masse atomique

Solide
Liquide
Gazeux
Inconnu

- Métaux alcalins
- Métaux alcalino-terreux
- Métaux de transition
- Métaux pauvres
- Lanthanides
- Actinides
- Métalloïdes
- Non-métaux
- Halogènes
- Gaz rares

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

General information on BP

Areas of application for pure elements

CE **Rare Earth**

- alloy;
- glass polishing
- additive in fuel
- cracking catalyst

Metalloids TE

- ➢ alloy;
- ➢ Optoelectronics and pyrotechnics
- ➢ Catalysts, in flame retardants, in the manufacture of glasses, optical disc players;
- ➢ Semiconductor;
- ➢ structural applications;

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Alloy Ce-Te

General information on BP

the experimental phase diagram

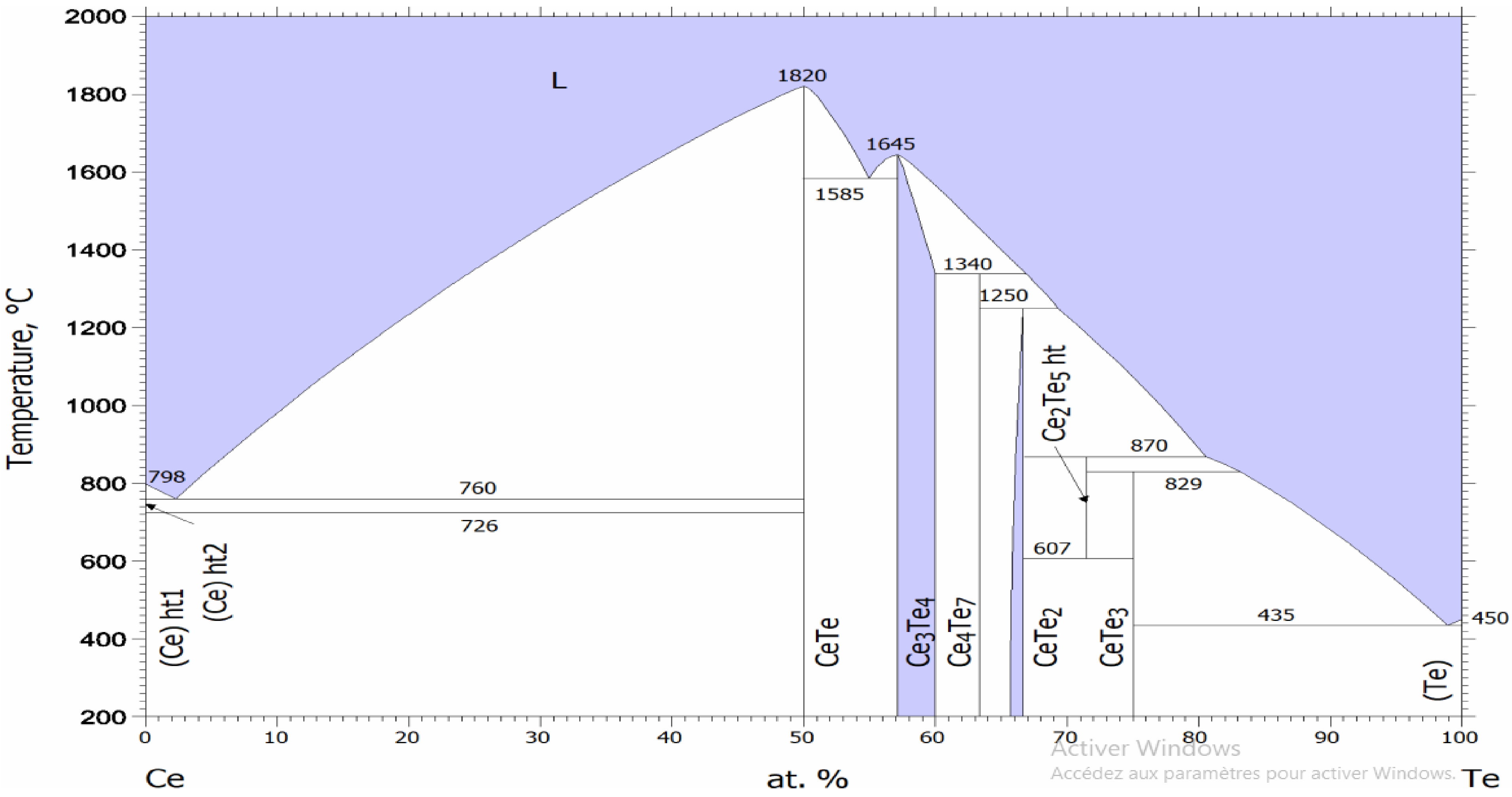


Figure 1. Experimental phase diagram of the Ce-Te system [1]

[1] H Okamoto, TB Massalski. Alloy Phase Diagrams. ASM handbook, volume 3. (1990)

Thermodynamic models

Gibbs energy calculation

1-Modeling of pure elements

$$G_i^{\varphi}(T) = {}^{o}G_i^{\varphi} - {}^{0}H_i^{SER}(298{,}15K) = a + bT + cT\ln T + dT^2 + eT^3 + fT^7 + gT^{-1} + hT^{-9}$$

2-Modeling of stoichiometric compounds

$${}^{0}G_{Ce_pTe_q} = \frac{p}{p+q}\,{}^{0}G_{Ce} + \frac{q}{p+q}\,{}^{0}G_{Te} + a + bT$$

3-Modeling of the non-stoichiometric compound

$${}^{0}G_{m}^{Ce_3Te_4} = Y_{Ga}\,{}^{0}G_{Ce:Te}^{Ce_3Te_4} + Y_{Sm}\,{}^{0}G_{Ce:Te}^{Ce_3Te_4} + RT(Y_{Ce}\ln Y_{Ce} + Y_{Te}\ln Y_{Te})$$

$$+Y_{Ce}Y_{Te}\sum_{i}^{v} L_{Ce:Ce,Te}(Y_{Ce} - Y_{Te})^{v}$$

Thermodynamic models

Gibbs energy calculation

3-Modeling of the liquid phase

Gibbs molar energy: $G_m^{\phi} = {}^{ref}G^{\phi} + {}^{id}G^{\phi} + {}^{ex}G^{\phi}$

Reference Gibbs Energy part: ${}^{ref}G^{\varphi} = \sum_{i=A,B} x_i^{\varphi}\, {}^{0}G_i^{\varphi}$

The ideal Gibbs energy part: ${}^{id}G^{\varphi} = RT \sum_{i=A,B} x_i^{\varphi} \ln(x_i^{\varphi})$

The excess Gibbs energy part: ${}^{ex}G^{\phi} = x_{Ce}^{\phi} x_{Te}^{\phi} L_{Ce,Te}^{\phi}$

redlich-kister model

$$ {}^{v}L_{Ga,Sm}^{\varphi} = {}^{v}a_{Ga,Sm}^{\varphi} + {}^{v}b_{Ga,Sm}^{\varphi} T $$

$$ {}^{ex}G^{\phi} = x_{Ce} x_{Te} \sum_{v=0} {}^{v}L_{Ce,Te}^{\phi} (x_{Ce} - x_{Te})^{v} $$

Thermodynamic models

Gibbs energy calculation

Associated species model

For a solution made up of the elements Ce and Te ⇒ $iCe + jTe \leftrightarrow Ce_iTe_j$

$$G^{liq} = {}^{ref}G + {}^{form}G + {}^{id}G + {}^{ex}G$$

$${}^{ex}G = \sum_{i=A}^{C} \sum_{j>i} y_i y_j \sum_{\nu=1}^{\nu} L_{i,j}(y_i - y_j)^{\nu}$$

$${}^{id}G = RT\sum_{i=A}^{C} y_i \ln y_i$$

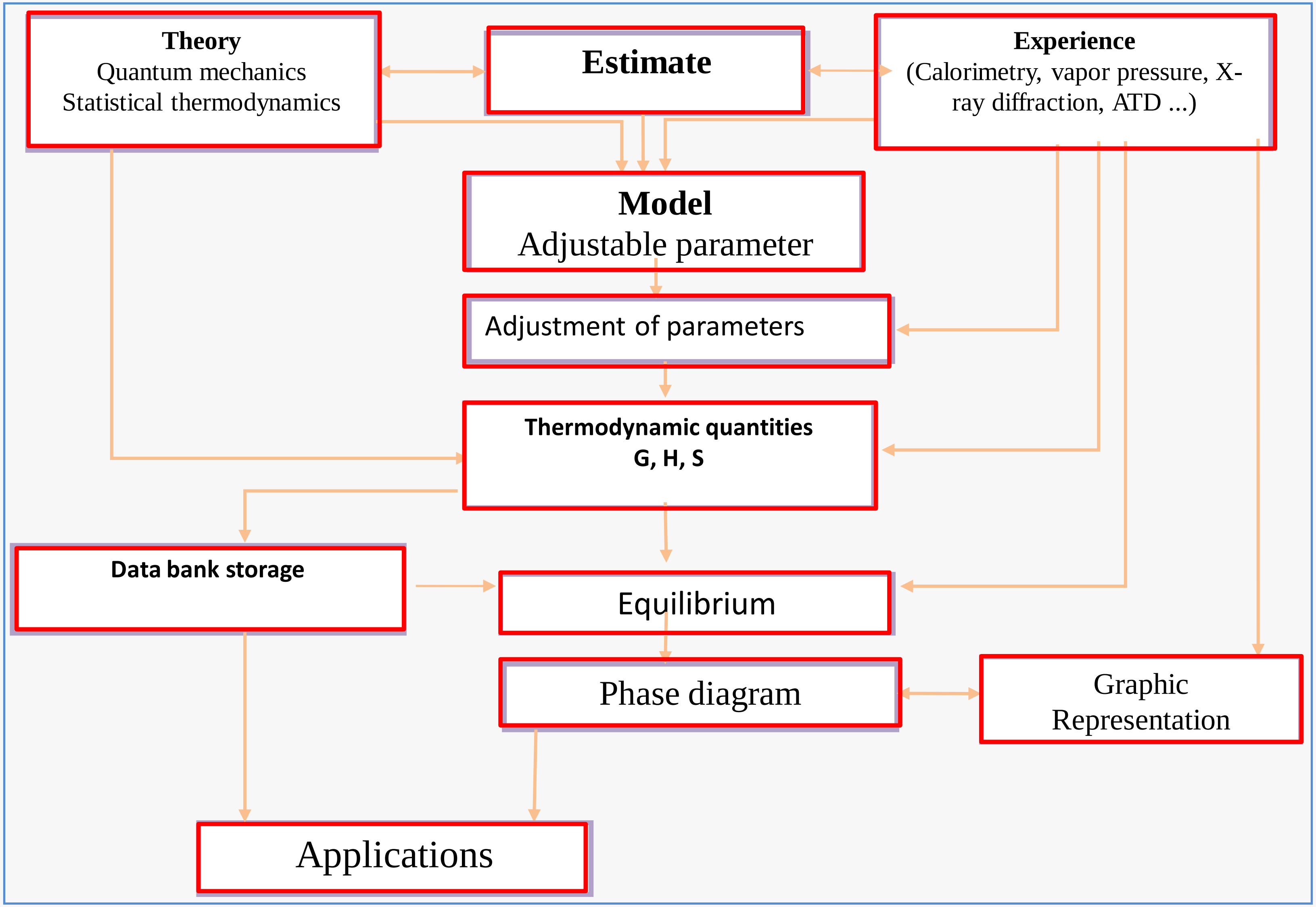
$${}^{form}G = y_C \Delta {}^0G^C$$

$${}^{ref}G = \left\{ x_{Ce}\left[{}^0G_{Ce}^{liq} - H_{Ce}^{SER}(298.15) \right] + x_{Te}\left[{}^0G_{Te}^{liq} - H_{Te}^{SER}(298.15) \right] \right\} (y_A + (i+j)y_C + y_B)$$

Objectives of modeling

- ➢ Determine the values of thermodynamic and energy quantities inaccessible to the experiment
- ❑ Test the consistency of thermodynamic quantities measured experimentally;
- ❖ Calculate the phase transformation temperatures and the domains of their existence;
- ✓ Establish an equilibria phase diagram based solely on the laws of thermochemistry;
- o Treat complex systems or n> 2

CALPHAD &Thermo-Calc software



Theory
Quantum mechanics
Statistical thermodynamics

Estimate

Experience
(Calorimetry, vapor pressure, X-ray diffraction, ATD ...)

Model
Adjustable parameter

Adjustment of parameters

Thermodynamic quantities
G, H, S

Data bank storage

Equilibrium

Phase diagram

Graphic Representation

Applications

Results and discussion

Results

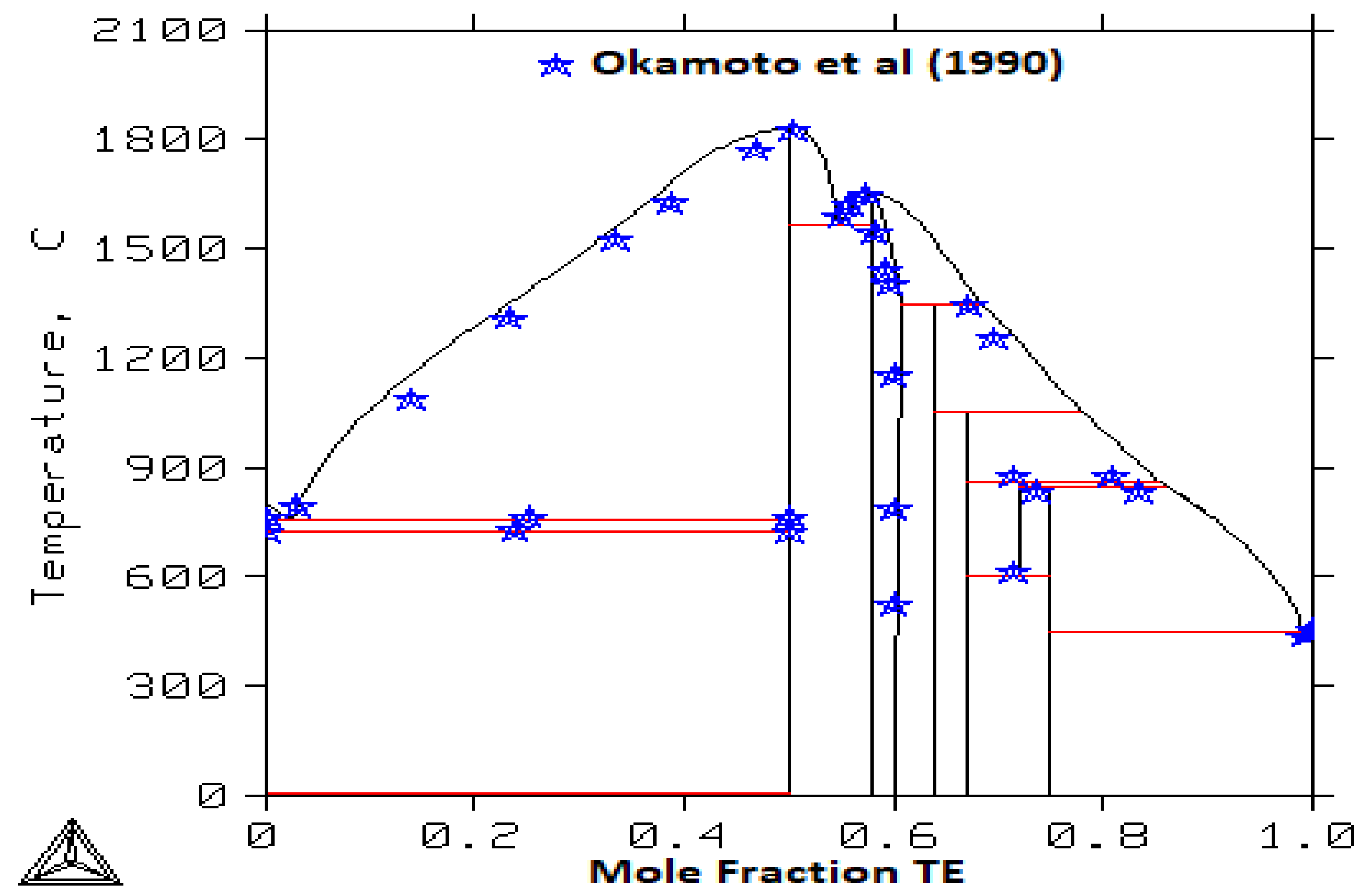


Figure 3. Phase diagram calculated in this work compared with the experimental results drawn in the literature.

Results and discussion

Results

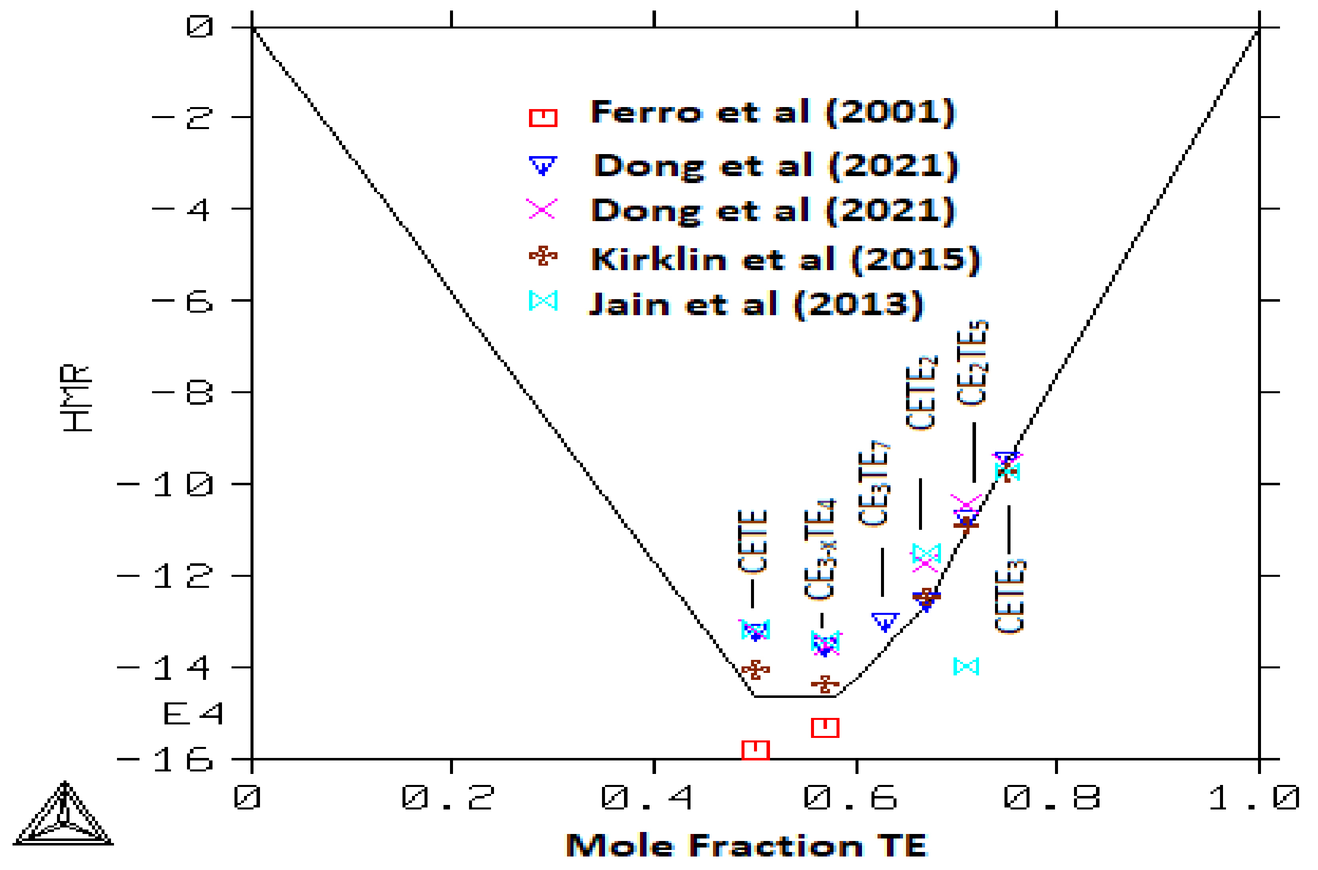


Figure 4. Comparison between the enthalpies of formation of the intermetallic compounds calculated in this work with the experimental data.

Results and discussion

Results

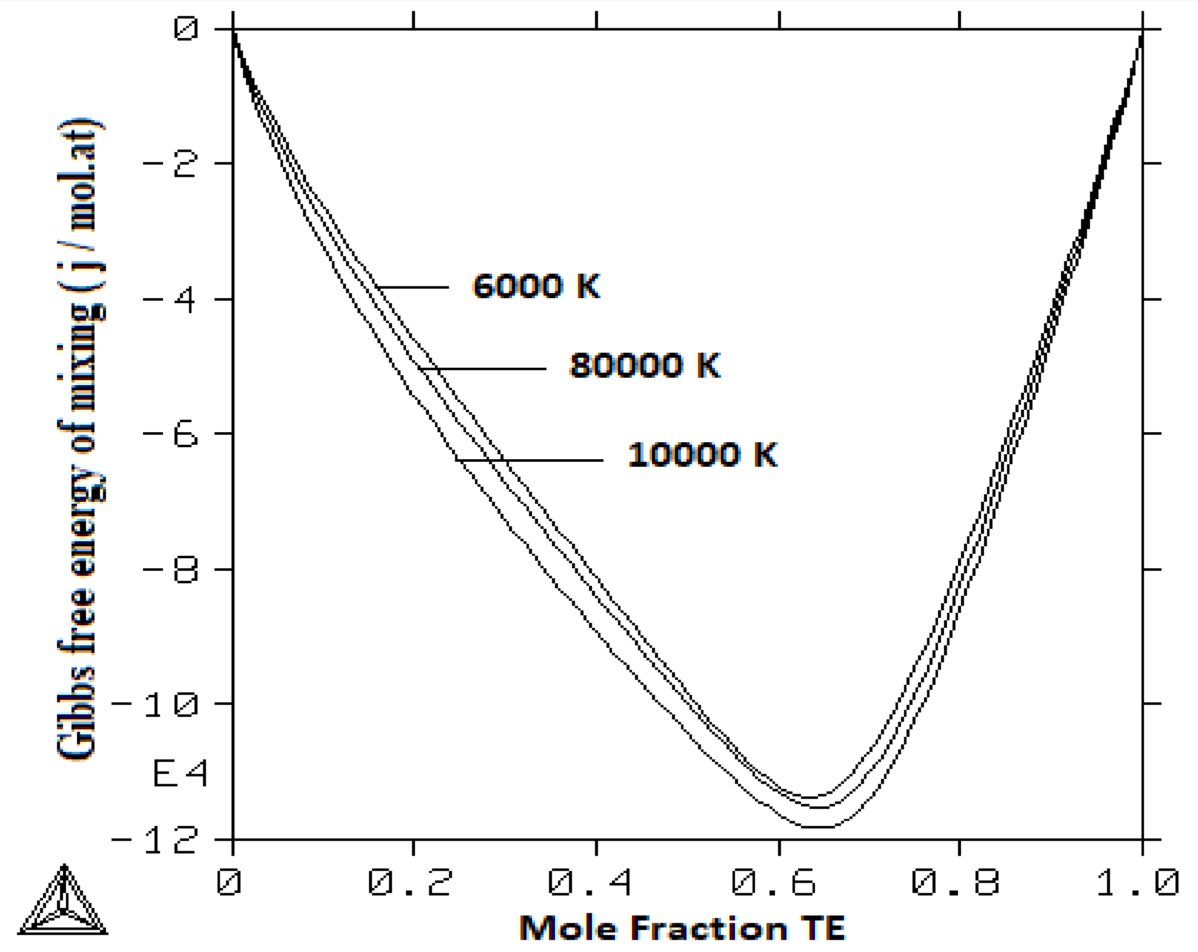


Figure 5 Calculated Gibbs free energy of mixing (in j /mol.at) of the liquid phase at different temperatures (6000 K, 8000 and 10000 K).

Results and discussion

Results

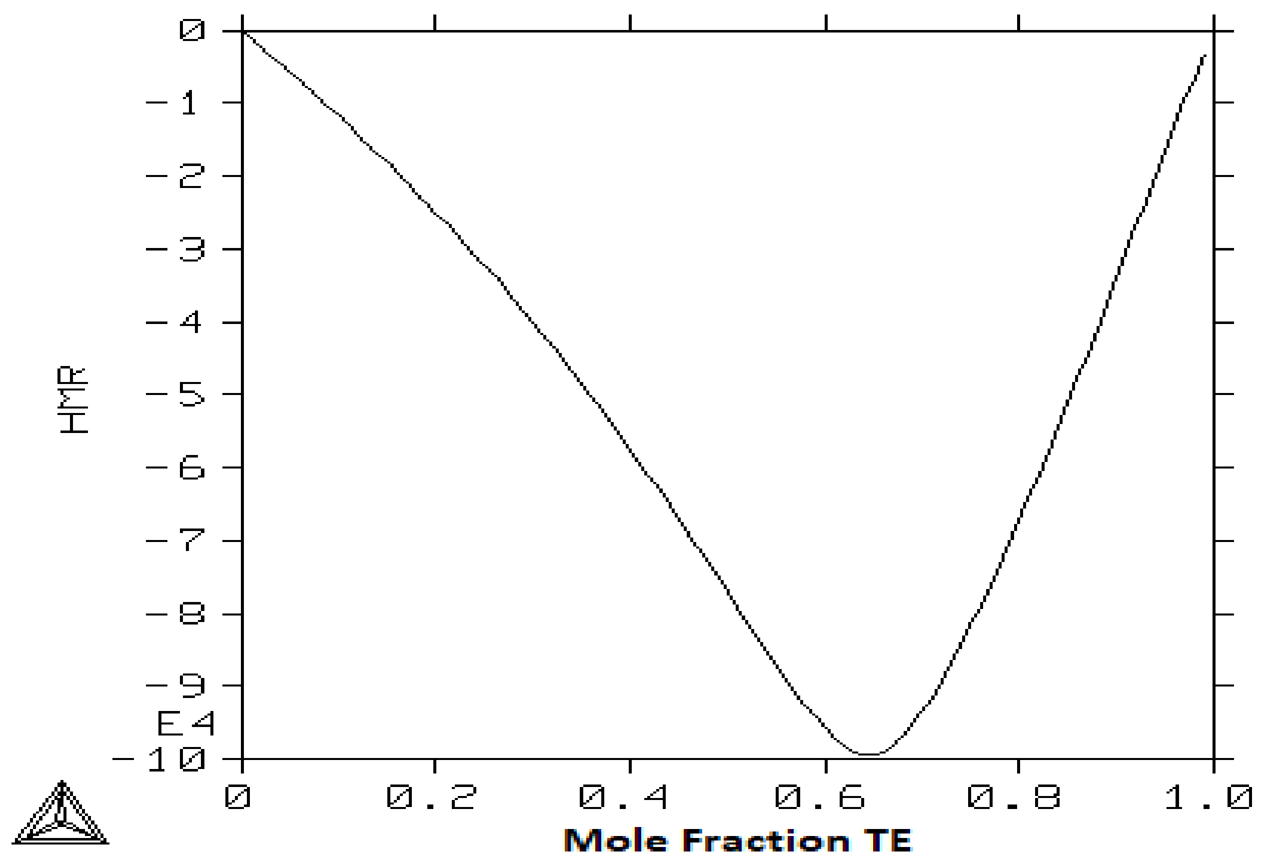


Figure 6. The enthalpy curve of integral formation of the liquid phase calculated at T = 1600 K, using the associated model.

Results and discussion

conclusion

- ❖ we have reproduced the phase diagram well, and we have calculated for the first time the enthalpies of the liquid phase and all intermediate phases

- ➢ We note a satisfactory agreement between the experimental diagram and the calculated one.

- ❑ The values of the enthalpies of formation calculated in this work are in agreement with the experimental values.

- ✓ Our calculations allow access to enthalpies, entropies and the energies of formation of all intermetallic compounds.

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Thank you for the kind attention!