ELSEVIER Thermochimica Acta 245 (1994) 21-43

Thermodynamic simulation in materials science and technology [☆]

G.K. Moiseev

Institute of Metallurgy, Ural Division Russian Academy of Sciences, 101 Amundsen Str., GSP-812, Ekaterinburg 620219, Russian Federation

Abstract

Computer simulation of the equilibrium states of multi-element heterogeneous systems is reviewed from the viewpoint of materials science and technology. A scheme is presented for carrying out the thermodynamic modeling (TM) discussing the individual steps and examples. Scientific problems delaying further developments are pointed out.

Keywords: HTS; Model; Simulation; Superconductor; Thermodynamic modelling

1. Introduction

The traditional approach used in chemical thermodynamics has usually been directed to studying the equilibrium systems of the individual reactions which are able to occur (partial thermodynamic analysis). In many cases, however, the possibilities of this approach have been exhausted. In connection with creation of theoretical methods [1-6] and the widespread application of computers, in the 1960s and 1970s it became possible to carry out complete thermodynamic analyses of systems. Various algorithms and programs were developed for this purpose [7-26].

[☆] Presented at the Czechoslovak-French-Polish Conference on Calorimetry and Experimental Thermodynamics: Applications to Contemporary Problems, Prague, Czech Republic, 4-7 September 1993.

SSDI 0040-6031(94)01814-W

As the next step the thermodynamic modeling i.e. numerical simulation and prediction of the composition and properties of heterogeneous multi-element systems [11,18,20,27-31], was developed. The necessary conditions for successful thermodynamic modeling are the availability of reliable thermodynamic properties for components of the system (elements, substances, ions) [32-36] and of the methods for optimum application of the complete thermodynamic analysis (CTA) programs (thermodynamic modeling (TM) methods) [20,37-40].

The main reasons for carrying out TM are to ascertain practical and technical requirements. Determination of the equilibrium compositions and properties of the system from the known properties of the constituents of its components, for example, would be of the greatest value for chemistry, metallurgy, and technology of inorganic and organic materials.

Two directions emerge from the solution of straightforward problems by thermodynamic modeling: (1) numerical simulation of the compositions and properties of the systems in a (usually) high-temperature process and the determination of optimal conditions for the various target products (TM(A)) [11,18,20,27-30]; (2) calculation of equilibrium diagrams of systems (TM(B)) [18,41-44].

Let us examine the direction TM(A), the main objects of which can be stated as follows: (1) To reveal the laws of behavior of substances and interaction between them in complex systems. This includes determination of the composition and properties in systems with phase and chemical transitions; selection of formation with phase and chemical transitions; selection of formation reactions of the most representative components and phases of the systems; predicting the phases that will form; verification of the applicability of the assumptions contained in the CTA program and the TM methods. (2) To solve specific practical problems, which include revealing the optimal conditions for producing the target products; determination of limits of the equilibrium compositions and properties of the system in the real processes; selection of optimal variants for treatment of various initial materials; creation of scientific bases for combined application of multi-element raw material, and so on.

As a rule, especially for high-temperature processes, the application of TM reduces the amount of experimental investigation necessary.

2. Method of investigation

Fig. 1 shows the main stages (blocks) of the TM [39,40,45].

2.1. Formulation of the problem

Here we need a representation of the problem in question in a form that is suitable for its TM. For determining the possibility of carrying out TM and the priority level of the solution, some questions arise with respect to the following stages: CTA program, TM method, Thermodynamic properties bank, and Computer. The answers to these questions specify the problem.

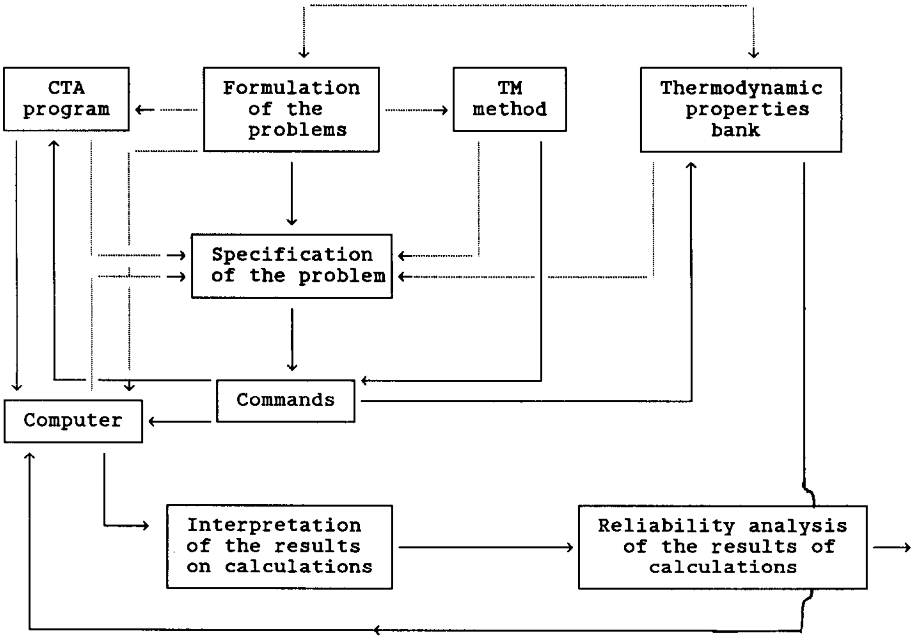

Fig. 1. Stages (blocks) in the thermodynamic modeling.

2.2. CTA program

The program should enable one to solve the formulated problem in principle and all its possibilities, merits and shortcomings must be questioned. At the present time many corrected versions of CTA programs have been written; seen in particular, Refs. 10–31 and 38.

The natural inclination of investigators is to use a program which is as universal and reliable as possible for solving various types of problems; mostly entire program packages such as ASTRA, SOLGASMIX, NASA(NNEPEQ), SELECTOR and CHEMIX [12,14,19–21,23–25,26] are used. We have used the ASTRA program [19,20,23] for TM.

2.3. Thermodynamic properties bank

At present, thermodynamic functions are known for several thousand elements, substances, and ions. The majority of these data are listed in Refs. 32–36. However when the investigator is studying a new system it is usually necessary to determine the properties of some new components of this system using various types of calculation [46–55] together with experiments [54–57]. In the thermodynamic properties bank we have data for more than 3000 compounds, gases and ions.

2.4. The method

This stage contains the recommended versions of optimal applications of TM for various processes.

The TM method always begins with the setting up of a physical picture (model) for the process, thus distinguishing the system and subsystems, which can attain equilibrium. Then a similar system is selected for the same process, for which the main properties (composition and the content of the condensed phases, partial pressures of the components in the gas phase, etc.) are known and available for a given range of variation of the parameters. Subsequent development of the method occurs according to the scheme shown in Fig. 1. The calculated results are compared with the known data, the possible reasons for the deviations between them are analyzed, requested corrections are made to the TM method, and calculations are repeated, as shown in the scheme of Fig. 1, to match the required level of deviations.

The main problems solved by performing TM are (1) separation of the main and secondary components in the system; (2) revealing the special conditions and assumptions superimposed on the system together with consideration of possibilities and limitations of the CTA program; (3) constructing the mass and phase compositions of the initial system and estimation of the phase composition of the system in the studied range of variation of parameters; (4) final definition of the parameters of the system and the ranges of their measurements together with construction of the procedures and sequences of the calculations.

We have the versions for studying the thermal dissociation and stability of condensed substances; reduction and refinement of metals; synthesis of refractory compounds, solid solutions $Me_xC_yN_zO_q$ and HTSC phase $YBa_2Cu_3O_y$; ionic compositions of molten alkali halides; phase compositions of powder, chemical vapor deposition (CVD) process, and so on [20,39,40,58-62].

2.5. Computer

For carrying out TM, a computer is required that enables one to apply the proper CTA program and the data from the database.

2.6. Specification of problem

After going though the above stages, the conditions are laid down for solving the problem and the data are summarized for setting up the commands. The contents of Commands and Interpretation ... blocks are not needed in the detailed explanations.

2.7. Reliability analysis of the results of calculations

This is an important step in TM. One should note that the TM results are frequently a unique source of information, but the possibilities of numerical modeling should not be exaggerated. The main sources of error in TM are, departure of the real system from equilibrium, the algorithm assumptions made for the CTA program in order to find the global extremes in the potential of the system [63], lack of precision and inconsistency between properties of the components of the system, inadequacy and incompleteness of representation of the components of the system, application of improper TM methods.

For determining the reliability of TM, it is desirable to use two methods: (1) calculation of presumed determinants of the composition and properties of the system taking into account all the sources of errors; (2) comparison between the TM results and reliable experimental data.

We note that the systematic investigation of TM errors has only just begun [11,18,40,63–69].

In order to leave out unreliable information we shall use some general propositions.

(1) The system chosen should be regarded as being in the equilibrium state for parameters of the process.

(2) A CTA program should be used, permitting an algorithm to be employed which does not cast any doubt on the main expected results.

(3) It is pointless carrying out the TM if even a single one of the most significant components is absent in the system, or if there are large errors in the values of the properties for any one of the significant components.

(4) The verified TM method must be used.

(5) The TM results should be selectively verified via experiments.

Let us compare the calculated and experimental data. The results of the thermal analysis of SiO_2 in initial atmosphere of argon are given in Tables 1 and 2. The product of reaction between Nb_2O_5 and Nb_3Al [74] is represented in Table 3. Data on partial pressure determinations [69] over molten Al–Me (Me is In, Ni, Si, Fe, Co, Mn or Cu) are presented in Table 4. The data on the heat of mixing have been

Table 1

Comparison between experimental (upright face) [a] [70] and calculated (italic face) [71] values of partial pressure of components over silica

Component	$\lg(p_i/\mathrm{atm}) = A - (B/T/\mathrm{K})$		p_i/atm	T/K
	A	*B*	1890	1890
SiO_2	8.67 ± 0.06	29663 ± 600	9.8×10^{-8}	5.1×10^{-7}
	8.67	*28660*	3.2×10^{-7}	1.6×10^{-6}
SiO	8.96 ± 0.06	27762 ± 600	1.9×10^{-6}	8.7×10^{-6}
	8.34	*26840*	4.3×10^{-6}	1.9×10^{-5}
O_2	9.26 ± 0.06	29028 ± 600	9.2×10^{-7}	4.6×10^{-6}
	7.87	*25690*	3.2×10^{-7}	7.8×10^{-6}
O	7.31 ± 0.06	26161 ± 600	3.4×10^{-7}	1.3×10^{-6}
	7.42	*26160*	3.8×10^{-7}	1.6×10^{-6}

1 atm = 1.01325 bar. [a] The results in upright face show data for experiments performed in the range 1890–1895 K. As a result, besides the values given in table, calculations were made to determine lg $p_i = f(T)$ for Si_3, Si_2, SiO^+, Si^-, e^-, O, O^+, O_2^-, O_2^+, O^- [21].

Table 2
Comparison between the properties of the "liquid–gas" transformation for silica

Property	TM results	Literature data		
		[48]	[72]	[73]
T_l^g/K	2950–3060	3546	2863–3223	3130
$\Delta_l^g H$/kJ mol^{-1}	654–625	517	–	509.7

Table 3
Weight and composition of the metallic solutions [74] [a]

Weight/(10^3 kg) at T/K							
2990	3000	2840	2860	2850	2850	3010	3015
16.40	16.5	15.21	11.6	17.1	17.0	17.0	17.2
16.31	*16.31*	*15.36*	*11.77*	*17.27*	*17.27*	*17.27*	*17.53*
Wt% Al							
–	0.15–0.08 *0.25*	–	–	1.1–1.2 *1.25*	–	–	

[a] Experimental data are upright face and calculated data are italic face.

taken from Ref. 75. As handbook data, we took those given in Ref. 76. The preparation conditions and composition of the alloys Nb–Mo–W–Zr–Al (alloy 1) and Nb–W Mo–Zr–Al–C (alloy 2) from the initial oxides be reducing Nb_3Al (according to Ref. 77) are presented in Table 5. The results of the syntheses of the solid Ti–C–N–O solutions [78] are given in Table 6.

One can see from Tables 1–6, the results of TM for different types of process are in satisfactory agreement with experimental data.

3. Results and discussion

The range of application of TM is illustrated in Fig. 2. Thermodynamic modeling is becoming more widespread as a method of investigation [11–15,18–31,37–39] and is being used to study diverse processes [11,12,15,18,20,23,25,27,28,30,31,38,39, 58–60,77,78].

Let us discuss the results of some studies in which we participated.

3.1. Thermal dissociation

We have studied the equilibrium thermal dissociation of more than 100 simple and complex substances (the possibility of formation of solutions was not consid-

Table 4
Comparison between calculated [69] and handbook [76] values of partial pressure of the components over the metallic solutions

[Al] in solution/ mole fraction	Partial pressure over the alloys/MPa	
	p(Al)/p(Al)/p(Al) (MIS) [a]/(MRS) [b]/[76]	p(Me)/p(Me)/p(Me) (MIS) [a]/(MRS) [b]/[76]
The system Al–Fe at 1873 K		
0.1	$0.175 \times 10^{-5}/0.862 \times 10^{-6}/0.261 \times 10^{-5}$	$0.7 \times 10^{-5}/0.701 \times 10^{-5}/0.449 \times 10^{-5}$
0.3	$0.381 \times 10^{-4}/0.135 \times 10^{-4}/0.182 \times 10^{-4}$	$0.609 \times 10^{-5}/0.532 \times 10^{-5}/0.217 \times 10^{-5}$
The system Al–In at 1373 K		
0.1	$0.2 \times 10^{-8}/0.26 \times 10^{-8}/0.131 \times 10^{-8}$	$0.754 \times 10^{-6}/0.755 \times 10^{6}/0.582 \times 10^{-6}$
0.3	$0.36 \times 10^{-8}/0.417 \times 10^{-8}/0.208 \times 10^{-8}$	$0.587 \times 10^{-6}/0.6 \times 10^{-6}/0.528 \times 10^{-6}$
0.5	$0.4 \times 10^{-8}/0.44 \times 10^{-8}/0.221 \times 10^{-8}$	$0.419 \times 10^{-6}/0.473 \times 10^{-6}/0.51 \times 10^{-6}$
0.7	$0.35 \times 10^{-8}/0.4 \times 10^{-8}/0.213 \times 10^{-8}$	$0.252 \times 10^{-6}/0.424 \times 10^{-6}/0.559 \times 10^{-6}$
0.9	$0.116 \times 10^{-8}/0.116 \times 10^{-8}/0.236 \times 10^{-8}$	$0.84 \times 10^{-7}/0.47 \times 10^{-6}/0.375 \times 10^{-6}$
The system Al–Si at 1973 K		
0.1	$0.47 \times 10^{-4}/0.13 \times 10^{-3}/0.12 \times 10^{-3}$	$0.284 \times 10^{-5}/0.283 \times 10^{-5}/0.285 \times 10^{-5}$
0.2	$0.141 \times 10^{-3}/0.15 \times 10^{-3}/0.126 \times 10^{-3}$	$0.221 \times 10^{-5}/0.206 \times 10^{-5}/0.217 \times 10^{-5}$
0.5	$0.234 \times 10^{-3}/0.243 \times 10^{-3}/0.462 \times 10^{-3}$	$0.158 \times 10^{-5}/0.132 \times 10^{-5}/0.135 \times 10^{-5}$
0.7	$0.329 \times 10^{-3}/0.295 \times 10^{-3}/0.542 \times 10^{-3}$	$0.946 \times 10^{-6}/0.978 \times 10^{-6}/0.613 \times 10^{-6}$
0.9	$0.423 \times 10^{-3}/0.42 \times 10^{-3}/0.518 \times 10^{-3}$	$0.315 \times 10^{-6}/0.321 \times 10^{-6}/0.144 \times 10^{-6}$
The system Al–CU at 1373 K		
0.1	$0.133 \times 10^{-7}/0.1 \times 10^{-8}/0.144 \times 10^{-8}$	$0.634 \times 10^{-7}/0.634 \times 10^{-7}/0.497 \times 10^{-7}$
0.3	$0.535 \times 10^{-7}/0.132 \times 10^{-7}/0.669 \times 10^{-8}$	$0.422 \times 10^{-7}/0.441 \times 10^{-7}/0.129 \times 10^{-7}$
0.5	$0.68 \times 10^{-7}/0.562 \times 10^{-7}/0.672 \times 10^{-7}$	$0.352 \times 10^{-7}/0.2 \times 10^{-7}/0.503 \times 10^{-8}$
0.7	$0.936 \times 10^{-7}/0.962 \times 10^{-7}/0.143 \times 10^{-6}$	$0.211 \times 10^{-7}/0.467 \times 10^{-8}/0.15 \times 10^{-8}$
0.9	$0.12 \times 10^{-6}/0.12 \times 10^{-6}/0.23 \times 10^{-6}$	$0.704 \times 10^{-8}/0.475 \times 10^{-9}/0.3077 \times 10^{-9}$

[a] Ideal solutions. [b] Regular solutions.

ered) [20,71,79–85]. Examples of the information obtined are cited in Tables 7 and 8. It was determined that extensions of schemes of the thermal decomposition of simple substances include the following three possibilities:

(1) Substance – gas. (Oxides of group I–III elements of the Periodic System, ZrO_2, HfO_2, SiO_2, VO, Nb_2O_5, Cr_2O_3, Ti_3O_5, Nb_2C, CeC_2, Ca_3P_2, AlN and FeSi.)

(2) Substance 1 – Substance 2 + gas. (TiO, V_2O_3, VO_2, V_2O_5, NbO_2, MoO_3, Fe_3O_4, FeO, Fe_2O_3, Ti_4O_7, TiO, TiO_2, Ti_2O_3, chromium carbides, NbC, NbN, CrN, NbO, MoO_2, WO_2, CaC_2, BN, TiN, Cr_2N, Nb_2N, CeN, Fe_2P, AlP, calcium aluminides, FeAl).

(3) Substance 1 – Substance 2 + Substance 3 + gas (VO_2 at 2100 K; Ti_2O_3 at 2700 K; SiC, Ce_2C_3, Fe_3P, $FeAl_2$, $NbAl_3$, Nb_3Al, $FeSi_2$, niobium silicides).

The first two variants of decomposition are well known [86]. Since TM was performed without considering any formation of solutions, an assumption was made that for condensed material of Scheme (3), the results of calculations do

Table 5
Comparison between calculated (upright face) [a] and experimental (italic face) [b] data [77]

Allowing element	θ fractional units		Alloy composition/wt%	
	Alloy 1	Alloy 2	Alloy 1	Alloy 2
W	1.0–1.1	1.1–1.0	4.7–6.5	10.2–11.5
	0.98	*0.98*	*4.9*	*9.98*
Mo	1.0–0.99	1.0–0.99	2.1–2.8	6.1–6.9
	0.885	*0.90*	*1.77*	*4.94*
Zr	0.02–0.41	0.03–0.05	0.02–0.61	0.04–0.06
	0.22	*0.12*	*0.22*	*0.15*
Al	0.126–0.078	0.15–0.08	1.02–0.88	1.15–0.74
	0.192	*0.25*	*1.33*	*1.445*
C	–	0.8–0.6	–	0.01–0.005
		0.25		*0.308*
Nb	0.986–0.69	0.897–0.763	99.25–89.12	82.48–80.56
	0.93	*0.92*	*91.36*	*83.06*

[a] Calculated data were in the range 3000–3500 K. [b] The experiments were performed at 3000 K; θ is the efficiency of extraction.

Table 6
Comparison between calculated (upright face) and experimental (italic face) data [78] for the synthesis of solid solutions $Ti–C_c–N_y–O_z$

T/K	$TiC_xN_yO_z$		
	x	y	z
1773	0.42 *0.42*	0.56 *0.57*	0.02 *0.03*
1873	0.42 *0.42*	0.56 *0.57*	0.02 *0.09*
1973	0.47 *0.42*	0.50 *0.56*	0.03 *0.03*
1973	0.47 *0.42*	0.52 *0.56*	0.01 *0.03*

indeed describe the dissociations, substances – solution of variable composition + gas. The points concerning this scheme need to be experimentally verified. However, IR and chemical analysis data confirmed Scheme (3) for the thermal dissociations of SiC [84].

We have made preliminary estimates of the thermal stabilities of some double nitrides of the type $Li_xMe_yN_z$. It was shown that Li_3AlN_2, LiMgN, Li_5TiN_3, Li_2ZrN_2, Li_7VN_4, Li_7NbN_4, Li_7TaN_4, Li_7SiN, Li_8SiN_4, Li_5SiN_3 and Li_6CrN_4 are stable [87]. The same was done for 34 compounds of the YBaCuO system [88].

From studies on the possibility of removing phosphorous from industrial concentrates optimal conditions were determined for dephosphorization and expenditure

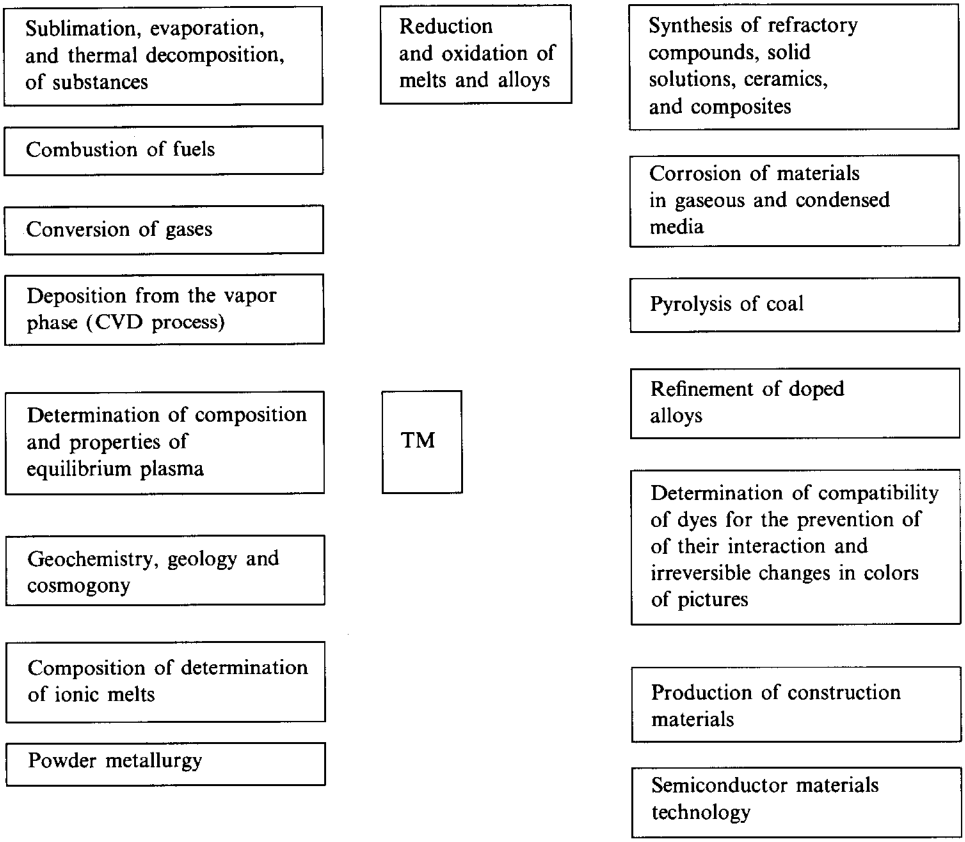

Fig. 2. Range of application of thermodynamic modeling.

of energy per unit mass for the initial molar mixture $2Ca_3P_2O_8 + Ca_2Nb_2O_7 + 3.57Fe_2SiO_4$ [89,90] (Table 9). The results of TM were used to organize the process with real concentrate and thus 80% of the phosphorus was removed [91].

3.2. *Reduction of metals*

We have investigated the reduction of niobium from its pentoxide by various reducing agents [20,74,92–100] as well as the reduction of niobium and the accompanying metals from a concentrate of the above mentioned composition with the object of determining the conditions for which the extraction of niobium is maximal in the metallic melt having minimal phosphorus content [101–104]. Some of the results are presented in Tables 10 and 11.

The information obtained by modeling the selective carbothermic reduction of phosphorus and iron from this concentrate (Table 9, process 2) enabled us to successfully carry out industrial experiments [105].

Table 7
Pressure of the components over $Ca_3P_2O_8$ initially in argon atmosphere at 2650–3600 K

No.	Component	$\lg(p_i/\text{Pa}) = A - B/(T/\text{K})$		T/K
		A	B	
1	P_4O_8	7.44	58610	2650–3450
		−59.46	−172110	3450–3600
2	P_4O_6	8.04	43470	2650–3450
		−46.65	−145100	3450–3600
3	PO	13.77	31400	2650–3450
		12.10	26330	3050–3450
4	P_4	11.4	67520	2650–3450
		−7.14	3590	3450–3600
5	P_2	11.85	39170	2650–3450
		2.54	7098	3450–3600
6	P	11.63	32800	2650–3450
		6.95	16680	3450–3600
7	P^+	11.84	61770	2650–3450
		4.61	36820	3450–3600
8	CaO	11.17	23990	2650–3450
		9.67	18710	3450–3600
9	Ca_2	10.61	42480	2650–3450
		19.72	73880	3450–3600
10	Ca	9.65	22340	2650–3450
		14.31	38320	3450–3600
11	Ca^+ and e	9.71	29420	2650–360
12	O_3	12.44	50180	2650–3450
		−6.02	−13870	3450–3600
13	O_2	12.37	28320	2650–3450
		0.08	−14060	3450–3600
14	O	12.22	27600	2650–3450
		5.97	6065	3450–3600
15	O_2^+	11.74	64390	2650–3450
		−3.23	−12750	3450–3600
16	O^+	11.12	70020	2650–3450
		2.62	40710	3450–3600
17	O_2^-	13.95	50990	2650–3450
		3.18	16110	3450–3600
18	O^-	10.92	42900	2650–3600

Table 8
Phase transition temperature for oxides as a function of $\sum_p (0)$

Transition	$T = \psi + \kappa(\sum_p (0))/\mathrm{K}$		Range of $\sum_p (0)$/MPa
	ψ	κ	
$Fe_2O_3 \rightarrow Fe_3O_4$	1580	175.4	0.128–0.098
$Fe_3O_4 \rightarrow FeO$	2940	360.4	0.0307–0.0743
$FeO \rightarrow$ gas	3120	345.2	0.0323–0.0559
$Nb_2O_5 \rightarrow$ gas	3540	151.8	0.0207–0.0543
$TiO_2 \rightarrow Ti_4O_7$	2915	302.6	0.0123–0.0965
$Ti_4O_7 \rightarrow Ti_3O_5$	3340	314.5	0.0169–0.0818
$Ti_3O_5 \rightarrow$ gas	3880	126.1	0.0179–0.0422
$V_2O_5 \rightarrow VO_2$	1790	161.0	0.0367–0.098
$V_2O_4 \rightarrow$ gas	2950	264.5	0.0166–0.0358
$Cr_2O_3 \rightarrow$ gas	3180	184.7	0.0096–0.0372
$CaO \rightarrow$ gas	3590	102.6	0.0101–0.0598
$SiO_2 \rightarrow$ gas	2900	201.2	0.0179–0.0604
$Al_2O_3 \rightarrow$ gas	3890	102.6	0.0417–0.0671

Table 9
Calculated indices of reprocessing of the concentrate

Process	L [a]/wt%	T/K	Degree of reduction of Nb/%	P [b]/wt%	Q_T [a]/kJ g^{-1}
(1) Thermal decomposition	–	3000	–	25	6.3
	–	3400	–	9.41	7.95
	–	3600–3700	–	0.1–0.01	11.5–12.8
(2) Selective reduction of P and Fe by carbon	16.7	2100	0	9.0	4.3
	–	2300	0	3.2	6.24
	–	2600	0	1.0	8.0
	–	2900	35	0	10.0

[a] L and Q_T are the content of the reducing agent in initial system and the energy expenditure, respectively.
[b] In the oxide (slag) solution (the P content was taken to be 100%).

The possibilities of the treatments of wastes for phosphorus production were also investigated [106] and we are also able to give some practical recommendations.

3.3. *Refinement of metallic alloys*

It was confirmed in Refs. 107 and 108 that production of steels with acid slags leads to conditions that are close to equilibrium (Table 12).

It was reported in Ref. 110 that the equilibrium degree of purification of niobium from the impurities increases with decreasing pressure and that, at a given pressure,

Table 10
Indices [a] for the equilibrium reduction of Nb from Nb_2O_5

Reducing agent	L/wt%	$(T/K)/(\theta/\%)$	$(\theta_{max}/\%)/(T/K)$	l/wt%	$Q_T \times 10^{-3}$/ kJ kg^{-1}
H_2	80	$\frac{2800-2600}{90}$	95/2300	–	24–36
H_2 [b]	65.3	$\frac{3200-3400}{90}$	95/3250	–	30–38
Li	20.7	$\frac{900-1200}{100}$	100/100	10^{-5}	−(2.3–2) [c]
Na	46.4	$\frac{1200-1400}{90}$	95/1250	5–1	−(2.5–1.5)
Be	14.5	$\frac{1000-1800}{90}$	100/1200	5×10^{-3}	−(2.8–2)
Mg	31.37	$\frac{1000-1800}{100-97}$	100/1400	$(5.5-5) \times 10^{-3}$	−(2.2–1.4)
Ca	43	$\frac{1000-2200}{100-97}$	100/1500	2	−(2.5–1.4)
Ba	72.1	$\frac{1000-2200}{100-98}$	100/1600	0.5–0.48	−(0–1)
B	16.9	$\frac{2400-3000}{95}$	98/2900	4–2	3.5–4.8
Al	30.0	$\frac{2350-2400}{90-98}$	99/2350	8–10	−(0.2–0.3)
Ce	63.73	$\frac{2600-2800}{98-97}$	98/2600	2–3	−(0.5–0.3)
Nb_3Al	80.83	$\frac{2500-2700}{95}$	99/2400	1–0.25	0.05–0.7
Si	34.57	$\frac{2500-3200}{92-99}$	99/2900	1–0.5	4.6–5.2
NbC	44.11	$\frac{3200-3400}{99}$	99.7/3200	0.25–0.5	5.25–5.3
C	18.43	$\frac{3300-3700}{98-99}$	99/3500	0.05–0.11	5.86–6.15
CH_4	23.18	$\frac{3300-3700}{97-98}$	99/3600	0.05–0.1	12.55–17.74
$C + CH_4$	4.68 + 15.63	$\frac{2900-3400}{84-87}$	87/3100	$(6-3.5) \times 10^{-3}$	8.37–11.5

[a] L, l, θ and Q are the contents of the reducing agent in the initial system and the alloy; efficiency of extraction of Nb in the alloy, and the amount of energy spent. [b] $p = 9.81$ MPa. [c] Minus sign means evolution of energy.

Table 11
Indices of reduction of the concentrate

Index	Reducing agents				
	C	CH_4	Al	Si (variant 1)	Si (variant 2)
T/K	3400-3700	2800-3000	2200-2600	2200-2600	2900-3200
L/wt%	19.15	22.5	27.65	36.5	36.5
θ/%	80-90	70-80	97-96	98-99	98-99
Q_T/kJ kg^{-1}	10700-11250	11650-14600	0-1100	2930-4640	7950-8700
Metallic components wt%					
Nb	97.02-98.8	80-96.5	28.35-33.74	62.9-69.4	76.12-90.8
Fe	2.54-0.91	19.5-3.2	34.22-44.26	34.0-27.0	20-5.8
P	0.6-0.3	0.025-0.00085	15.26-4.46	0.1-0.06	0.0194-0.00054
Si	0.31-0.21	0.05-0.025	1.72-2.26	3-3.5	3.64-3.33
C	0.017-0.047	0.01-0.005	-	-	-
Al	-	-	20.44-15.22	-	-
Ca	0.061-0.04	0.08-0.055	0.021-0.061	0.4-0.2	0.18-0.88

[a] L, θ and Q_T are, respectively, the content of the reducing agent in the initial working body, efficiency of extraction of Nb in the alloy, and amount of energy spent.

Table 12
Comparison between calculated and experimental indices of the production process of steel with acid slags

Indices	Process (experiment)		(p/MPa) = $9.8 \times 10^{-1}/1.96 \times 10^{-1}$ Calculated at 1850-2100 K
	Bessemer	Experiments	
Composition of steel at the end of final adjustment/wt%			
[C]	0.1	0.3	(0.055-0.09)/(0.67-0.18)
[P]	0.06	0.06	(0.06-0.058)/(0.062-0.06)
[Si]	0.1	0.3	(0.07-0.38)/(0.04-0.3)
[Mn]	0.1	0.4	(0.01-0.05)/(0.07-0.05)
[N]	0.02	-	(0.005-0.03)/(0.07-0.05)
Composition of the slag/wt%			
(SiO_2)	68-70	57-62, 42-45 [a]	(48-28)/(44-40)
(FeO)	17-18	10-20, 32-35 [a]	(37-44)/(42-44)
(MnO)	13-15	4-6	(12-14)/(9.9-11)
(Fe_2O_3)	1.0	0.3	(0.003-0.01)/(0.007-0.01)
Composition indices/kg/t			
Loss of metal metal	70-90	-	(78-86)/(77-80)
Weight of slag	60-100	-	(63-50)/(72-54)

[a] Data obtained for slage free of (CaO) and (MgO).

the degree of purification decreases in the sequence Al > Fe > Si > Ti > O > N > C. The experimental (electron-beam remelting (EBR) data) and calculated values are comparable for the loss of niobium. Increasing time and decreasing pressure of

Table 13
Ratios $[C_i]_{p,T}/[C_i]_{start}$ [a] of impurity elements in iridium at 2800 K and different pressures [111] and after EBR [112]

Element	Results of TM [111] at p/MPa					After EBR [112]
	9.8×10^{-2}	1.3×10^{-2}	1.3×10^{-4}	1.3×10^{6}	1.3×10^{-8}	
Ga	5.3×10^{-1}	1.3×10^{-1}	1.4×10^{-3}	2.5×10^{-6}	6.1×10^{-8}	1×10^{-2}
Ca	1.1×10^{-1}	1.5×10^{-2}	1.5×10^{-4}	2.7×10^{-7}	4.4×10^{-9}	1.4×10^{-2}
Mn	3.3×10^{-1}	6.1×10^{-2}	2.6×10^{-4}	1.1×10^{-6}	2.4×10^{-8}	8×10^{-3}
Zn	9.1×10^{-3}	1.0×10^{-3}	9.6×10^{-6}	1.7×10^{-7}	2.5×10^{-10}	4×10^{-2}
Pd	8.1×10^{-1}	2.3×10^{-1}	2.9×10^{-3}	5.3×10^{-6}	2.6×10^{-7}	4×10^{-5}
Si	1.0	9.6×10^{-1}	2.5×10^{-1}	3.1×10^{-4}	1.1×10^{-5}	9×10^{-2}
Al	8.3×10^{-1}	3.8×10^{-1}	5.9×10^{-3}	1.1×10^{-5}	2.9×10^{-7}	1×10^{-2}
Fe	9.6×10^{-1}	7.5×10^{-1}	2.9×10^{-2}	5.5×10^{-5}	1.8×10^{-6}	1×10^{-3}
Ni	9.8×10^{-1}	8.1×10^{-1}	3.9×10^{-2}	7.2×10^{-4}	2.6×10^{-6}	3×10^{-3}
C	1.0	1.0	1.0	1.7	1.8×10^{-1}	2.3×10^{-1}
W	1.0	1.0	1.0	7.9	1.9×10^{-2}	1.0
Zr	1.0	1.0	0.99	1.5×10^{-1}	9.7×10^{-3}	–
Pt	1.0	1.0	9.3×10^{-1}	2.2×10^{-2}	1.4×10^{-2}	1×10^{-1}
Rh	1.0	1.0	7.5×10^{-1}	5.3×10^{-3}	3×10^{-4}	2×10^{-2}

[a] Ratio at the concentration of an impurity at p and T to its initial concentration in the purified metal.

EBR will promote greater purification from all impurities except for carbon. Therefore, for producing high-purity niobium, it is expedient to use pure metallic aluminum or niobium aluminide as the reducing agent for niobium from its pentoxide.

While studying the behavior of 15 impurity elements contained in unredefined iridium, it was shown [111], that upon decreasing the total pressure, the impurity concentrations decrease for all elements except tungsten and carbon (Table 13). The TM results at $p = 1.3 \times 10^{-4}$ to 1.3×10^{-6} MPa are in agreement with the data after EBR [112] considering the fact that, during EBR [113], the total pressure is higher in the melt zone than in the reaction chamber [113]. The same investigation was carried out in an oxidizing atmosphere [114]. The information obtained by these investigations [111,114] enabled us to propose an industrial method for purifying iridium.

3.4. *Solid state chemistry [18,28-31,37,39,60-62,71,115-127]*

The conditions for producing individual carbides and binary solid solution carbides of some less-common metals have been determined [115-118] (Tables 14 and 15). It was found for the solid solutions $MeC_xN_yO_z$ (where Me is Nb, Ti or V) at the compositions given in Table 16 are stable over wide temperature ranges [119-121]. These can be used, for example, as the raw materials for the creation of ceramic cutting instruments.

Since 1987 we have been using TM to study the YBaCuO system. For example, the synthesis of HTSC-phase $YBa_2Cu_3O_{7-\delta}$ from Y_2O_3, CuO and $BaCO_3$ under

Table 14
Conditions of formation of some carbides

Z [a]	Carbide	Composition/wt%	Energy expenditure $Q_T \times 10^{-3}$/kJ kg^{-1}	T/K
7.0	NbC	100	3.4–3.8	1300–2000
7.0	$NbC + Nb_2C$	$Nb_2C \leq 2.5$	3.8–4.8	2000–3400
6.5	$NbC + Nb_2C$	$Nb_2C = 33$	3.2–5.1	2000–3400
7.1	$NbC + C$	$C \leq 5$	3.4–4.9	1400–3000
4.0	$WC + \psi - W_2C$	WC from 33 (100 K) to 5 (3000 K)	1.6–2.9	1000–3000
3.0	TiO	100	4.0–5.8	1500–3000
3.0	ZrO	100	4.3–5.8	1900–3800
7.0	VC	100	3.4–6.2	1400–3000
4.0	MoC	$MoC = 90$ $C = 4$ $MoC_2 = 6$ [b]	1.4–3.5	1000–2800

[a] Molar ratio of carbon to oxide. [b] Experimental data.

Table 15
The conditions of formation solid solution on a base of some carbides

No.	Solution	The range of formation/K	The efficiency of formation %	Energy of expenditure $Q_T \times 10^{-3}$/kJ kg^{-1}
1	Nb–Ti–C	1500–3000	100–98	3.5–5.5
2	Nb–Zr–C	1800–3800	100–98	3.5–5.5
3	Nb–W–C	1400–3000	[a]	2–4.2
4	Nb–V–C	1400–3000	100	3–5.5
5	Nb–Mo–C	1500–2800	100	2.2–4.7

[a] The efficiency of formation can change; it is dependent upon the composition and temperature. At a concentration of $NbC \geq 86$ wt% the efficiency is approximately 100%.

Table 16
Some stable solid $MeC_xN_yO_z$ solutions

Initial composition of the system at TM	Composition of solid solution	Temperture range/K
$NbO_2 + 2C + 250N_2$	$Nb_{0.05-0.75}N_{0.9-0.85}O_{0.05-0.075}$	1400–2400
$NbO_2 + 2.5C + 250N_2$	$NbC_{0.5}N_{0.48}O_{0.02}$	1200–2400
$TiO_2 + 2C + 500N_2$	$TiC_{0.075-0.1}N_{0.85-0.8}O_{0.075-0.1}$	1600–2500
$TiO_2 + 2.5C + 250N_2$	$TiC_{0.5}N_{0.48}O_{0.02}$ [a]	1000–2500
$V_2O_3 + 4C + 250N_2$	$VC_{0.48}N_{0.5}O_{0.02}$	1600–2600
$V_2O_3 + 3C + 250N_2$	$VC_{0.025-0.075}N_{0.95-0.85}O_{0.025-0.075}$	1400–2600

[a] The composition calculated by TM agrees with experimental data.

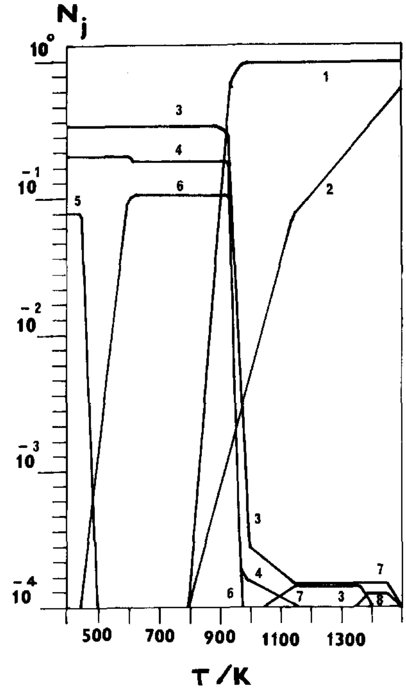

Fig. 3. System Y–Ba–Cu–O [60]. The formation of the phases in initial O_2 atmosphere from $BaCO_3$, CuO and Y_2O_3 (where curve 1 is the ideal solution $YBa_2Cu_3O_6 + YBa_2Cu_3O_7$; curve 2 is the content of $YBa_2Cu_3O_6$ in the solution; curve 3 is CuO, curve 4 is $BaCO_3$, curve 5 is Y_2O_3, curve 6 is Y_2BaCuO_5, curve 7 is $BaCuO_2$ and curve 8 is Cu_2O). N_j is the mole fraction of compounds.

various conditions was modeled together with its thermal decomposition [60,88,122–125] (Fig. 3). It was shown that at equilibrium, CVD processes with the halide precursors render it impossible to obtain superconducting $YBa_2Cu_3O_{7-\delta}$. Accordingly [62], only the tetragonal phase $YBa_2Cu_3O_{7-\delta}$ can be formed (Fig. 4).

The interaction of $YBa_2Cu_3O_{6.85}$ with the metals and substances which can be used as possible functional and constructional materials was investigated at 100–1500 K (Table 17).

Here only the main results of our investigations are shown, but in our opinion, one can see that TM can be successfully used to study and solve various problems in materials' science and technology.

4. Problems

One must consider the creation of methods by which to determine the global nature of the extremes of thermodynamic potentials of complex systems. For systems consisting of individual phases and/or ideal solutions, analysis showed that there are unique extremes [18], i.e. there is a unique solution. In systems with

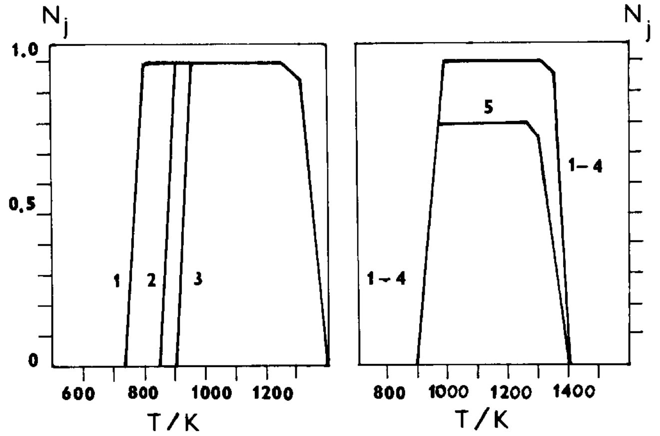

Fig. 4. Some results of CVD-process in the YI_3–BaI_2–CuI–H_2O–O_2 system [62]. (a) Yield of $YBa_2Cu_3O_6$ related to temperature and pressure, curves 1–3 signify $p = 1.01325 \times 10^{-5}$, 1.01325×10^{-4} and 1.01325×10^{-3} bar respectively. (b) Yield of $YBa_2Cu_3O_6$ related to temperature and $\lg(\Sigma(0)/\sigma(\mathrm{Me}))$ in systems (mol ratio) at $p = 1.01325 \times 10^{-3}$ bar, where regions 1–5 represent the ratios 3, 2, 4 and 5, respectively. N_j is the mole fraction of compounds.

Table 17
Characteristics of interactions and structures of contacting phase

Initial system: $123 - O_y$ + Ar + contracting material; 100–300 K; $y = 0.85$		Notes
I	Ag, Pd, Pt, Au, $SrTiO_3$, MgO, $MgAl_2O_4$, Ba_2SiO_4 Y_2BaCuO_5, $BaCuO_2$ $BaHfO_3$, $BaZrO_3$, $BaTiO_3$	There is no chemical interaction. The differences of structure parameters of initial contraction phases are always found to be ≤10%
I.	Y_2O_3, AgO, HfO_2, ZrO_2, TiO_2, CuO, Nb_2O_5, $SrSiO_3$, Al_2O_3	There is some chemical interaction. The retaining part of $123\text{-}O_y$ phase continues to have superconducting properties ($y = 6.6$–6.85). Differences of structure parameters of initial contacting phases are found such as <10% and >10%
III.	Cu, V_2O_3, VO_2, C	There is chemical interaction. The retaining part of $123\text{-}O_y$ phase does not have superconducting properties ($y = 6.6$–6.4). The differences of structure parameters of initial contacting phases are usually more than 10%
IV.	Si, W., V, Ti, Zr, Hf, Fe, Nb, Sn, In, Ga, SiO_2, GdN, SiC	There are strong chemical interactions. The 123-O phase does not exist. The differences of structure parameters of initial contracting phases are always more than 10%

nonideal solutions we cannot rule out the possibility of the presence of several local extremes, which can be the cause of the non-unique nature of the determination of phase and chemical compositions [18,63,66].

For TM with participation of multicomponent (multielement) melts it is impossible in practice to use the well known models of binary, quasibinary or ternary solutions (regular, sub-regular, quasichemical approaches and so on) [128-130]. Therefore, it seems very attractive to use for this purpose the various variances of models for ideally clustered solutions [131-133].

We suggest the ideal solution of products of chemical interactions (ISPI) model [134]. In this model the clusters are real substances with their thermodynamic functions and properties. Those substances could form from elements of a given system and could dissolve in the base substance of a solution. For example, as components, the metallic solution not only included metals but also intermetallides, carbides, nitrides and phosphides which could form from elements of this system, and could dissolve in the base metal under the given conditions. Our experience shows that the ISPI model can be used [20,40,58,59,69,74,77,91,93,94-109,111,114] in these circumstances. A more complex and inadequately studied problem is that of the applicability of the above model of solutions to the determination of the vapor phase composition.

There is an opinion [24,25,135] that it is necessary to use the real activities of the components of the solution. In principle, this is correct. However, one must consider the fact that the real activities are known for a limited number of binary and ternary systems, and selectively for some components of the multielement solutions, where the conditions of their experimental determination can usually be fairly easily removed from the conditions of the process being studied.

Investigations of systems with the help of TM give rise to an urgent need to construct rapid methods to determine the properties of new substances, or unknown properties of well known compounds and phases. This is difficult to do rapidly by experimental methods, but is possible by applying the various reliable calculational methods (see, e.g., Refs. 46-53). We have used those methods extensively (see, e.g., Refs. 53, 136, 137), and we have now calculated the thermodynamic and thermochemical propeties of more than 500 condensed compounds.

The widespread and fully fledged application of TM is also hindered by lack of scientific organization. In our country this includes, in our opinion, the absence of a unified database on chemical thermodynamics and thermochemistry, which is closely connected to foreign information sources. Such a database could be expediently created by using the experience of the Institute of High Temperature of the Academy of Sciences of Russia (Moscow) [32,138].

At least, it is obvious that development of a new scientific direction is impossible without learned investigators. Therefore, it is expedient to introduce for the University students the approprite specialized courses, which may also be offered on an optional basis to graduate specialists.

5. Conclusion

In this report are presented the principal results of investigations carried out by a group of researchers in the Laboratory of Phase Compositions of the Institute of

Metallurgy, Ural Division Russian Academy of Sciences, Ekaterinburg, Russian Federation, using the thermodynamic modeling method from 1976 to 1993.

Acknowledgments

The work was carried out with the constant attention and support of Academician N.A. Vatolin and with the help of my colleagues S.K. Popov, L.A. Marshuk, O.V. Yavoiskya, S.I. Zaitzeva and N.I. Ilyinych to whom I express my sincere gratitude.

It is a great pleasure to thank very much Professor J. Šesták and Dr. B. Štěpánek of the Institute of Physics, Prague, and also the Organizing Committee of the Czechoslovak–French–Polish Conference on Calorimetry and Experimental Thermodynamics.

References

[1] R. Brinkley, J. Chem. Phys., 15 (1947) 107.
[2] W.S. Dorn, J. Chem. Phys., 32 (1960) 1490.
[3] W.B. White, S.M. Johnson and G.B. Dantzig, J. Chem. Phys., 28 (1958) 751.
[4] G.M. Harris, J. Chem. Phys., 31 (1959) 1211.
[5] F.P. Boynton, J. Chem. Phys., 32 (1960) 1880.
[6] G.B. Sinyarev, Izv. Vyssch. Uchebn. Zaved. Transp. Energ. Mashinostr., 2 (1966) 89 (in Russian).
[7] J. Marek and R. Holub, Collect. Czech. Chem. Commun., 29 (1964) 1085.
[8] W.B. White, J. Chem. Phys., 46 (1967) 4171.
[9] F.Y. Zeleznik and S. Gordon, Ind. Eng. Chem., 60 (1968) 27.
[10] G.B. Sinyarev, B.G. Trusov and L.E. Slyn'ko, Tr. Mosk. Vyssh. Tech. Uchil., 159 (1973) 60 (in Russian).
[11] V.E. Alemasov, A.F. Dregalin, A.P. Tishin et al., in V.P. Gluschko (Ed.), Thermodynamic and Thermophysical Properties of the Products of Combustion, Vols. 1–10, Moscow, 1971–1980 (in Russian).
[12] S. Gordon, H. Sanford, B.J. McBride and J. Bonnie, NASA Spec. Publ. No. 273, 1971.
[13] G. Eriksson, Acta Chem. Scand., 25 (1971) 2651.
[14] L.A. Kaz'min, O.A. Khalinlina and I.K. Karpov, Algorithms and Programs, Inf. Byull. Number 3, 1975, p. 18 (in Russian).
[15] F.A. Kushnetsov, G.A. Kokovin and Y.M. Buzhdan, Isv. Sib. Otd. Akad. Nauk USSR, 2 (1975) 5 (in Russian).
[16] I.V. Rozhdestvenski and K.K. Olevinski, in Thermophysical Properties of the Systems with Chemical Interactions, Energ. Inst., Moscow, 1975, p. 145 (in Russian).
[17] Yu.V. Shvarov, Dokl. Akad. Nauk SSSR, 229 (1976) 1224.
[18] G.F. Voronin, in Ya.M. Kolotyrkin (Ed.), Physical Chemistry, Khimiya, Moscow, 1984, p. 112 (in Russian).
[19] G.B. Sinyarev (Ed.), Tr. Mosk. Vyssh. Tekh. Uchil., Number 268 (1978) (in Russian).
[20] G.B. Sinyarev, N.A. Vatolin, B.G. Trusov and G.K. Moiseev, Application of Computers to Thermodynamic Calculations of Metallurgical Processes, Nauka, Moscow, 1982 (in Russian).
[21] A.G. Turnbull, CALPHAD, 7 (1983) 137.
[22] W.R. Smith and R.W. Misson, Chemical Reaction Equilibrium Analysis, Theory and Algorithm, John Wiley, New York, 1982.
[23] B.G. Trusov and G.B. Sinyarev, Isv. Sib. Otd. Akad. Nauk SSSR, 10 (1987) 31.

[24] G. Eriksson and E. Rozen, Chem. Scr., 8 (1975) 100.
[25] G. Eriksson, CALPHAD, 8 (1984) 15.
[26] L.N. Fishbach and S. Gordon, Trans. ASME, 111 (1989) 114.
[27] A.L. Suris, Thermodynamic Analysis of High-Temperature Processes, Metallurgy, Moscow, 1985 (in Russian).
[28] Y.M. Bestman and E.K. Spear, J. Electrochem. Soc., 124 (1977) 786.
[29] C.F. Wan and E.K. Spear, CALPHAD, 7 (1983) 149.
[30] A.V. Emyashev, Vapor Phase Metallurgy of Refractory Compounds, Metallurgy, Moscow, 1987 (in Russian).
[31] V.M. Glazov (Ed.), Thermodynamics and Material Science of Semiconductors, Metallurgy, Moscow, 1992 (in Russian).
[32] V.P. Gluschko (Ed.), Thermodynamic Properties of Individual Substances, 4th edn., Vols. 1–4, USSR Academy of Sciences, Moscow, 1978–1982 (in Russian).
[33] JANAF Supplement. J. Phys. Chem. Ref. Data, 3 (974)311; 4 (1975) 1; 7 (1978) 7693; 11 (1982) 695.
[34] JANAF Supplement. J. Phys. Chem. Ref. Data, 11 (1982) 1.
[35] I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1973.
[36] I. Barin, P. Knacke, and O. Kybashewski, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1976.
[37] E.K. Spear, in T.O. Sedwick and H. Lydtin (Eds.), Proc. VIIth Int. Conf. on CVD, Electrochem. Soc., New York, 1979 p. 25.
[38] G. Eriksson and T. Johanssen, Scand. J. Met., 7 (1989) 264.
[39] G.K. Moiseev, V.V. Chernyaeva, B.V. Mitrofanov and L.A. Marshuk, Formation and Stability of Transition-metal Nitrides under Equilibrium Conditions, Institute of Chemistry Ural Scientific Center, Sverdlovsk, 1989 (in Russian).
[40] G.K. Moiseev and B.G. Trusov, Thermodynamic Modeling in High-Temperature Inorganic System, Principles, Operating Instructions, Ural State University, Sverdlovsk, 1989 (in Russian).
[41] L. Kaufman and H. Bernstein, Computer Calculation of Phase Diagrams with Special Reference to Refractory Metals, Academic Press, New York, 1970.
[42] Y.L. Khazin, P.V. Kovtunenko and A.A. Mayer, Calculation of Phase Diagrams Using the Model of Quasiideal Solutions, Metallurgy, Moscow, 1988 (in Russian).
[43] P.L. Lin, A.D. Petton and C.W. Bate, CALPHAD, 4 (1988) 47.
[44] A.L. Udovski, in E.V. Prichodko, G.I. Zmoidin and A.G. Ponomarenko (Eds.), Physicochemical and Technological Database for Optimizing Metallurgical Techniques, Institute of Black Metals, Dnepropetrovsk, 1988, p. 172 (in Russian).
[45] G.K. Moiseev and N. A. Vatolin, in Proc. IXth Conf. on Physical Chem. and Electrochem., Institute of Electrochemistry, Sverdlovsk, Vol. 1, 1987 p. 156 (in Russian).
[46] M.Kh. Karapet'yants, Methods of Comparative Calculations of Physico-Chemical Properties, Nauka, Moscow, 1985 (in Russian).
[47] V.A Kireev, Methods of Practical Calculations in Thermodynamics of Chemical Reactions, Khimiya, Moscow, 1970 (in Russian).
[48] L.P. Ruzinov and B.S. Gulyanitski, Equilibrium Transformation in Metallurgical Reactions, Metallurgy, Moscow, 1975.
[49] I.B. Sladkov, Methods of Approximate Calculations of Physico-Chemical Properties of Covalent Inorganic Compounds, Leningrad State University, 1978, (in Russian).
[50] E.A. Stolyarov and G. Orlova, Calculation of Physico-chemical Properties of Liquids, Khimiya, Leningrad, 1976 (in Russian).
[51] D.S. Tzagareishvili, Methods of Calculating Thermal and Elastic Properties of Crystalline Inorganic Substances, Metsniereba, Tbilisi, 1977 (in Russian).
[52] A.G. Morachevski and I.B. Sladkov, Thermodynamical Calculations in Metallurgy, Metallurgy, Moscow, 1985 (in Russian).
[53] G.K. Moiseev, Deposited with VINITI, Paper Number 2845-B92 (1992) (in Russian).

[54] L.N. Sidorov, M.V. Korobov and L.V. Zhuravleva, Thermodynamic Investigations by Mass Spectroscopy, Moscow State University, 1985 (in Russian).
[55] G.G. Gvelesiani, D.Sh. Tzagareishvili and A.A. Nadiradze, Thermodynamics of Oxygen Compounds of Rare-Earth Metals at High Temperatures, Metsniereba, Tbilisi, 1983 (in Russian).
[56] P.P. Arsent'ev, V.V. Yakovlev and M.G. Krasheninnikov, Physicochemical Methods of Investigating Metallurgical Processes, Metallurgy, Moscow, 1988 (in Russian).
[57] I.M. Zharski and G.I. Novikov, Physical Investigation Methods in Inorganic Chemistry, Vysshaya Shkola, Moscow, 1988 (in Russian).
[58] G.K. Moiseev, N.A. Vatolin and A.N. Men, Melts, 2 (1988) 3 (in Russian).
[59] G.G. Zalazinski, T.L. Shennikova, G.K. Moiseev and O.V. Yavoiskaya, Melts, 3 (1989) 120 (in Russian).
[60] G.K. Moiseev, N.A. Vatolin, D.S. Tzagareishvili, O.V. Yavoiskaya, G.G. Grelesiani and I.B. Baratashvily, Dokl. Akad. Nauk SSSR, 307 (1989) 902.
[61] G.K. Moiseev, O.V. Yavoiskaya, S.I. Zaitzeva, N.A. Vatolin, D.Sh. Tzagareishvili, G.G. Grelesiani and I.B. Baratasvily, Deposited with VINITI, Paper Number 5283-B89 (1989) (in Russian).
[62] N.I. Ilynych, G.K. Moiseev, N.A. Vatolin and J. Šesták, Thermochim. Acta, 198 (1992) 357.
[63] H.G. Othmer, Chem. Eng. Sci., 31 (1976) 993.
[64] O.D. Khramov, L.A. Kuznetzova and Yu.Yu. Kuzyakov, in Application of Mathematical Methods for Describing and Studying Physicochemical Equilibria, IRGeOChim, Irkutsk, 1982, p. 37 (in Russian).
[65] A.D. Rusin, Vestn. Mosk. Univ., 6 (1972) 714 (in Russian).
[66] R.A. Heidemann, Chem. Eng. Soc., 33 (1978) 1517.
[67] L.A. Marshuk, G.K. Moiseev and S.K. Popov, in Rep. VIth Conf. Struct. Props. Metallic and Slag Melts, Institute of Metallurgy, Sverdlovsk, Part I, 1986, p. 303 (in Russian).
[68] L.A. Marshuk, G.K. Moiseev and S.K. Popov, in Rep. VIth Conf. Struct. Props. Metallic and Slag Melts, Institute of Metallurgy, Sverdlovsk, Part I, 1986, p. 301 (in Russian).
[69] G.K. Moiseev, L.A. Marshuk and S.K. Popov, Izv. Akad. Nauk SSSR Met., 6 (1987) 45.
[70] E.K. Kazenas, G.I. Zviadadze and M.A. Bol'shikh, Izv. Akad. Nauk SSSR, 1 (1985) 46.
[71] G.K. Moiseev, N.A. Vatolin, G.B. Sinyarev, B.G. Trusov and L.E. Slynko, Phase Compositions of Some Oxides During Their Equilibrium Heating to High Temperatures, Institute of Metallurgy, Sverdlovsk, 1979 (in Russian).
[72] E.K. Kazenas and D.M. Chizhikov, Vapor Pressure and Composition over Oxides of Chemical Elements, Nauka, Moscow, 1976 (in Russian).
[73] I.S. Kulikov, Thermodymanics of Oxides, Metallurgy, Moscow, 1986 (in Russian).
[74] G.K. Moiseev, N.A. Vatolin, S.K. Popov and V.S. Kadyshevsci and T.K. Samiltyrov, Izv. Akad. Nauk SSSR Neorg. Mater., 17 (1981) 659.
[75] G.I. Batalin, E.A. Beloborodova and V.I. Kazimirov, Thermodynamics and Structure of Liquid Aluminium-Based Alloys, Metallurgy, Moscow, 1983 (in Russian).
[76] O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, 4th edn., Pergamon, Oxford, 1969.
[77] G.K. Mosieev, S.K. Popov, I.V. Rathnikova, V.I. Tzuchkov and N.A., Vatolin, Izv. Akad. Nauk SSSR Met., 2 (1985) 21.
[78] G.K. Moiseev, V.D. Lubimov and T.A. Timoschuk, in Nitrides: methods of production, properties and applications. Rep. Vth All-Union Conference, Sinatne, Riga, Vol. 1, 1984, p. 38 (in Russian).
[79] G.K. Moiseev and N.A. Vatolin, Phase Compositions of Carbides, Nitrides, Aluminides, Silicides and Phosphides of Some Metals During Equilibrium Heating to High Temperature, Institute of Metallurgy, Sverdlovsk, 1981 (in Russian).
[80] G.K. Moiseev and N.A. Vatolin, Izv. Akad. Nauk SSSR Neorg. Mater., 14 (1978) 1462.
[81] G.K. Moiseev and N.A. Vatolin, Izv. Akad. Nauk SSSR Met., 3 (1979) 30.
[82] N.A. Vatolin and G.K. Moiseev, Izv. Akad. Nauk SSSR Neorg. Mater., 15 (1979) 1838.
[83] G.K. Moiseev and N.A. Vatolin, in Thermal Analysis and Phase Equilibria, Permski State University, 1982, p. 22 (in Russian).

[84] S.V. Baranov, A.G. Vodop'yanov, G.K. Moiseev, N.A. Vatolin and G.N. Kozevnikov, Izv. Akad. Nauk SSSR Neorg. Mater., 18 (1982) 1300.

[85] G.K. Moiseev and N.A. Vatolin, Dokl. Akad. Nauk SSSR, 246 (1979) 656.

[86] I.S. Kulikov, Thermal Dissociation of Compounds, Metallurgy, Moscow, 1969 (in Russian).

[87] G.K. Moiseev, N.Y. Ilynych, S.I. Zaitzeva and N.N. Batalov, Rep. Xth Conf. Physical Chem. and Electrochem., Institute of Electrochemistry, Ekaterinburg, Vol. 3, 1992, p. 28 (in Russian).

[88] G.K Moiseev, S.I. Zaitzeva, N.I. Ilynych and N.A. Vatolin, Dokl. Russian Akad. Nauk, 326 (1992) 662.

[89] G.K. Moiseev and N.A. Vatolin, Isv. Akad. Nauk SSSR Neorg. Mater., 16 (1980) 686.

[90] N.A. Vatolin, G.K. Moiseev, B.G. Trusov and G.B. Syniyrev, Kompl. Ispolsovanie Miner. Syr'ya, Number 8 1979, p. 13 (in Russian).

[91] G.K. Moiseev, G.E. Melnik and N.A. Vatolin, Kompl. Ispolsovanie Miner. Syr'ya, Number 1 (1984) 40 (in Russian).

[92] G.K. Moiseev and B.G. Trusov, in Proc IVth Conf. Struct. and Props. Metallic and Slag Melts, Vol. 3, Sverdlovsk, 1980, p. 85 (in Russian).

[93] N.A. Vatolin and G.K. Moiseev, Deposited with VINITI, Paper Number 1083-81, (1981) (in Russian).

[94] N.A. Vatolin and G.K. Moiseev, Deposited with VINITI, Paper Number 2042-81, (1981) (in Russian).

[95] N.A. Vatolin and G.K. Moiseev, Deposited with VINITI, Paper Number 1084-81, (1981) (in Russian).

[96] G.K. Moiseev, N.A. Vatolin, B.G. Trusov and G.B. Syniyarev, Dokl. Akad. Nauk SSSR, 252 (1980) 598.

[97] N.A. Vatolin, G.K. Moiseev, B.G. Trusov and G.B. Syniyarev, in Repts. IIIrd Symp. Plasma Chem., Nauka, Moscow, Vol. 1, 1979, p. 168 (in Russian).

[98] G.K. Moiseev, S.K. Popov, V.S. Kadyshevski, N.A. Vatolin and T.K. Samyltirov, Izv. Akad. Nauk SSSR Met. Number 4 (1981) 55.

[99] G.K. Moiseev, S.K. Popov, V.S. Kadyshevski, N.A. Vatolin and T.K. Samyltirov, Zh. Prikl. Khim., 57 (1985) 2425 (in Russian).

[100] G.K. Moiseev, S.K. Popov, V.V. Kovalev and N.A. Vatolin, Izv. Akad. Nauk SSSR Met., Number 2 (1984) 71.

[101] G.K. Moiseev and N.A. Vatolin, Izv. Akad. Nauk SSSR Met., Number 1 (1981) 3.

[102] N.A. Vatolin and G.K. Moiseev, Izv. Akad. Nauk SSSR Met., Number 6 (1980) 43.

[103] N.A. Vatolin and G.K. Moiseev, Kompl. Ispolsovanie Miner Syr'ya, Number 9 (1979) 27 (in Russian).

[104] G.K. Moiseev, N.A. Vatolin, B.G. Trusov and G.B. Syniyrev, in Proc. IVth Conf. Thermodynamics of Metallic Alloys, Vol. 1, Nauka, Alma-Ata, 1979, 106 (in Russian).

[105] G.K. Moiseev, G.E. Melnik and N.A. Vatolin, Kompl. Ispolsovanie Miner. Syr'ya, Number 2 (1982) 43 (in Russian).

[106] G.K. Moiseev, V.P. Khan, S.I. Zaitzeva, L.I. Ilynych and N.A. Vatolin, Rep. IInd Int. Symp. on Thermodynamics of Natural Processes, Novosibirsk, 1982, p. 118.

[107] E.K. Borodulin, G.K. Moiseev and N.A. Vatolin, Dokl. Akad. Nauk SSSR, 259 (1981) 596.

[108] N.A. Vatolin, G.K. Moiseev, E.K. Borodulin, B.G. Trusov and G.B. Synivarev, Izv. Akad. Nauk SSSR Met., Number 4 (1982) 36.

[109] G.K. Moiseev, N.A. Vatolin, E.K. Borodulin, B.G. Trusov and G.B. Synivarev, Izv. Akad. Nauk SSSR Met., Number 4 (1983) 17.

[110] G.K. Moiseev and N.A. Vatolin, Izv. Akad. Nauk SSSR Met., Number 6 (1983) 33.

[111] N.A. Vatolin, G.K. Moiseev, P.A. Matynkhin and Timofeev, Izv. Akad. Nauk SSSR Met., Number 2 (1986) 50.

[112] A.V. Elyntin, V.M. Koltygin and O.Yu. Pasechnik, in Nonferrous Metallurgical Processes at Low Pressure, Nauka, Moscow, 1982, p. 230 (in Russian).

[113] B.E. Paton (Ed.), Electron-Beam Melting and Refinement of Metals and Alloys, Naukova Dumka, Kiev, 1973 (in Russian).

[114] N.A. Vatolin, A. I. Timofeev, G.K. Moiseev and P.A. Matykhin, Izv. Akad. Nauk SSSR Met., Number 2 (1987) 18.

[115] G.K. Moiseev, S.K. Popov, L.A. Ovchinnikova and N.A. Vatolin, Izv. Akad. Nauk SSSR Neorg. Mater., 18 (1982) 1304.

[116] G.K. Moiseev, S.K. Popov, L.A. Ovchinnikova and N.A. Vatolin, Izv. Akad. Nauk SSSR Neorg. Mater., 18 (1982) 1521.

[117] G.K. Moiseev, S.K. Popov, L.A. Ovchinnikova, B.V. Mitrofanov and N.A. Vatolin, Izv. Akad. Nauk SSSR Neorg. Mater., 19 (1982) 72.

[118] G.K. Moiseev, N.A. Vatolin and S.K. Popov, Izv. Akad. Nauk SSSR Neorg. Mater., 19 (1983) 1378.

[119] G.K. Moiseev, V.D. Lubimov and T.A. Timoschuk, Zh. Neorg. Khim., 30 (1985) 152 (in Russian).

[120] G.K. Moiseev, S.K. Popov, B.V. Mitrofanov, L.A. Ovchinnikova and N.A. Vatolin, Isv. Akad. Nauk. SSSR Neorg. Mater., 21 (1985) 63.

[121] G.K. Moiseev and N.A. Vatolin, Proc. IInd Symp. on Solid State Chemistry, Pardubice, Czechoslovakia, 1989, p. 151.

[122] G.K. Moiseev, I.N. Dubrovina and N.A. Vatolin, Dokl. Akad. Nauk SSSR, 302 (1988) 376.

[123] I.N. Dubrovina, G.K. Moiseev, R.G. Sakharov, N.A. Vatolin and V.F. Balakirev, Deposited with VINITI, Paper Number 2040-B89 (1989) (in Russian).

[124] N.A. Vatolin and G.K. Moiseev, Abstr. MahTech-91, Finland, Helsinki, 1991, p. 262.

[125] G.K. Moiseev S.I. Zaitzeva, D.S. Tzagareishvili and N.A. Vatolin, Superconductivity: Physica, Chemica, Technica, 4 (1991) 1999 (in Russian).

[126] G.K. Moiseev S.I. Zaitzeva, J. Sestak and N.A. Vatolin, Thermochim. Acta, 216 (1993) 301.

[127] S.I. Zaitzeva, G.K. Moiseev and N.A. Vatolin, in Abstr. 1st Int. Conf. on Material Science of High-Superconductors, Institute of Monocrystals, Vol. 1, Kharkov, Ukraine Rep., 1993, p. 20.

[128] K. Lupic, Chemical Thermodynamics of Materials, North-Holland, New York, 1989.

[129] V.A. Grigorian, A.Ja. Stomachin and A. G. Ponomarenko, Physicochemical Calculation Electromelting Processes of Steel, Metallurgy, Moscow, 1989 (in Russian).

[130] N.A. Svidunovich, V.P. Glyibin and L.K. Svirko, The Interaction of Components in Alloys, Metallurgy, Moscow, 1989 (in Russian).

[131] I. Prigogine and R. Defay, Chemical Thermodynamics, Longman and Green, New York, 1954.

[132] A.G. Morachevskii and E. A. Mairov, in Physicochemical Investigations of Metallurgical Processes, Sverdlovsk, 1980, p. 36 (in Russian).

[133] K.Y. Shunyaev, N.K. Tkachev and A.N. Men, Melts, 2 (1988) 11 (in Russian).

[134] G.K. Moiseev, L.A. Marshuk and N.A. Vatolin, Rep. Xth Conf. Physicochemical Base of Metallurgical Processes, Vol. 1, Chermet Information, Moscow, 1991, p. 23 (in Russian).

[135] A.G. Ponomarenko, E.N. Inosemtzev and S.A. Khrapko, in Physicochemical and Technical Databases for Optimizing Metallurgical Techniques, Dnepropetrovsk, 1980, p. 147 (in Russian).

[136] G.K. Moiseev, N.A. Vatolin, S.I. Zaitzeva, N.I. Ylynych, D.Sh. Tzagareishivili, G.G. Grelesiani, I.B. Baratashsivili and J. Šesták, Thermochim. Acta, 198 (1992) 267.

[137] G.K. Moiseev, N.Y. Ylynych, S.I. Zaitzeva and N.N. Batalov, Rep. Xth Conf. on Physical Chem. and Electrochem., Ekaterinburg, Vol. 3, 1992, p. 26 (in Russian).

[138] L.V. Gurvich, Vestn. Akad. Nauk SSSR, Number 3, (1988) 54 (in Russian).