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Review

Application of chemical thermodynamics to the description of processes of special inorganic materials preparation

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The paper reviews the possibilities of chemical thermodynamics for the description of processes for preparing special inorganic materials with exactly defined final properties. The first part is devoted to general conditions of thermodynamic equilibrium, and describes a procedure for calculating the equilibrium composition of multiphase and multicomponent systems by minimizing the total Gibbs energy of the system while satisfying mass balance conditions. A stoichiometric algorithm convenient especially for equilibrium composition calculations of simple systems is described. Special attention is paid to input data needed for equilibrium calculations. Data characterizing the thermodynamic properties of individual pure substances are discussed, as are data describing the nonideal behaviour of multicomponent condensed phases. The second part of the paper gives a summary of some applications of chemical thermodynamics to the description of processes of special inorganic materials preparation. Case studies on thermodynamic analysis are described for three industrial processes: (1) chemical vapour deposition of titanium carbonitride, (2) growth of Si-doped GaAs single crystals by Bridgman's method, and (3) refining of technical boron nitride by reductive chlorination. The results of equilibrium calculations for all the three systems are in very good agreement with available experimental data.

1. Introduction

The current scientific and technological advances are very closely related to research, development, preparation and production of new materials with exactly defined mechanical, electrical, optical, magnetic and other properties. Clearly, these final properties are determined primarily by the chemical composition and structure of the particular material. Thus the development of new materials involves the solution of the following two circles of questions:

(1) How are the required final properties related to the chemical composition and structure of the given material?

(2) What methods and technological conditions to choose in order to obtain a material of the desired chemical composition and structure?

These relations can be represented by the scheme shown in Fig. 1.

The solution of the first circle of questions falls largely within the field of solid state physics, while the second circle offers a wide scope for chemical technologists engaged in materials research.

The above mentioned relations between chemical composition, structure and technological conditions of materials production can be studied experimentally, but such studies are generally time consuming and expensive. The tendency therefore has been to use theoretical approaches which treat mathematically various physicochemical models of the processes of interest, either quite *a priori* or on the basis of a limited number of experimental data. An important position in this field is held by chemical thermodynamics, some applications of which to the description of high temperature processes of making special inorganic materials will be reviewed in the present paper.

2. Thermodynamic analysis

The simplest model concept of the course of a process is that of the establishment of a thermodynamic equilibrium, either throughout the reactor or in some part of it (usually where the actual chemical conversion takes place, for example, at the interface of two reacting phases). The state of thermodynamic equilibrium is well-defined for closed systems. When applying the equilibrium model to flow systems, which are more frequently encountered in practice, we therefore usually assume that the process studied occurs under steady-state conditions, with all intensive variables taking equilibrium values corresponding to the given temperature and pressure. In this approach, the influence of all transport and kinetic processes on the course and result of the process investigated is neglected.

In spite of these considerable simplifications, the thermodynamic analysis is commonly used as an introduction to a general analysis of the process

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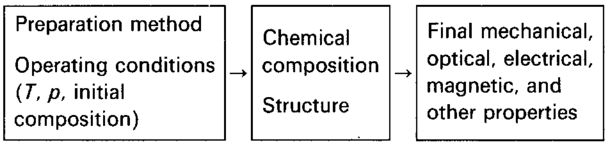

Figure 1 Scheme showing relationship between preparation method, operating conditions and properties of materials.

investigated. It allows the feasibility of the process to be assessed, and the theoretical effectiveness (yield, degree of conversion), and in some cases also the maximum possible rate of solid phase formation, to be determined from the calculated equilibrium composition. The results obtained in this way are limiting values for the real process. What can be predicted fairly well on the basis of thermodynamic analysis are general patterns of the dependences of the actual (experimentally determined) composition on the temperature, pressure and initial composition. In some cases, such as the deposition of ternary and quaternary solid solutions of $A^{III}B^{V}$-type semiconductors by vapour-phase epitaxy, the agreement between the calculated and experimental data is very good, so that the results of thermodynamic analysis can be used directly to determine optimum technological conditions.

2.1. General conditions of thermodynamic equilibrium and methods for calculating the equilibrium composition

A closed system at a constant temperature and pressure, which can perform no work other than that in changes of volume, attains the equilibrium state at a point of the absolute minimum in the total Gibbs energy, provided that mass balance conditions are satisfied. The condition for thermodynamic equilibrium can be written down in the following concise form [1–4]

$$\begin{aligned} &\min G: G = G(T, p, n_1, n_2, \ldots, n_N) \\ &\sum_{j=1}^{N} a_{ji} n_i = b_j \qquad j = 1, 2, \ldots, H \\ &n_i \geqslant 0 \qquad i = 1, 2, \ldots, N \end{aligned} \tag{1}$$

where n_i is the amount of ith substance, a_{ji} is the constitution coefficient of ith substance (indicating the number of atoms of jth kind in a molecule of ith substance), b_j is the fixed number of moles of the jth element in the system, N is the number of substances in the system, and M is the number of elements that make up these substances. The symbol H denotes the rank of a matrix of constitution coefficients, which is such that $H \leqslant M$ (usually $H = M$). So formulated condition for thermodynamic equilibrium can be used directly to calculate the equilibrium composition of a given system. We shall express the total Gibbs energy as a function of the composition of the system

$$G = \sum_{i=1}^{N} n_i \mu_i = \sum_{i=1}^{N} n_i(\mu_i^0 + RT \ln a_i) \tag{2}$$

where μ_i and μ_i^0 are, respectively, the chemical potential and the standard chemical potential of ith substance, and a_i is the activity of ith substance defined as the ratio of the fugacities of the substance in the state considered and the standard state: $a_i = f_i/f_i^0$. In view of the usual choice of the standard states*, we can express the activities of the gaseous substances, assuming the ideal behaviour of the gas phase, in the form

$$a_i = p_{i,\mathrm{rel}} = \frac{n_i}{n(\mathrm{g})} p_{\mathrm{rel}} \tag{3}$$

where $p_{i,\mathrm{rel}}$ and p_{rel} are, respectively, the relative partial and total pressures (with respect to the standard pressure $p^0 = 101.325$ kPa), and $n(\mathrm{g})$ is the total number of moles of the gas phase. The activities of the substances that form condensed solutions can be expressed as

$$a_i = x_i \gamma_i \tag{4}$$

where x_i and γ_i are, respectively, the mole fraction and the activity coefficient of ith component of the solution (for the ideal solution, $\gamma_i = 1$). For the activities of one-component condensed phases, we have

$$a_i = 1 \tag{5}$$

After substituting Equations 3 to 5 for the activities of individual substances in Equation 2, we search for the minimum in the function $G = G(T, p, n_1, \ldots, n_N)$, subject to constraints 1. This problem can be solved using some of the mathematical procedures described in detail in [1, 3, 4], or in a number of original papers such as [5–14]. This general method has primarily been used to calculate chemical equilibria of multiphase and multicomponent systems.

Chemical equilibria of relatively simple systems are frequently calculated by applying the so-called stoichiometric algorithm, which makes use of equilibrium conditions for individual reactions chosen to describe the overall chemical conversion in the system. Assuming that all the substances involved in the set of chosen reactions are present in non-zero amounts at equilibrium, one can derive from the general relationship 1 equilibrium conditions in the form

$$\sum_{i=1}^{N} \nu_{ir} \mu_i = 0 \qquad r = 1, 2, \ldots, C \tag{6}$$

where C (C=N–H) is the number of independent chemical reactions chosen to describe the chemical conversion of the system. The stoichiometric coefficient ν_{ir} indicates the number of moles of ith substance in rth reaction (positive for products and negative for initial substances). Combining Equations 2 and 6, we obtain the well-known relationship

$$\mathrm{K}_r = \prod_{i=1}^{N} a_i^{\nu_{ir}} \qquad r = 1, 2, \ldots, C \tag{7}$$

The equilibrium constant of rth reaction, K_r, can be derived from the equation

$$RT \ln \mathrm{K}_r = -\Delta G_r^0 = -\sum_{i=1}^{N} \nu_{ir} \mu_i^0 \qquad r = 1, 2, \ldots, C \tag{8}$$

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*For gases: pure substance in the ideal gas state at the temperature of the system and the pressure $p^0 = 101.325$ kPa; for condensed substances: pure substance at the temperature and pressure of the system.

The activities of individual substances in Equation 7 may be expressed in terms of Equations 3 to 5. This set of C equilibrium conditions will be supplemented by H mass balance equations in the form

$$\sum_{i=1}^{N} a_{ji} n_i = \sum_{i=1}^{N} a_{ji} n_i^0 \qquad j = 1, 2, \ldots, H \quad (9)$$

where n_i^0 is the amount of ith substance at the beginning of the reaction. The resulting set of N nonlinear equations with variables n_i $(i = 1, 2, \ldots, N)$ can be solved by any convenient numerical method [15].

The chemical equilibrium can also be calculated using the so-called stoichiometric representation of mass balance equations in the form

$$n_i = n_i^0 + \sum_{r=1}^{C} \nu_{ir} \xi_r \qquad i = 1, 2, \ldots, N \quad (10)$$

where ξ_r is the reaction coordinate of rth reaction. By combining the equilibrium relationship, Equation 7 with the activities of individual substances expressed in terms of Equations 3 to 5 and the mass balance Equation 10, we obtain a set of N-H nonlinear equations for the unknown ξ_r $(r = 1, 2, \ldots, N\text{-}H)$, which can be solved numerically [15]. The equilibrium amounts of all n_i substances involved $(i = 1, 2, \ldots, N)$ are then calculated by substituting for ξ_r back into Equation 10.

In some cases, special one-purpose procedures have been developed for the calculation of equilibrium composition. An example is Vieland's method [16, 17] for calculating the equilibrium between the solid phase and the melt in binary and ternary A^{III}–B^{V} systems (A^{III} = Al, Ga, In; B^{V} = P, As, Sb).

2.2. Input thermodynamic data

The calculation of chemical and phase equilibria requires the knowledge of data on thermodynamic properties of pure substances and on nonideal behaviour of multicomponent phases. The input data used for pure substances are usually either standard molar Gibbs energies (i.e., standard chemical potentials), $G_i^0(T) = \mu_i^0(T)$, or standard molar Gibbs energies of formation, $\Delta G_f^0\,(i, T)$. Input data of one type must always be used for all the substances involved. Values of $G_i^0(T)$ or $\Delta G_f^0\,(i, T)$ have been published for many compounds (see below). If necessary, these values can be calculated from other thermodynamic properties using the following relationships:

$$G_i^0(T) = T[(G_T^0 - H_{298}^0)/T]_i + \Delta H_f^0\,(i, 298) \quad (11)$$

$$G_i^0(T) = \Delta H_f^0\,(i, 298) + \int_{298}^{T} C_{p,i}(T)\,\mathrm{d}T - T\left[S_i^0(298) + \int_{298}^{T} \frac{C_{p,i}(T)}{T}\,\mathrm{d}T\right] \quad (12)$$

$$\Delta G_f^0\,(i, T) = \Delta H_f^0\,(i, 298) + \int_{298}^{T} \Delta C_{p,i}(T)\,\mathrm{d}T - T\left[\Delta S_f^0\,(i, 298) + \int_{298}^{T} \frac{\Delta C_{p,i}(T)}{T}\,\mathrm{d}T\right] \quad (13)$$

where $(G_T^0 - H_{298}^0)/T$ is the G-function, $\Delta H_f^0\,(i, 298)$ is the standard molar enthalpy of formation of ith substance at 298.15 K, $\Delta S_f^0\,(i, 298)$ and $S_i^0(298)$ are, respectively, the standard molar entropy of formation and standard absolute entropy of ith substance at 298.15 K, $C_{p,i}(T)$ is the temperature dependence of the molar heat capacity of ith substance at constant pressure, and $\Delta C_{p,i}(T)$ is the temperature dependence of the difference in the molar heat capacities of ith substance and the elements that make up a molecule of this substance, so that $\Delta C_p(T) = (\partial \Delta H_f^0/\partial T)_p$.

In the case of multicomponent phases that cannot be regarded as having ideal behaviour, further data are needed for equilibrium calculations. This is true especially for multicomponent condensed phases, where the concept of ideal solution is merely a rough approximation. In order to account for deviations from the ideal behaviour, various empirical and semi-empirical equations have been used for the excess Gibbs energy ΔG^E as a function of temperature and composition of the given solution [18, 19]. Hence, on the basis of the general relationship

$$RT \ln \gamma_i = \left(\frac{\partial \Delta G^E}{\partial n_i}\right)_{T,p,n_{j\neq i}} \quad (14)$$

it is possible to derive equations relating the activity coefficients of the components of the solution to the temperature and composition. In order to evaluate numerical values of the activity coefficients, it is necessary to know the values of the constants appearing in these equations.

The simplest model for representing nonideal properties of condensed solutions is that of the strictly regular solution, which has been derived on the basis of the so-called zero approximation of Guggenheim's lattice theory [20]. Here, the molar excess Gibbs energy of an S-component solution is given by

$$\Delta G^E = \sum_{i,j=1}^{S} \Omega_{ij} x_i x_j, \quad \Omega_{ij} = \Omega_{ji} \text{ and } \Omega_{ii} = 0 \quad (15)$$

where Ω_{ij} is the interaction parameter of i-j binary system, which is not a function of either the temperature or the solution composition. A better representation of experimental data may be obtained by introducing an empirical temperature dependence of the parameter Ω_{ij} (the so-called simple solution model). On the basis of Equation 14, the expression for the activity coefficients of the components of the strictly regular (as well as simple) solution is obtained in the form

$$RT \ln \gamma_i = \sum_{j=1}^{S} x_j \left(\Omega_{ij} - \frac{1}{2}\sum_{k=1}^{S} x_k \Omega_{kj}\right), \quad \Omega_{ij} = \Omega_{ji} \text{ and } \Omega_{ii} = 0 \quad (16)$$

The corresponding values of the binary interaction coefficients, Ω_{ij}, can generally be obtained from experimental data, and in some cases even by a semi-empirical estimation.

Thermodynamic data for many inorganic substances are available from various data collections and monographs. Among the best known and most comprehensive are the monograph by Hultgren and co-workers

[21] (giving C_p, $H_T^0 - H_{298}^0$, S^0, $(G_T^0 - H_{298}^0)/T$, and vapour pressures for 86 elements), the tables of Barin and co-workers [22] (C_p, H^0, S^0, and G^0 for over 1830 substances), the monograph of Mills [23] (C_p, $H_T^0 - H_{298}^0$, S^0, $(G_T^0 - H_{298}^0)/T$, and ΔH_f^0 (298) for 730 inorganic compounds of sulphur, selenium, and tellurium), the tables of Glushko and colleagues [24] (C_p, $H_T^0 - H_0^0$, S^0, $(G_T^0 - H_0^0)/T$, ΔH_f^0 (0), and ΔH_f^0 (298) for over 1350 substances), and the JANAF tables [25] (C_p, $H_T^0 - H_{298}^0$, S^0, $(G_T^0 - H_{298}^0)/T$, ΔH_f^0, and ΔG_f^0 for over 1460 substances). The values for the thermodynamic functions in the above sources are given for temperatures increasing in steps of 100 K.

Data for thermodynamic properties of multicomponent condensed phases are generally less readily available. Values for some binary systems of primarily metal elements are summarized in the tables of Hultgren and co-workers [26] and in the monograph of Kubaschewski and Alcock [27]. Further data for binary and pseudobinary systems are given in various reviews, for example in [28–33]. In many cases, however, one must resort to the original literature to get the necessary data.

In addition to the printed forms of data sets, extensive computer banks of thermodynamic data for inorganic substances have been built which contain values for pure substances as well as condensed solutions stored on memory media. The software packages of such data banks include programs for calculation of phase and chemical equilibria, mass and enthalpy balances, etc., and the whole system is usually accessible on-line through a terminal network [34–38].

3. Examples of application

The application of thermodynamics in the field of materials preparation and production is most widespread in metallurgy and in the technology of classical ceramic materials and oxide glasses. The potential of thermodynamics for the description of these systems has been discussed in several monographs [27, 39–41] and a number of reviews [42–48]. Recent work in this area has been concerned with calculations of equilibria for very complex multiphase and multicomponent systems, great emphasis being placed on an adequate description of thermodynamic properties of nonideal multicomponent condensed phases [49–56].

Currently, considerable attention is paid to the application of chemical thermodynamics to the field of special materials preparation, especially the materials for electronics and optoelectronics. Thermodynamic analyses have been performed for the preparation of glass preforms for pulling optical fibres [57–59], the synthesis of single crystals of $A^{III}B^{V}$ semiconductor compounds [60, 61], deposition of semiconductor epitaxial layers from the liquid and gas phases (a number of original papers on this subject are cited in [62, 63]), the preparation of special chalcogenic glasses [64–66], the preparation of superconducting materials of A-15 type (Nb_3Ga, Nb_3Ge) [67, 68], the preparation of SiC- and Si_3N_4-based ceramic materials [67–74], and many other processes. In a number of studies, good agreement was found between the results obtained from equilibrium calculations and experimental data. For illustration, three case studies on thermodynamic analysis of processes of making special inorganic materials will be given which document the utility of equilibrium calculations for optimizing technological conditions of the processes.

3.1. Chemical vapour deposition of titanium carbonitride

Abrasion-resistant titanium carbide and carbonitride coatings are used worldwide to increase the lifetime of sintered-carbide cutting tools. The Ti(C, N) coatings are usually deposited by the CVD method under atmospheric or reduced pressure. The starting materials for the high temperature process (at about 1300 K) are $TiCl_4$, CH_4 or other hydrocarbons or their chlorine derivatives, N_2 or NH_3 and H_2. Carbonitrides of various compositions are formed depending on the initial vapour-phase composition, the pressure in the reactor, and the deposition temperature. Information on these dependences can be derived *a priori* from a thermodynamic analysis of the system Ti–C–N–Cl–H [75].

The chemical equilibrium for this system was calculated using a method based on minimizing the total Gibbs energy of the system (Equations 1–5). The solid phase composition was assumed to be represented by the stoichiometric formula TiC_xN_{1-x}, where $0 < x < 1$. The thermodynamic properties of titanium carbonitride were described in terms of the sublattice model [76, 77], with the nonideal properties of the mixture of C and N atoms on the interstitial sublattice expressed in terms of the model of strictly regular solution. The value of the interaction parameter Ω_{C-N} appearing in the relationship for the activity coefficients of the solution components (Equation 16) was optimized using available experimental data on chemical vapour deposition of solid TiC_xN_{1-x}. Solid carbonitride–gas phase equilibria were considered for 17 gases ($TiCl_4$, $TiCl_3$, $TiCl_2$, CH_4, C_2H_6, C_2H_4, C_2H_2, CH_3Cl, HCl, Cl, H_2, H, N_2, NH_3, HCN, ClCN, and C_2N_2) selected on the basis of preliminary calculations for a set of 47 gaseous substances composed of the elements Ti, C, N, Cl, and H. The thermodynamic data for the pure substances were taken from published tables [22, 24].

The calculated dependences of the solid TiC_xN_{1-x} equilibrium composition on the pressure and initial vapour-phase composition are represented in Fig. 2, where experimental results are also plotted for comparison. The comparison shows that the thermodynamic analysis of the system Ti–C–N–Cl–H in the range of technological conditions investigated allows the resulting solid-phase composition to be predicted with an accuracy of about +/− 0.05 in the mole fraction x. This is comparable with the error in the solid carbonitride composition as determined by X-ray analysis from the lattice parameter of the unit cell.

3.2. Growth of silicon-doped GaAs single crystals

Gallium arsenide single crystals are among important semiconducting materials used in electronics and optoelectronics. The material is prepared by Bridgman's

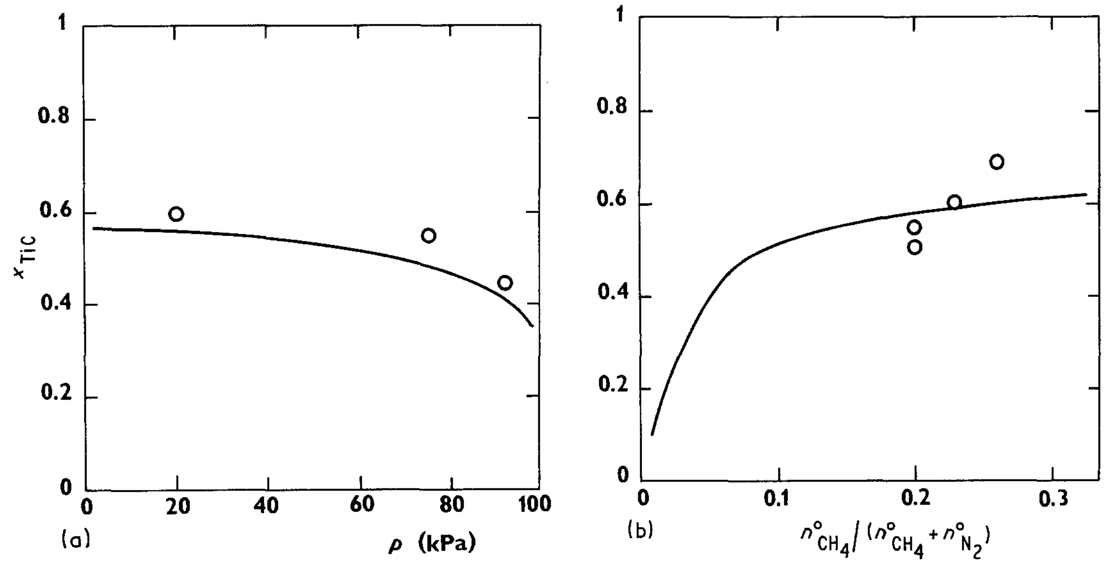

Figure 2 (a) Dependence of the equilibrium composition of solid TiC$_x$N$_{1-x}$ on pressure at 1293 K and the initial gas-phase composition TiCl$_4$ – 2.7, CH$_4$ – 4.3, N$_2$ – 27.8, and H$_2$ – 62.5 (mol %). (b) Dependence of the equilibrium composition of solid TiC$_x$N$_{1-x}$ on the ratio $n^0_{CH_4}/(n^0_{CH_4} + n^0_{N_2})$ at 1293 K, a pressure of 12 kPa, and the initial gas-phase composition TiCl$_4$ – 3, CH$_4$ + N$_2$ – 25, and H$_2$ – 72 (mol %). (——) Calculated dependence, (○) experimental data.

method, in which a GaAs melt solidifies in a quartz boat placed in a sealed ampoule at a constant pressure of arsenic vapour. At its melting point (1513 K), gallium arsenide reacts with SiO$_2$, so that the melt becomes contaminated with silicon.

The residual concentration of Si in GaAs single crystals was calculated on the assumption of a chemical equilibrium established in the system SiO$_2$(s)–GaAs(l)–gas phase. Further, dependences of Si content of silicon-doped GaAs single crystals on the amount of Si subsequently added to the melt were evaluated [61].

The overall chemical conversion in the system studied was described by the following reactions

$$\mathrm{SiO_2(s) = Si(GaAs\text{-}l) + 2O(GaAs\text{-}l)} \quad (A)$$

$$\mathrm{Si(GaAs\text{-}l) + O(GaAs\text{-}l) = SiO(g)} \quad (B)$$

$$\mathrm{2Ga(GaAs\text{-}l) + O(GaAs\text{-}l) = Ga_2O(g)} \quad (C)$$

where the symbol (GaAs-l) denotes elements dissolved in liquid gallium arsenide. The equilibrium composition was calculated using the stoichiometric algorithm (Equations 7–9). Thermodynamic data for the pure substances were taken from published tables [22, 24, 25], the value used for the limiting activity coefficient of silicon was that published by Akai and co-workers [78], and the limiting activity coefficient of oxygen was evaluated in the above cited paper [61]. The calculations were performed for a temperature of 1523 K, and the results were compared with experimental values.

The calculated value of the residual concentration of silicon, $N_{Si}{}^* = 1.39 \times 10^{16}$ atoms cm^{-3}, is in excellent agreement with the result obtained from measurement of free carrier concentration, $N_{Si}{}^* = (1\text{–}3) \times 10^{16}$ atoms cm^{-3}. Fig. 3 shows a comparison of calculated and experimental dependences of Si content of silicon-doped GaAs single crystals on the initial concentration of silicon in the melt. In the concentration range $N_{Si} = 3 \times 10^{18}$ to 3×10^{19} atoms cm^{-3}, the calculated values agree fairly well with results of spectrophotometric analysis. At lower silicon contents, however, the analysis is subject to considerable error, and the concentration of Si was therefore determined indirectly by measuring the free carrier concentration. The agreement of so obtained and calculated results is very good up to a silicon concentration of 5×10^{18} atoms cm^{-3}. Thus, equilibrium calculations for the system Ga–As–Si–O allows us to determine the amount of silicon to be added in order to reach a preassigned Si concentration in GaAs single crystals.

3.3. Refining of technical boron nitride

Boron nitride is an important ceramic material, which is currently finding use in many technological applications. The parameters of the final sintered product depend largely on the physical and chemical properties

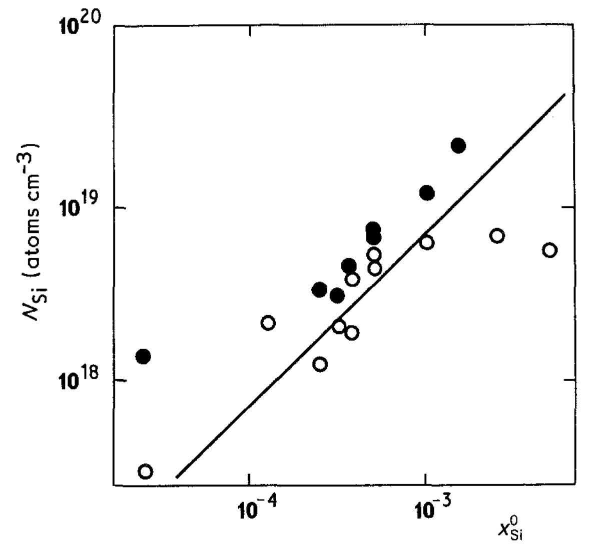

Figure 3 Comparison of calculated and experimentally determined dependences of silicon concentration in GaAs single crystals on the initial silicon concentration in the melt at 1523 K. (——) Calculated dependence, (●) results of spectrophotometric analysis, (○) results of electrical measurements (free electron concentration determined by Van der Pauw's method). (^{0} denotes initial composition).

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*Denotes residual conc.

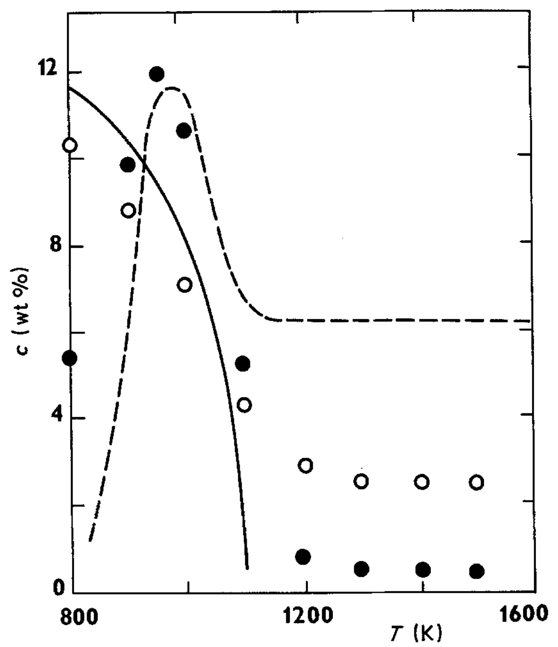

Figure 4 Comparison of calculated and experimentally determined solid phase compositions after refining of technical boron nitride by a mixture of $CHCl_3$ and NH_3 (20.5 mol % $CHCl_3$). (——) Oxygen, calculated dependence; (– – –) carbon, calculated dependence; (○) oxygen, experimental data; (●) carbon, experimental data.

of the starting powder material, of primary importance being the content of residual oxygen. One of the ways of lowering the oxygen content to the required level is by reductive chlorination. This method employs a gaseous mixture of a chlorine derivative of methane (CCl_4 or $CHCl_3$) and hydrogen or ammonia. In order to assess the effect of technological conditions on the outcome of the refining process, a detailed thermodynamic analysis of the system B–N–O–C–Cl–H has been made [79].

The chemical equilibrium in the system was calculated by a method based on minimizing the total Gibbs energy (Equations 1–5). A total of 30 gaseous substances (BCl_3, BCl_2, BCl, B_2Cl_4, BH_3, BH_2, BH, B_2H_6, $BHCl_2$, BH_2Cl, BHCl, BOCl, BOH, B_2O_3, HCl, H_2O, H_2, O_2, Cl, CO, CO_2, $COCl_2$, CCl_4, $CHCl_3$, CH_4, C_2H_4, C_2H_2, HCN, N_2 and NH_3) and five one-component condensed phases, B_2O_3(l), BN(s), B_4C(s), B(s) and C(s) were included in the calculations. All the oxygen present in the solid phase was assumed to be bound in the form of boron trioxide. Thermodynamic data for the pure substances were taken from published tables [22, 24].

The calculated and experimentally determined compositions of the solid phase after the refining by a $CHCl_3 + NH_3$ mixture are compared in Fig. 4. In the temperature range 800 to 1100 K, the agreement is very good. The results for higher temperatures indicate that all the initially present boron trioxide reacts and the oxygen passes to the gas phase. In contrast to this, residual oxygen was detected in the refined product. This contradiction may be explained by the presence of another, thermodynamically more stable oxygen-containing solid in the starting material. At temperatures above 1100 K, the agreement between calculated and experimentally determined carbon contents is only qualitative. The lower experimentally found carbon content may be due to the fact that in the refining process chemical equilibrium is not attained throughout the gas–phase volume, and so part of the input amount of $CHCl_3$ will not react, especially at higher flow rates of the gas phase.

On the basis of equilibrium calculations for the system B–N–O–C–Cl–H, technological conditions have been identified under which the initially present oxygen is substantially eliminated, while contamination of the product with carbon remains at a minimum level. The suitability of these conditions has been verified experimentally [80].

4. Conclusion

The above case studies document the importance of chemical thermodynamics and equilibrium calculations for optimizing the conditions of special inorganic materials production. The currently employed mathematical tools are sufficiently sophisticated to permit, in general, the equilibrium calculations for systems of any complexity. A point that has become of prime interest is therefore the availability of accurate thermodynamic data, not only for pure substances, but primarily for nonideal multicomponent condensed phases. Considerable effort has been expended worldwide to acquire such data, and in addition to numerous original papers, compilations have been published which give critically evaluated and consistently selected thermodynamic data. In the future, further development may therefore be expected in the application of chemical thermodynamics to the field of special inorganic materials preparation.

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