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DESIGN OF EXPERIMENTAL ROUTES AND DATA PROCESSING FOR THE DETERMINATION OF THE DEPTH-DISTRIBUTION OF ENERGY IN REAL SOLIDS

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Abstract

No adequate thermodynamic definition of non-equilibrated solids is available at present. In this paper a method is suggested for the energetic characterization of solids by estimation of the distribution of the differential molar internal energies – as they appear during the breakdown of sample e.g. by chemical reaction, i.e. the 'depth distribution of differential energies' (DDE) of samples. Thermodynamic considerations are presented for approximating this quantity – and experimental possibilities proposed to attain the needed input information by thermoanalytical methods. Application of the suggested procedure is supposed to contribute to the better understanding of structure – energy – reactivity relations in real solids.

Keywords: energy distribution, solid, state determination, test reaction

Introduction

The thermodynamic state of real, grained solids – as they are commonly used both in industry and laboratory research usually differs from their equilibrium state. This is caused by their specific structure, with non-equilibrium (extended and extrinsic) defects and in consequence by their excess energy, volume and entropy. It follows from this that their physical properties and chemical reactivity change significantly in dependence on their structure and on the changed driving forces of their reactions. Consequently, both the concepts and kinetic data concerning solids show many inconsistencies and contradictions [1]. Although the effects of these 'active' states of solids have been observed as early as the beginning of our century (De Forcrand, 1902) and intensively studied in the thirties and forties (Fricke R., Ziemens K.F., Hüttig G.F., Flügge S., Schwab G., Cremer E.) with a wealth of new, qualitative observations – the problem of thermodynamic state definition of real solids has still remained open. Furthermore, the precision of the majority of thermodynamic data – which should relate to equilibrium state – is qualified as 'moderately good – re-

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determination desirable' or 'better than nothing' [2]. A revival of interest in the problem was stimulated in the last decades by needs of materials science, mechanochemistry, and by the intrinsic interest in thermodynamics – as novel, highly developed thermoanalytical techniques promise new possibilities for better approaches.

Possibilities to define the state of solids

For equilibrated crystals, modifications of Einstein's 'one parameter model' provide a possibility of evaluation of their thermodynamic functions. 'State equations' proposed for solids may also be used. However, they are useful only for high-pressure/temperature equilibria [3]. Quantum chemistry has also provided in the last decades a wealth of information concerning structure-energy relations for crystalline molecular solids [4].

For unequilibrated states of 'homogeneous' samples, the determination of their state can be achieved by measuring their $C_p(T)$ values down to 10 K and lower, including the determination of their 'zero-point entropy'. This permits evaluation of the average values of their thermodynamic functions. However, custom-made technique and time consuming measurements are the reason that data of this kind are routinely not accessible [5].

With finely grained porous, defect solids appears the problem even more complicated, which is caused by surface and adsorption effects. It should be realized that each kind of defect represents a specific local energy. Thus, the recognition is essential that all thermodynamic functions of a real solid sample are statistical quantities and therefore they should be described by corresponding distribution functions of their local values (analogously as it is common with the distribution of adsorption energies). This has been recently postulated from kinetic considerations [6] and shown by simulations of the energy distribution of ideal and disorganized 'two-dimensional solids' [7]. Applying this approach to real samples would require the knowledge of their – not accessible – microstate [8], i.e. the positions as well as the potential-distance functions of all particles including steric and shielding effects.

Nevertheless, the increased interest in the problem stimulated different approaches for differing structure types as they differ in the kind of prevailing defects. In mixtures of inorganic oligomers, e.g. silicate glasses, the distribution of excess energy has been studied on the basis of calorimetry and appropriate thermodynamic cycles [9]. Long-term investigations on samples with ionic bonds enabled to ascribe contributions of different types of defects (surface, crystallite size, lattice strain, amorphization) to the total excess energy of mechanically activated materials [10].

Thus, it is at present not possible to define exactly the state of a real solid by routinely applicable procedures.

Because of the lack of an exact definition of state, it is common practice to give values of three sets of data:

– structure parameters (chemical composition, distribution of grain and pore radii, of crystallite sizes, phase composition, X-ray amorphous fraction etc.),

– parameters of the history of sample (i.e. the exact description of its preparation – best starting from a well-defined state),

– set of nonstructure property values (physical ones, standard properties, and others being in relation to the aimed use of sample. The term 'property means in general the quantifiable manifestation of the system studied – when submitted to a defined procedure).

It is not hard to realize that such sets of data cannot replace an exact and exhausting definition of state. However, combinations of data from the three sets above seem to be sufficient for technical/industrial needs and they are commonly used also in laboratory practice and research.

There is a growing tendency of standardization of newly developed and produced powders of commercial importance [11]. The problem treated in this paper is not without interest from this point of view, as efforts in the last three decades directed to quantification of particle shape (being a non-negligible structure parameter) failed to bring the expected results [12].

Thus, the problem remains topical in solid-state chemistry.

The aim of this paper is to suggest possibilities of determining quantities being in relation with the distribution of internal energies of real solids – accessible by thermoanalytical methods.

The depth distribution of local energies

A powdered real solid is characterized by a series of extrinsic and extended defects, residual strains, and differences in the quality and specific sizes of surface and grain boundaries. Each of these frozen-in defects contribute to the energy state of the sample. As mentioned above, it is not possible to determine local values of standard Helmholtz's energies of a sample, neither their distribution – which would provide an exact statistical thermodynamic definition of the sample. As an alternative compensation, the suggestion has been made that the internal energy/enthalpy distribution of a powdered solid – as it appears during its breakdown, e.g. by a chemical reaction – will be still characteristic of its 'structure' [13].

In a chemical reaction of the solid with another reactant being in a defined state (gas, liquid, and also with a specified solid), the process will proceed – roughly speaking – from the surface of grains towards their centre, and from the smaller particles – reacting quickly – to the coarser ones. During the course of reaction the apparent differential molar energy (ADME) of the sample – relating to an infinitesimal change of the conversion (x) will thus change in dependence on the latter (x). This dependence (i.e. frequency of ADME's) might be called the 'depth distribution of apparent molar energies' (DDE).

To realize the essence of this idea let us imagine the following extreme cases:

– in a monodisperse sample with energetically homogeneous bulk of grains there are, on the whole, two distinct energy levels: that of the surface and that of the bulk (see also [7]); with coarser samples the surface term will be negligible,

– in a polydisperse sample with energetically homogeneous bulk of grains there should be a dispersion of ADME anticipated as the value and share of surface energy depend on the particle sizes (radii of curvature). The same holds for monodisperse homogeneous porous samples with a distribution of pore diameters,

– in a monodisperse sample a radial (depth) distribution of energies may occur as a consequence of the method of sample preparation (grinding, precipitation, quenching, plasma spraying, etc.).

Commonly all the above effects appear in superposition and combined with the topical – very variable – advancement of the reaction boundary, depending on the structure of sample and on the chosen test reaction (nature of the other reactant). Thus, with a fixed test reaction the ADME will sensitively reflect the 'structure' of sample on all – micro- and macro-levels.

Recently we have shown – on the basis of thermodynamic considerations – the principal possibility of determination of the DDE [13]. The proposal assumes the experimental determination of the dependence of the heat evolved in the reaction on the conversion in the test reaction. The supposition of this dependence opposes the common convention in evaluating thermoanalytical measurements, where a direct proportionality between both quantities is being presupposed. In the following, experimental techniques and thermodynamic relations are presented, which permit determination of DDEs.

Design of experimental approaches to the determination of DDE

As mentioned above, the experimental device has to enable determination of the dependence of the enthalpy change of the system, ΔH, on the conversion of the solid reactant x for the test reaction with a sufficiently high precision. As no commercial calorimeters provide such output information, it can be equivalently replaced by measuring simultaneously the dependence of the evolved heat and of the conversion as a function of the time: $\Delta H(t)$ and $x(t)$. These functions provide the needed input in parametric form, and they are equivalent to $\Delta H(x)$ as they can be easily transformed to the latter. However, a crucial point in the treated problem is that both of these dependencies have to relate to the process itself – and do not mean the direct outputs (φ_{op}, ψ_{op}) of the measuring arrange-

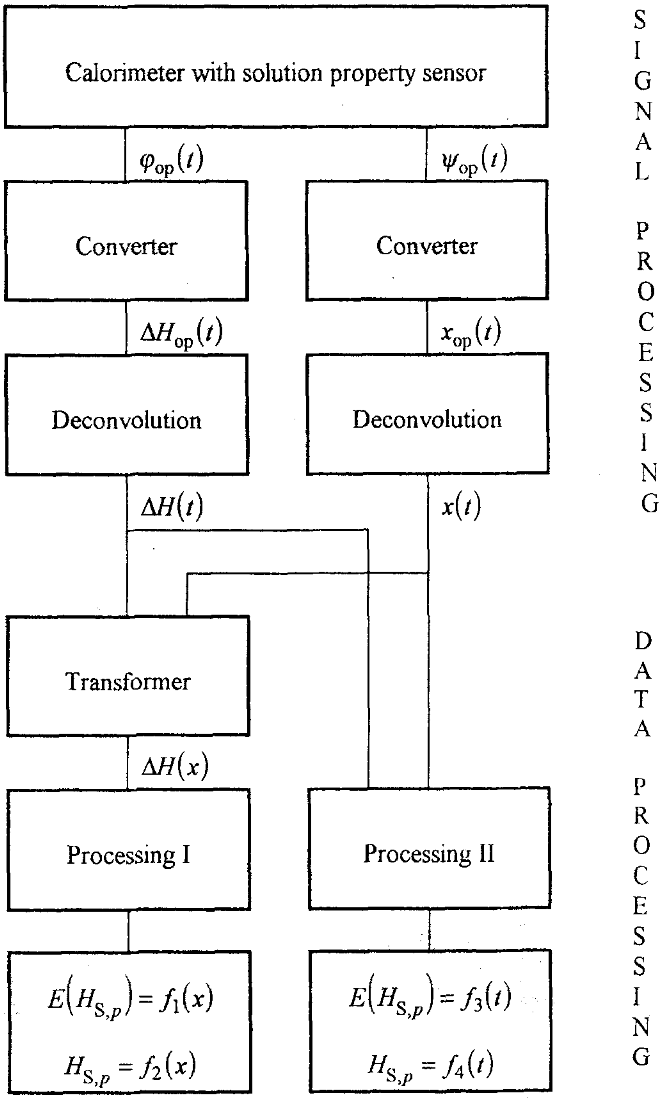

Fig. 1 Scheme of signal processing routes; $\varphi_{op}(t)$, $\psi_{op}(t)$-direct output from a calorimeter and from a solution property sensor. $\Delta H_{op}(t)$, $x_{op}(t)$, direct output converted to the corresponding enthalpy and conversion. $\Delta H(t)$, $x(t)$, deconvoluted values of enthalpy and conversion. $H_{S,p}$, the apparent differential molar energy (ADME) of the tested solid. $E(H_{S,p})$, differential distribution function of ADME's.

ments (Fig. 1). It means that the output signals of the measuring devices – being delayed in relation to the process – have to be deconvoluted after determination of their transfer functions.

Arrangement for test reactions of the type

Solid + Solution→Products (sln)

Supposedly the $\Delta H(t)$ and $x(t)$ dependencies could be best acquired via test reactions of this type, e.g.

$$MgO(s)+2HCl(sln)=MgCl_2(sln)+H_2O \tag{1}$$

The reaction path in the solution can be visualized by a straight line in the ternary diagram $HCl–H_2O–MgCl_2$. The $\Delta H(t)$ function can be derived from the output $\varphi_{op}(t)$ of a high-precision calorimeter, where the sample cell has to be equipped with a low-heat-capacity sensor – measuring some quantity $\psi_{op}(t)$ related to the composition of the solution and thus allowing to convert the sensor signal to the $x_{op}(t)$ function. Furthermore, the calorimeter should enable mixing of the solution to ensure stable hydrodynamic conditions. Fulfilling of this requirement will surely lower the parameters of the calorimeter, because of the energy additionally introduced into the reacting system and the heat escaping through the mixer's shaft. However, a twinned construction of the calorimeter with both sample and reference cell being mixed would allow compensation of these effects to a great extent. There are no commercial devices fulfilling all the requirements mentioned above but the Heat flow, Calvet-type D-80, the MS-80 or the Micro DSC III (SETARAM, France) seem to be best adaptable. Thus the whole signal processing arrangement might be devised according to the scheme in Fig. 1. The complete thermodynamic evaluation procedure is given below for this case only.

Testing via solid decomposition reaction

A(s)→B(s) + C(g)

Another possibility might be the testing of solid decomposition reactions (sulphides, oxyhydroxides, carbonates, etc.) at elevated temperatures under dynamic conditions (i.e. linear temperature-time program) in a controlled purge-gas atmosphere, where a constant pressure of the evolved gas component C(g) is being maintained. The $x(T)$ and $H(T)$ functions can be derived from simultaneous TG/DSC (DTA) measurements. Supposing that at sufficiently slow heating the process approaches equilibrium at each temperature, i.e. the Gibbs energy of the decomposition reaction should vanish during the whole run. Of course the precision of these measurements will not compete with that of a calorimeter described above, first of all because of the 'base-line problem' involved in the evaluation of DSC (DTA) curves, although great progress has been made in the last decades in TA technique (e.g. TG-DSC 111, TG-DSC LABSYS^{TM}-SETARAM, France and TG-DSC NETZSCH, FRG). However, for high-temperature measurements it has been realized that annealing (relaxation) of non-equilibrium defects can proceed before or simultaneously with the decomposition reaction [14].

The principal premises of both the dispersion of ADME and of the possibility of acquiring the *H*(*t*) and *x*(*t*) functions with test reactions of this type may be qualitatively illustrated by the following example of the partial decomposition of dolomite:

$$\mathrm{CaMg(CO_3)_2(s) = MgO(s) + CaCO_3(s) + CO_2(g)} \tag{2}$$

TG and DTA measurements were carried out with two samples of the same chemical composition: a pure natural dolomite of Eastern Slovakia. One of the samples (1) has been ground shortly – as it is common for TA determinations,

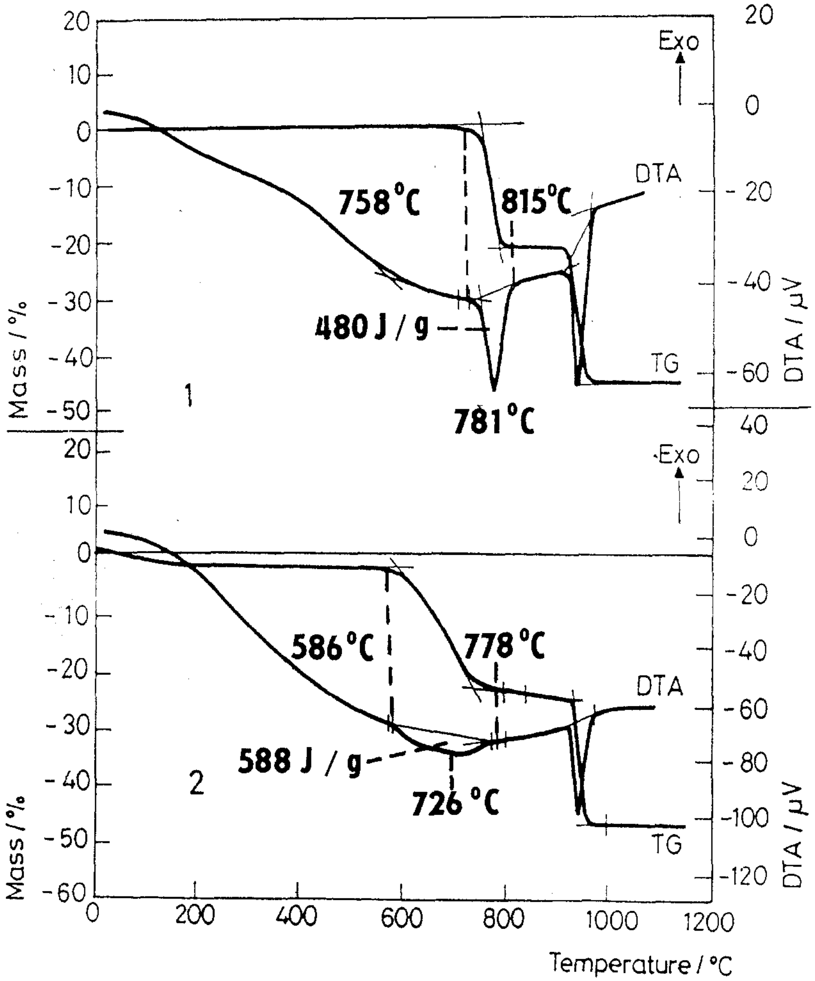

Fig. 2 TG/DTA records taken of natural dolomite in a CO_2 atmosphere before (1) and after (2) mechanical activation

the other one (2) mechanically activated by 4 h vibration milling. Both samples (provided by Mrs. L. Turčányiová from the Institute of Geotechnic of the Slovak Academy of Sciences) were measured under the same conditions in a CO_2 atmosphere (100 cm^3 min^{-1}) with a NETZSCH STA 409 instrument. Figure 2 shows the results of both runs. We are concerned here with the first, endothermic 'magnesite decomposition peak', where defect generation by milling caused its impressive broadening and shifting to lower temperatures (Table 1). Comparing the thermal effect (DTA curve) with the TG signal it is seen that different fractions of sample (2) generate different reaction enthalpies and provide – however with low precision – the needed $H(x)$ input information for the evaluation of the DDE.

Table 1 TA-parameters of the "Magnesite decomposition peak" of dolomites

Sample	1 (Reference)	2 (Activated)	Difference
Starting temp. of decomposition/K	758.8	586.1	172.7/K
Peak temp./K	781.2	725.7	65.5/K
Temp. range of decomposition/K	56.3	192.3	135.5/K
Enthalpy effect of decomposition/J g^{-1}	–480	–588	Excess enthalpy 108/J g^{-1}

Testing with a heterogeneous reaction of the type

A(s)+B(g)=C(s)

This type of reaction – A(s) being the sample tested – often proceeds at ambient and low temperatures. Thus the needed information can be obtained by means of TG and DSC technique, where the precision of determination is higher compared with high-temperature measurements.

Furthermore, this kind of test reaction provides the advantage of the possibility of testing also changes in the distribution of ADME of a sample (A(s)) with temperature, i.e. the annealing of its non-equilibrium defects independently of the reaction itself.

Testing with a solid-state reaction of the type

A(s)+B(s)=C(s)+D(g)

Reactions of this kind, e.g.

$$SiO_2(s)+2BaCO_3(s)=2BaO{\cdot}SiO_2(s)+2CO_2(g) \qquad (3)$$

where SiO_2 represents the tested sample and $BaCO_3$, supposedly very finely grained e.g. precipitated and present in great stoichiometric excess, proceed below the decomposition temperature of the carbonate. Thus CO_2 is being released only according to the reaction scheme: thus the conversion of SiO_2 (x) can be detected by TG and the thermal effect by high-temperature DSC. In this way it is possible to acquire $H(x)$ dependencies. However, the expected precision is even lower than with the decomposition reactions described above as a consequence of problems with the reproducible homogenization and compacting of the reactants.

Thermodynamic definition of the apparent differential molar energy (ADME)

Let us suppose that the tested powdered active solid sample S(s) reacts with a solution containing other reactants, or solvents, R_i ($i=1,2,\ldots,k$), as for example in reaction (1). Using the convention that the stoichiometric coefficients of the reactants on the left-hand side of the equation are negative and separating the term for the solid reactant from those for the solution, the stoichiometric equation may be written as follows:

$$\sum_i \nu_i R_i\,(\mathrm{sln}) + \nu_S S\,(\mathrm{s}) = 0 \tag{4}$$

Furthermore, the stoichiometric coefficient of the solid reactant S will be assumed to be $\nu_S=-1$. If only a physical change takes place, (e.g. dissolution), S(sln) has to be formally treated as one of the reaction products.

Let the starting system contain a solution with amounts of substances n_i^o of the components R_i and n_S^o of the solid reactant S(s). After the extent of reaction has reached ξ, the unreacted amount of S(s) is

$$n_S = n_S^o - \xi \tag{5}$$

and the amounts of R_i in the solution are

$$n_i = n_i^o + \nu_i \xi \tag{6}$$

or, in terms of the conversion of S(s) denoted as x:

$$\xi = n_S^o x \tag{7}$$

$$n_S = n_S^o\,(1-x) \tag{8}$$

and

$$n_i = n_i^o + \nu_i n_S^o x \tag{9}$$

The overall enthalpy change of the system is

$$\Delta H = H - H^o \tag{10}$$

where H and H^o are the actual and the starting enthalpy of the system, respectively. If the extent of reaction increases by dξ and the temperature by dT, the differential enthalpy change of the system will be

$$\mathrm{d}\Delta H = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}\xi + \left(\frac{\partial H}{\partial T}\right)_{\xi,p} \mathrm{d}T \tag{11}$$

The first partial derivative on the right-hand side of Eq. (11) is the actual (i.e. not the standard) reaction enthalpy $\Delta_r H$, corresponding to the actual composition of the solution, temperature and state of the unreacted rest of the solid, and the second one represents the overall heat capacity of the system, C_p:

$$C_p = \sum_i n_i \overline{C}_{p,i} + n_S C_{pS} \tag{12}$$

where $\overline{C}_p$ are the partial molar heat capacities of R_i in the solution, and C_{ps} is the mean molar heat capacity of the unreacted portion of S(s). Introducing $\Delta_r H$ and C_p into Eq. (11) with respect to Eq. (7), we get:

$$\mathrm{d}\Delta H = \Delta_r H \cdot n_S^o \,\mathrm{d}x + C_p \,\mathrm{d}T \tag{13}$$

so that

$$\Delta_r H = \frac{\mathrm{d}\Delta H - C_p \,\mathrm{d}T}{n_S^o \,\mathrm{d}x} \tag{14}$$

On the other hand, the reaction enthalpy may be expressed as

$$\Delta_r H = \sum_i \nu_i \overline{H}_i - H_{S,p} \tag{15}$$

where $\overline{H}_i$ are the partial molar enthalpies of the components of the solution and $H_{S,p}$ is the ADME of the solid corresponding to conversion x and temperature T. Then from Eq. (13) follows:

$$\mathrm{d}\Delta H = \left(\sum_i \nu_i \overline{H}_i - H_{S,p}\right) n_S^o \,\mathrm{d}x + C_p \,\mathrm{d}T \tag{16}$$

and from Eqs (14) and (15):

$$H_{S,p} = \sum_i \nu_i \bar{H}_i - \frac{\mathrm{d}\Delta H - C_p\,\mathrm{d}T}{n_S^0\,\mathrm{d}x} \tag{17}$$

Thus, Eq. (17) is the definition of the ADME on the basis of the heat effect of the chosen test reaction.

Depth distribution of differential molar energies (DDE)

This topic has been treated in [13]. Further considerations concern processes realized at constant temperature (e.g. in a quasi-isothermal calorimeter) where $H_{S,p}$ of the sample for the given test reaction and also $\bar{H}_i$ and ΔH depend only on the conversion x, therefore they will be further denoted $H_{S,p}(x)$, $\bar{H}_i(x)$, and $\Delta H(x)$, respectively.

Let $I(H_p)$ denote the integral distribution function of ADME of S(s), i.e. the fraction of S(s) with $H_{S,p}$ less than or equal to H_p and $E(H_p)$ the differential one. Derivations below hold only on the supposition that the dependence of $|H_{S,p}(x)|$ on ΔH is monotonously descending, which presumably covers the majority of practical cases. With this supposition

$$I(H_p) = 1 - x(H_p) \tag{18}$$

and

$$E(H_p) = \frac{\mathrm{d}I\,(H_p)}{\mathrm{d}H_p} = \frac{1}{\dfrac{\mathrm{d}H_{S,p}\,(x)}{\mathrm{d}x}} \tag{19}$$

where $x(H_p)$ is the conversion of S(s) at which $H_{S,p} = H_p$.

The mean value of ADME, $H_{S,f}$, is the average molar enthalpy of the whole sample:

$$H_{S,f} = \int_0^1 H_{S,p}\,(x)\mathrm{d}x = \frac{\Delta H\,(1)}{n_s^0} \tag{20}$$

Here $\Delta H(1)$ is the enthalpy change corresponding to the complete reaction of the solid. The central statistical moments which are necessary for calculation of the parameters of the distribution like dispersion, tortuosity and excess are:

$$\mu_q = \int_0^1 [H_{S,p}\,(x) - H_{S,f}]^q\,\mathrm{d}x \tag{21}$$

where q equals 2, 3 or 4, respectively.

Processing of data

If the measurement proceeds at constant temperature, Eqs (16) and (17) simplify to

$$\mathrm{d}\Delta H(x) = [\sum_{\mathrm{i}} \nu_{\mathrm{i}} \overline{H}_{\mathrm{i}}(x) - H_{\mathrm{S,p}}(x)]\ n_{\mathrm{S}}^{\mathrm{o}}\ \mathrm{d}x \tag{22}$$

$$H_{\mathrm{S,p}}(x) = \sum_{\mathrm{i}} \nu_{\mathrm{i}} \overline{H}_{\mathrm{i}}(x) - \frac{\mathrm{d}\Delta H(x)}{n_{\mathrm{S}}^{\mathrm{o}}\ \mathrm{d}x} \tag{23}$$

According to the experimental arrangement, in principle two different types of input may be provided for further consideration (Fig. 1):

1) If x and ΔH relate to the same moment, sets of corresponding values t_{j}, x_{j}, ΔH_{j} are available. Then ΔH may be expressed explicitly as a function of x, $\Delta H(x)$, using a convenient empirical relation, e.g. a polynomial (I in Fig. 1)
2) dependencies $\Delta H(t)$ and $x(t)$ (II in Fig. 1) are available.

According to Eqs (15)–(17), for evaluation of $H_{\mathrm{S,p}}$ the knowledge of the partial molar enthalpies of all components of the solution is necessary at least along the reaction path in the ternary liquid system $x(0\rightarrow1)$ (a). However, their values are accessible in very rare cases only. This problem may be eliminated in two ways:

– via experiment with a high excess of the solution (including also the reaction products) in comparison with the solid reactant; in this case the composition of the solution will change negligibly during the reaction and the partial molar enthalpies may be considered as being constant (b)
– via experiment with some reference solid sample with defined state (e.g. a monocrystalline solid) (c).

Thus, processing of data is given for two alternatives of pre-processed experimental output (Fig. 1):

$$\mathrm{I} - \Delta H(x)$$

$$\mathrm{II} - \Delta H(t),\ x(t)$$

For both cases three further alternatives are derived:

a) known $\overline{H}_{\mathrm{i}}(x)$ values (general case),
b) constant $\overline{H}_{\mathrm{i}}$ values,
c) experiment with reference sample.

I. Processing $\Delta H(x)$ being the input

I. a)

For $H_{S,p}(x)$ Eq. (23) holds. The derivative $dH_{S,p}(x)/dx$ is:

$$\frac{dH_{S,p}(x)}{dx} = \sum_i \nu_i \frac{d\overline{H}_i(x)}{dx} - \frac{d^2\Delta H(x)}{n_S^o dx^2} \qquad (24)$$

and after inserting into Eq. (19)

$$E(H_{S,p}) = \frac{1}{\dfrac{d^2\Delta H(x)}{n_S^o dx^2} - \sum_i \nu_i \dfrac{d\overline{H}_i(x)}{dx}} \qquad (25)$$

Equations (23) and (25) are parametric expressions of the dependence of $E(H_{S,p})$ on $H_{S,p}$ with x as parameter, i.e. they represent the DDE function.

I. b) Experiment with constant $\overline{H}_i$ values

Experiments of this kind may be realized with a high excess of all components in the starting solution (including the reaction products) in comparison with $S(s)$: ($n_i^o(sln) >> n_S^o$). In this case the composition of the solution will change negligibly during the reaction and the partial molar enthalpies of the components of the solution along the whole reaction path $\overline{H}_i(x)$ may approximate constant values equal to those in the starting solution, $\overline{H}_i^o$: $\overline{H}_i(x) = H_i^o$ = *const.*, so $dH_i/dx=0$ and Eqs (23) and (25) simplify to

$$H_{S,p}(x) = \sum_i \nu_i \overline{H}_i^o - \frac{d\Delta H(x)}{n_s^o dx} \qquad (26)$$

and

$$E(H_{S,p}) = \frac{1}{\dfrac{d^2\Delta H(x)}{n_s^o dx^2}} \qquad (27)$$

I. c) Experiment with a reference sample

An additional experiment may be carried out with a well-defined reference sample (e.g. a coarse-grained monocrystalline solid), for which $H_{S,p}= H_S^* =$const. Furthermore, all quantities relating to the experiment with the reference sample will be denoted by an asterisk superscript. In both experiments, the composition of the starting solution and the proportion of S(s) should be the same:

$$\frac{n_i^{*o}}{n_S^{*o}} = \frac{n_i^o}{n_S^o} \tag{28}$$

Conveniently, in practice, if $n_S^{*o}=n_S^o$, then $n_i^{*o} = n_i^o$. If (28) is valid, according to (6) the dependence of n_i on x and consequently also the composition of the solution and the partial molar enthalpies along the reaction path will be identical in both experiments at $x=x^*$ also $\overline{H}_i(x)=H_i^*(x^*)$ and

$$\sum_i \nu_i \overline{H}_i(x) = \sum_i \nu_i \overline{H}_i^*(x^*) \tag{29}$$

For the reference sample, (22) is

$$\mathrm{d}\Delta H^*(x^*) = [\sum_i \nu_i \overline{H}_i^*(x^*) - H_S^*]\, n_S^{*o}\, \mathrm{d}x \tag{30}$$

from which

$$\sum_i \nu_i \overline{H}_i^*(x^*) = H_S^* + \frac{\mathrm{d}\Delta H^*(x^*)}{n_S^{*o}\, \mathrm{d}x^*} \tag{31}$$

and, since $H_S^*=const.$

$$\sum_i \nu_i \frac{\mathrm{d}\overline{H}^*(x^*)}{\mathrm{d}x^*} = \frac{\mathrm{d}^2\Delta H^*(x^*)}{n_S^{*o}\, \mathrm{d}x^{*2}} \qquad \text{at} \quad x=x^* \tag{32}$$

After substitution from (31) into (23)

$$H_{S,p}(x) = H_S^* + \left[\frac{\mathrm{d}\Delta H^*(x^*)}{n_S^{*o}\, \mathrm{d}x} - \frac{\mathrm{d}\Delta H(x)}{n_S^o\, \mathrm{d}x}\right]_{x=x^*} \tag{33}$$

differentiation gives

$$\frac{\mathrm{d}H_{S,p}(x)}{\mathrm{d}x} = \left[\frac{\mathrm{d}^2\Delta H^*(x^*)}{n_S^{*o}\, \mathrm{d}x^2} - \frac{\mathrm{d}^2\Delta H(x)}{n_S^o\, \mathrm{d}x^2}\right]_{x=x^*} \tag{34}$$

From (19) and (34) it follows:

$$E(H_{S,p}) = \frac{1}{\left[\frac{\mathrm{d}^2\Delta H(x)}{n_S^o\, \mathrm{d}x^2} - \frac{\mathrm{d}^2\Delta H^*(x^*)}{n_S^{*o}\, \mathrm{d}x^2}\right]_{x=x^*}} \tag{35}$$

Equations (33)–(35) may be written more briefly as:

$$H_{S,p}(x) = H_S^* - \frac{d}{dx}\left[\frac{\Delta H^*(x^*)}{n_S^{*o}} - \frac{\Delta H(x)}{n_S^o}\right]_{x=x^*} \tag{36}$$

$$\frac{dH_{S,p}(x)}{dx} = \frac{d^2}{dx^2}\left[\frac{\Delta H^*(x^*)}{n_S^{*o}} - \frac{\Delta H(x)}{n_S^o}\right]_{x=x^*} \tag{37}$$

$$E(H_{S,p}) = \frac{1}{\frac{d^2}{dx^2}\left[\frac{\Delta H(x)}{n_S^o} - \frac{\Delta H^*(x^*)}{n_S^{*o}}\right]_{x=x^*}} \tag{38}$$

Thus, the first step of processing data will be the conversion of dependencies $\Delta H(x)$ and $\Delta H^*(x^*)$ into the dependence

$$\left[\frac{\Delta H(x)}{n_S^o} - \frac{\Delta H^*(x)}{n_S^{*o}}\right]_{x=x^*} = f(x) \tag{39}$$

which will further be processed according to Eqs (36) and (38) giving the DDE again in parametric form.

II. Processing of ΔH(t), x(t) being the input

II. a)

Equations (33) and (35) have to be transformed by substituting for derivatives $d\Delta H(x)/dx$ and $d^2\Delta H(x)/dx^2$, namely

$$\frac{d\Delta H(x)}{dx} = \frac{\frac{d\Delta H(t)}{dt}}{\frac{dx(t)}{dt}} \tag{40}$$

and

$$\frac{d^2\Delta H(x)}{dx^2} = \frac{\frac{d^2\Delta H(t)}{dt^2}\cdot\frac{dx(t)}{dt} - \frac{d\Delta H(t)}{dt}\cdot\frac{d^2x(t)}{dt^2}}{\left[\frac{dx(t)}{dt}\right]^3} \tag{41}$$

Inserting $d\Delta H(x)/dx$ from (40) into (23) we get:

$$H_{S,p} = \sum_i \nu_i \overline{H}_i(x) - \frac{\dfrac{d\Delta H(t)}{n_S^o dt}}{\dfrac{dx(t)}{dt}} \tag{42}$$

and analogously from (41) into (25):

$$E(H_{S,p}) = \frac{\left[\dfrac{dx(t)}{dt}\right]^3}{\dfrac{d^2\Delta H(t)}{n_S^o\, dt^2}\cdot\dfrac{dx(t)}{dt} - \dfrac{d\Delta H(t)}{n_S^o\, dt}\cdot\dfrac{d^2x(t)}{dt^2} - \left[\dfrac{dx(t)}{dt}\right]^3 \cdot \sum_i \nu_i \dfrac{d\overline{H}_i(x)}{dx}} \tag{43}$$

(42) and (43) express the dependence of $E(H_{S,p})$ on $H_{S,p}$ in parametric form with t being the parameter.

II. b) Experiment with constant $\overline{H}_i$ values

From (26) and (40) follows:

$$H_{S,p} = \sum_i \nu_i \overline{H}_i^o - \frac{\dfrac{d\Delta H(t)}{n_S^o\, dt}}{\dfrac{dx(t)}{dt}} \tag{44}$$

and from (27) and (41)

$$E(H_{S,p}) = \frac{\left[\dfrac{dx(t)}{dt}\right]^3}{\dfrac{d^2\Delta H(t)}{n_S^o\, dt^2}\cdot\dfrac{dx(t)}{dt} - \dfrac{d\Delta H(t)}{n_S^o\, dt}\cdot\dfrac{d^2x(t)}{dt^2}} \tag{45}$$

c) Experiment with a reference sample

Since the reactivity of the tested sample and that of the reference one are different, reaction rates and consequently the dependencies $x(t)$ and $x^*(t)$ will differ, too: $x(t) \neq x^*(t)$. Nevertheless, if the starting compositions of both solutions and proportions of their amounts to the corresponding amounts of solid reactant are the same in both experiments, i.e. if condition (28) is fulfilled, then (32) will also hold. Then from Eqs. (33) and (40) follows

$$H_{\mathrm{S,p}}(x) = H_{\mathrm{S}}^{*} + \left[\frac{\dfrac{\mathrm{d}\Delta H^{*}(t)}{\mathrm{d}t}}{n_{\mathrm{S}}^{*\mathrm{o}}\dfrac{\mathrm{d}x^{*}(t)}{\mathrm{d}t}} - \frac{\dfrac{\mathrm{d}\Delta H(t)}{\mathrm{d}t}}{n_{\mathrm{S}}^{\mathrm{o}}\dfrac{\mathrm{d}x(t)}{\mathrm{d}t}} \right]_{x=x^{*}} \tag{46}$$

and from (35) and (41)

$$E(H_{\mathrm{S,p}}) = \tag{47}$$

$$= \frac{1}{\left\{ \dfrac{\dfrac{\mathrm{d}^{2}\Delta H(t)}{n_{\mathrm{S}}^{\mathrm{o}}\,\mathrm{d}t^{2}}\cdot\dfrac{\mathrm{d}x(t)}{\mathrm{d}t} - \dfrac{\mathrm{d}\Delta H(t)}{n_{\mathrm{S}}^{\mathrm{o}}\,\mathrm{d}t}\cdot\dfrac{\mathrm{d}^{2}x(t)}{\mathrm{d}t^{2}}}{\left[\dfrac{\mathrm{d}x(t)}{\mathrm{d}t}\right]^{3}} - \dfrac{\dfrac{\mathrm{d}^{2}\Delta H^{*}(t)}{n_{\mathrm{S}}^{*\mathrm{o}}\,\mathrm{d}t^{2}}\cdot\dfrac{\mathrm{d}x^{*}(t)}{\mathrm{d}t} - \dfrac{\mathrm{d}\Delta H^{*}(t)}{n_{\mathrm{S}}^{*\mathrm{o}}\,\mathrm{d}t}\cdot\dfrac{\mathrm{d}^{2}x^{*}(t)}{\mathrm{d}t^{2}}}{\left[\dfrac{\mathrm{d}x^{*}(t)}{\mathrm{d}t}\right]^{3}} \right\}_{x=x^{*}}}$$

It has to be pointed out that the expressions in Eqs (46) and (47) relate to the same value of x : $x=x^{*}$ and not $t=t^{*}$.

Discussion

It is believed that the proposed determination of DDE values will contribute to the understanding of structure – energy – reactivity relations in real solids. The needed input information has been shown to be accessible by modifying today's thermoanalytical techniques. Results of thermodynamic considerations lead to the aimed distribution functions of differential internal energies of samples, i.e. to the dependencies of $E(H_{\mathrm{S,p}})$ on $H_{\mathrm{S,p}}$ in parametric form – both quantities being functions of the conversion (x): (26), (27); (36), (38) – or of the reaction time (t): (42), (43); (46), (47), respectively. As the latter relations are derived from primary experimental outputs, i.e. from $\Delta H(t)$ and $x(t)$ dependencies and contain both second-order derivatives and third power of derivatives as well – high precision of the inputs is required. Thus a pre-processing of experimental signals cannot be avoided.

The example presented for the decomposition of dolomite may show only qualitatively the correctness of the concept proposed, although no thermodynamic proofs are given here.

It is to be pointed out that the determined DDE values depend on the test reaction chosen and its conditions. Thus, the states of different samples of identical chemical composition can be compared using a defined test reaction. On the other hand, differences of DDE values of identical samples – treated with different test reactants or under different conditions will reflect differences in the progress of the reaction boundaries – as it is familiar with corrosion tests, or with chemical etching and/or polishing.

The determined DDE curves can be interpreted directly – looking for their physical meaning, i.e. for the relation between the types and proportions of the prevailing defects and their contribution to the total excess energy. On the other hand, the DDE of samples can be used to define their state – expressing the DDE curves by their statistical moments.

Excess energy is usually connected with an excess of molar volume and entropy. Consequently, the reactivity of 'active' samples is enhanced both by loosening of sample structure and by increased values of local driving forces of the reaction.

It is to be stressed that the determined DDE relates to the state of sample at the temperature and pressure of the test reaction. Non-equilibrium defects are successively annealed (relaxed) at higher temperatures – a process which may be connected with the decrease of the upper limit of the distribution function i.e. of $(H_{S,p})_{max}$. Thus, for high-temperature reactions of samples analyzed by means of the procedure proposed, only a fraction of the determined excess energy will be of use.

However, it is anticipated that the procedure proposed will be a valuable completion of other methods used to study defect solids – topical in the fields of advanced materials, structural ceramics, mechanochemistry and thermodynamics.

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