Journal of Thermal Analysis, Vol. 45 (1995) 1265-1276

ON THE EVALUATION OF DYNAMIC X-RAY DIFFRACTOMETRIC DATA FOR KINETIC AND STRUCTURAL PURPOSES

M. Epple

Institute of Inorganic and Applied Chemistry, Martin-Luther-King-Platz 6, University of Hamburg, D-20146 Hamburg, Germany

(Received February 7, 1995)

Abstract

Possible errors made due to incorrect evaluation of time- or temperature-resolved X-ray data (TXRD) are described. The extraction of compositional information, e.g., for kinetic purposes, can be highly erroneous when neglecting the influence of the changing mass absorption coefficient and a proper conversion of mass fractions to molar fractions. When structural data are computed, care should be given to a possible volume change of the sample. The correct way of evaluation and the extent of these errors is demonstrated for the thermal decarboxylation of calcium carbonate.

Keywords: $CaCO_3$, dynamic X-ray diffractometry, kinetics, solid-state reactions

Introduction

The investigation of solid state reactions and solid-state phase transitions is an important application of thermal analysis. Leaving aside general objections to the intrinsic nature of the kinetic parameters (mechanism, activation energy, pre-exponential factor) for solid state processes [1–3], it is in principle possible to evaluate a set of α/t- or α/T-values to obtain formal kinetic parameters [4, 5]. Differential scanning calorimetry (DSC) and thermogravimetry (TG) are useful methods for measuring these data.

Due to the more complex nature of solid state reactions and solid-state phase transitions as compared to homogeneous reactions [6, 7], complementary techniques are often applied. Examples are evolved gas analysis (EGA) by Fourier-transform infrared spectroscopy (FTIR, [8]) or mass spectroscopy (MS, [8, 9]), emanation thermal analysis (ETA, [10]) and time- or temperature-resolved X-ray diffractometry (TXRD). Numerous examples of the last method have recently been reviewed [11]. Structural as well as compositional data can be derived from X-ray diffractometry [12, 13]. This explains the wide applicability of this method, especially for the complex processes in the solid state.

0368–4466/95/ $ 5.00

John Wiley & Sons, Limited
Chichester

When X-ray diffractometry is applied during a defined temperature program, be it with a constant heating rate β or isothermally ($\beta = 0$), it fits the definition of a thermoanalytical method by ICTAC standards [14]. In this case, X-ray diffractograms are recorded continuously, i.e., one after the other. Then conclusions about reaction kinetics and structural changes can be drawn [11, 15].

Unfortunately, not all user groups pay sufficient attention to the fundamentals of crystallography, which are essential for a correct evaluation of the measured data. This is most important for the extraction of compositional information that may be used for a kinetic evaluation. Care must also be given when computing structural data (e.g., changing lattice parameters) during a solid state reaction or solid-state phase transition.

In this article, possible errors due to an incorrect evaluation are pointed out. The effect of neglecting the necessary corrections is demonstrated on the classical example of the decarboxylation of calcium carbonate $CaCO_3$. To improve the readability of the text, in all the following examples the reaction

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

is referred to. However, the considerations apply to any process studied by TXRD.

Errors made during the determination of the sample composition

For our example, the reaction extent α is defined as

$$\alpha = x(CaO) = 1 - x(CaCO_3) \tag{1}$$

with x the molar fractions in the reaction mixture.

Frequently, the intensity I of an X-ray peak, determined either as height or (better) as integral, is taken as a direct measure of reaction extent in a mixture. For the example of $CaCO_3$ decarboxylation, this means

$$\alpha = 1 - \frac{I(CaCO_3;\ t)}{I(CaCO_3;\ t = 0)} = \frac{I(CaO;\ t)}{I(CaO);\ t = \infty)} \tag{2}$$

Here $I(CaCO_3)$ and $I(CaO)$ denote the intensity of a calcium carbonate peak and a calcium oxide peak, respectively. Generally, all peaks of one compound should behave identically within the error limits.

This simple proportionality between reaction extent and intensity ratio is true only in some special cases. Decomposition reactions with the release of a gaseous compound generally do not follow this simple equation. In the following, the correct way for evaluation is demonstrated.

The intensity of an X-ray peak in a mixture (like a reacting system) is given by Eq. (3) [11, 13, 16]:

$$I_{ij} = \frac{K'_{ij}\, w_j}{\rho_j \cdot \mu_T^*} = K_{ij} \cdot \frac{w_j}{\mu_T^*} \tag{3}$$

with I_{ij} the intensity of the i-th peak of compound j, w_j the mass fraction of compound j in the mixture, ρ_j the density of compound j and μ_T^* the mass absorption coefficient of the mixture. K'_{ij} is a temperature-dependent constant characteristic for each peak and compound. K_{ij} is another constant defined as $K_{ij} = K'_{ij}/\rho_j$.

For our example, substitution in equation 2 yields

$$\frac{I_{i1}(\mathrm{CaO};\, t)}{I_{i1}(\mathrm{CaO};\, t=\infty)} = \frac{K_{i1}(\mathrm{CaO};\, t)\cdot w(\mathrm{CaO};\, t)\cdot \mu_T^*(\mathrm{Mixture};\, t=\infty)}{K_{i1}(\mathrm{CaO};\, t=\infty)\cdot w(\mathrm{CaO};\, t=\infty)\cdot \mu_T^*(\mathrm{Mixture};\, t)}$$

$$= \frac{K_{i1}(\mathrm{CaO};\, t)\cdot w(\mathrm{CaO};\, t)\cdot \mu_T^*(\mathrm{CaO})}{K_{i1}(\mathrm{CaO};\, t=\infty)\cdot \mu_T^*(\mathrm{Mixture};\, t)} \tag{4}$$

because $w(\mathrm{CaO};\, t=\infty) = 1$ and $\mu_T^*(\mathrm{Mixture};\, t=\infty) = \mu_T^*(\mathrm{CaO})$.

For the simple proportionality of Eq. (2) to hold, K_{i1} and μ_T^* must be constant. During a solid state reaction, all K_{ij} may often be assumed to be constant, giving

$$\frac{I_{i1}(\mathrm{CaO};\, t)}{I_{i1}(\mathrm{CaO};\, t=\infty)} = w(\mathrm{CaO};\, t)\cdot \frac{\mu_T^*(\mathrm{CaO})}{\mu_T^*(\mathrm{Mixture};\, t)} \tag{5}$$

and consequently

$$w(\mathrm{CaO};\, t) = \frac{I_{i1}(\mathrm{CaO};\, t)\cdot \mu_T^*(\mathrm{Mixture};\, t)}{I_{i1}(\mathrm{CaO};\, t=\infty)\cdot \mu_T^*(\mathrm{CaO})} \tag{6}$$

However, the mass absorption coefficient μ_T^* of the mixture changes with changing composition. Also note that the peak integral ratio gives the mass fraction w_j of compound j, not the molar fraction x_j. For a kinetic evaluation, the molar fraction is required.

The mass absorption coefficient μ_T^* of the mixture depends on its composition, i.e., the mass fraction of all elements in the mixture, regardless of valence, bonding state, etc. It can be calculated for every given mixture (see textbooks of crystallography).

Briefly, μ_T^* is

$$\mu_T^* = \sum w_E \cdot \mu_E^* \tag{7}$$

with w_E the mass fraction of each element E (Ca, O, C, ...) in the mixture and μ_E^* the mass absorption coefficient of the element. The mass absorption coefficients (also called cross sections) are tabulated for all elements. They depend on the X-ray wavelength. They increase strongly with rising atomic number.

When gaseous products are released, as during the decarboxylation of $CaCO_3$, the mass fractions of the elements in the sample change, and so does the mass absorption coefficient. This in turn influences the peak intensity in Eq. (3). The first necessary correction is therefore the calculation of the mass absorption coefficient during the reaction [13].

For copper K_α radiation ($\lambda = 1.54$ Å), the mass absorption coefficient of $CaCO_3$ is 74.26 $cm^2 \cdot g^{-1}$, and of CaO 125.35 $cm^2 \cdot g^{-1}$. It changes considerably during the decomposition. For a mixture of $CaCO_3$ and CaO, the mass absorption coefficient is additive, therefore

$$\begin{aligned}\mu_T^*(\text{Mixture}) &= w(CaCO_3)\cdot\mu_T^*(CaCO_3) + w(CaO)\cdot\mu_T^*(CaO)\\ &= \mu_T^*(CaCO_3) + w(CaO)\cdot[\mu_T^*(CaO) - \mu_T^*(CaCO_3)]\\ &= 74.26 + w(CaO)\cdot(125.35 - 74.26) \quad [cm^2g^{-1}]\\ &= 74.26 + 51.09\cdot w(CaO) \quad [cm^2g^{-1}]\end{aligned} \tag{8}$$

The *a priori* unknown factor w(CaO) in Eq. (8) can be determined by an iteration procedure, starting with $w(CaO) \approx I_{i1}(CaO; t)/I_{i1}(CaO; t = \infty)$ computing μ_T^* (Mixture) from Eq. (8), then substituting μ_T^* (Mixture) in Eq. (6) and computing the next value for w(CaO). Usually this iteration leads to convergence after a few steps. An equivalent operation is used for an educt peak of $CaCO_3$.

An alternative way to allow for the change in μ_T^* (Mixture) is the addition of an internal standard that does not take part in the reaction [16]. This could be any unreactive crystalline compound. The intensity of a peak of this inert standard changes according to Eq. (3) as well. By setting I_{ij} constant, the mass absorption coefficient of the mixture can be computed from Eq. (3), because K_{ij} and w_j are also constant. The disadvantage of this method is the necessity to assure the complete inertness of the standard (no influence on the reaction!) and the occurrence of further lines in the diffractogram. There may also be a temperature change in the intensity of a standard, rendering K_{ij} variable. For reactions involving a mass change, w_j changes too. In this case an interation procedure as described above has to be applied (Eq. (6) and (8)).

After taking into account the changing mass absorption coefficient, the mass fractions $w(\mathrm{CaO})$ and $w(\mathrm{CaCO_3}) = 1 - w(\mathrm{CaO})$ can be computed. For a kinetic evaluation, they must now be converted into the molar fractions $x(\mathrm{CaO})$ and $x(\mathrm{CaCO_3})$. Mass fractions and molar fractions are related by the molar masses.

For such a single-step reaction, one obtains [13]

$$x(\mathrm{CaO}) = \frac{1}{1 + \dfrac{M(\mathrm{CaO})}{M(\mathrm{CaCO_3})}\dfrac{1 - w(\mathrm{CaO})}{w(\mathrm{CaO})}} \tag{9}$$

and

$$x(\mathrm{CaCO_3}) = \frac{1}{1 + \dfrac{M(\mathrm{CaCO_3})}{M(\mathrm{CaO})}\dfrac{1 - w(\mathrm{CaCO_3})}{w(\mathrm{CaCO_3})}} \tag{10}$$

with $M(\mathrm{CaCO_3}) = 100.09\ \mathrm{g{\cdot}mol^{-1}}$ and $M(\mathrm{CaO}) = 56.08\ \mathrm{g{\cdot}mol^{-1}}$, this becomes

$$x(\mathrm{CaO}) = \frac{1}{1 + 0.560\dfrac{1 - w(\mathrm{CaO})}{w(\mathrm{CaO})}} \tag{11}$$

and

$$x(\mathrm{CaCO_3}) = \frac{1}{1 + 1.785\dfrac{1 - w(\mathrm{CaCO_3})}{w(\mathrm{CaCO_3})}} \tag{12}$$

In the following, it will be graphically demonstrated how the neglect of these two corrections influences the calculation of reaction extent.

Figure 1 shows a simulated reaction of $\mathrm{CaCO_3}$ to CaO. A sigmoidal α/t-curve was created using an A2 mechanism ($\alpha = 1 - \exp(-0.0004{\cdot}t^2)$). The solid line shows the "true" reaction extent of Eq. (1), i.e., $x(\mathrm{CaO})$. Also plotted are the calculated mass fraction of calcium oxide $w(\mathrm{CaO})$ and the intensity ratios for a calcium oxide and a calcium carbonate peak, respectively. It is obvious that one would obtain completely erroneous values for the reaction extent when calculating it simply from the intensity ratio of a calcium oxide peak, as in Eq. (2).

If one takes into account only the change of the mass absorption coefficient during the reaction, the corrected intensity ratio of a calcium oxide peak gives the mass fraction of CaO (Eq. (6)). This still deviates considerably from the true reaction extent.

However, the uncorrected intensity ratio of a calcium carbonate peak is almost identical with the reaction extent. This comes from the counteracting effects of increasing mass absorption coefficient (decreases I/I_o with rising α) and higher molar mass of $CaCO_3$ than CaO (increases I/I_o with rising α due to $w(CaCO_3) > x(CaCO_3)$). This is not at all a general feature of solid state reactions, just an accidental extinction of two errors.

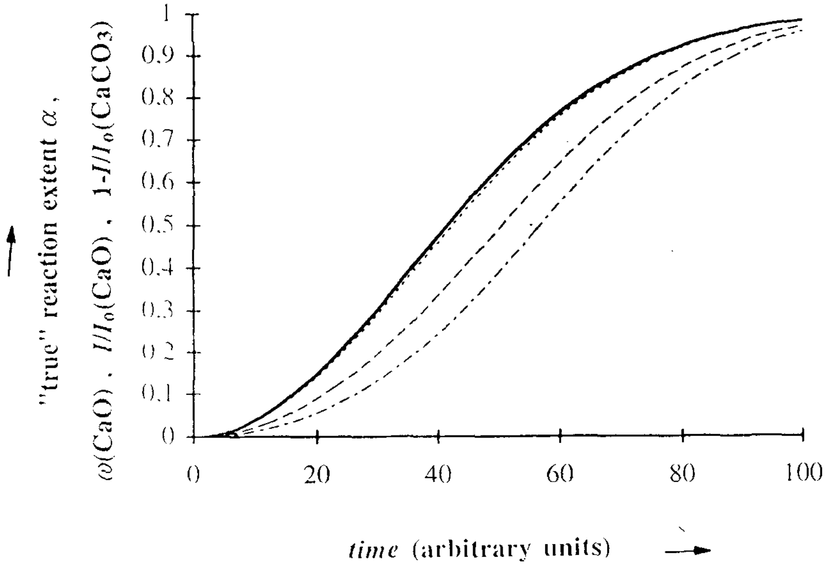

Fig. 1 One "true" and three "false" α/t-curves for the decarboxylation of $CaCO_3$. Thick solid line: "true" reaction extent $\alpha = x$ (CaO); dotted line: $1\text{-}I(t)/I(t = 0)$ for a $CaCO_3$ peak; dashed line w(CaO); point-dashed line: $I(t)/I(t = \infty)$ for a CaO peak. The α/t-curve was created with an A2-mechanism

The errors made by improper evaluation are illustrated also in Fig. 2. Here the variables of Fig. 1 are plotted against the true reaction extent α. Note that this graph is characteristic for the decarboxylation of $CaCO_3$ and invariant from the type of valid reaction mechanism. The possible error in α is about 0.2 in the worst case. For a kinetic evaluation, it is easily seen that these deviations would give different activation energies and probably also different mechanisms for each of the four curves.

Before finishing this section, it should be clearly noted that the assumption of constant values for K_{ij} during a reaction or phase transition may not always be true (Eq. (5)). Especially during structural changes, peak intensities may show a noticeable temperature-dependence. For all peaks which are used for a kinetic evaluation one should check the validity of the assumption of constant

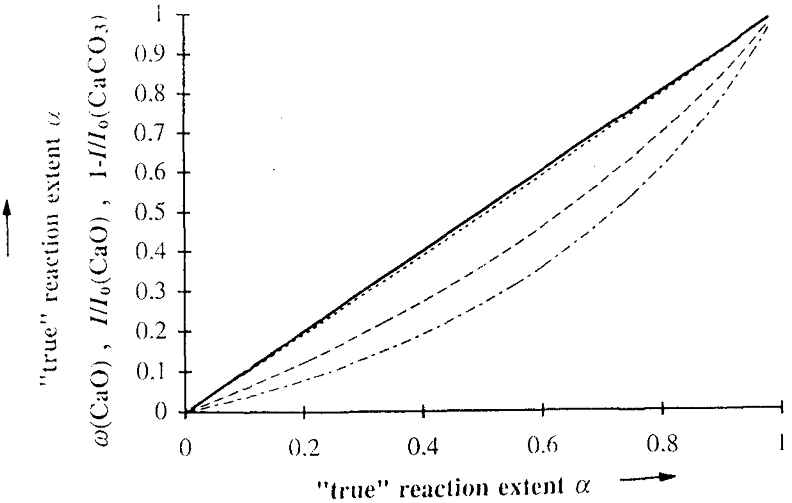

Fig. 2 Reaction extent $\alpha = x(\text{CaO})$ (thick solid line), $1\text{-}I(t)/I(t = 0)$ for a $CaCO_3$ peak (dotted line) $w(\text{CaO})$ (dashed line), $I(t)/I(t = \infty)$ for a CaO peak (point-dashed line) plotted against the reaction extent α. These curves are characteristic for the reaction $CaCO_3 \rightarrow CaO + CO_2$ and independent from the reaction mechanism

K_{ij}. This can be done for educt peaks by extrapolation of I_{ij} *vs.* T from the region before the reaction into the reaction range. For product peaks, the temperature-dependent intensities can be conveniently measured by heating up the reacted sample once more after the reaction and following $I_{ij}(T)$.

Errors made by neglect of sample volume change

The position of an X-ray peak is related to the lattice spacing by Bragg's equation:

$$n\lambda = 2d\sin(\Theta) \tag{13}$$

with n the order of diffraction, λ the X-ray wavelength, d the lattice spacing, and Θ the diffraction angle. Knowledge of the unit cell allows the calculation of the lattice parameters a, b, c, α, β, γ from suitable reflections (see textbooks of crystallography for details). Temperature-dependent experiments give temperature-dependent lattice parameters that are especially interesting during solid-state phase transformations and solid state reactions. Moreover, expansion coefficients $\mathrm{d}l/\mathrm{d}T$ can be determined.

Many authors make use of this easy computation of changing structural parameters from peak positions (°2 Θ). Structural changes are found and interpreted to shed light on the occurring process.

However, any volume change of the sample during the experiment leads to strong errors in the lattice parameters. This comes from "defocusing" of the sample in the goniometer, known as "sample displacement error" [16].

For the most common Bragg-Brentano geometry, we have

$$\Delta 2\Theta = -2\,\Delta h\,\frac{\cos\Theta}{R} \tag{14}$$

with Δh the displacement of the sample, i.e., the distance between sample surface and sample holder, Θ the diffraction angle, R the radius of the goniometer circle (instrument-dependent, of the order of 200 mm) and $\Delta 2\Theta$ the resulting error in diffraction angle [in radians]. For typical conditions, a sample displacement of only $\Delta h = 100$ µm leads to an error of $\Delta 2\Theta \approx 0.05°$.

The defocusing is displayed in Fig. 3, where *a* is a correctly aligned sample and *b* is a shrunk (defocused) sample.

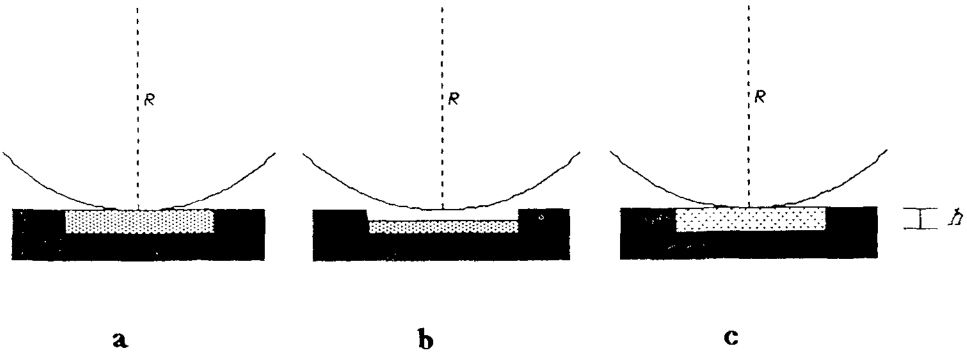

Fig. 3 The position of a powder sample in a sample holder during a solid-state process; **a** shows a correctly aligned sample with a surface tangential to the goniometer circle (radius *R*). Assuming a volume decrease as in the case of the calcium carbonate decomposition, we can either have a defocusing (case **b**) or the retaining of a loose network (case **c**). Both cases lead to errors in the determination of *d*-values

For the decarboxylation of $CaCO_3$, the effect of this displacement during the experiment will be demonstrated in the following.

The volume of the sample decreases considerably during the reaction, due to the loss of CO_2 and also due to the higher density of CaO (3.3 $g\cdot cm^{-3}$) as compared to $CaCO_3$ (2.7 $g\cdot cm^{-3}$). We have

$$V_m(CaCO_3) = \frac{M(CaCO_3)}{\rho(CaCO_3)} = \frac{100.1}{2.7} = 36.94\ [cm^3\cdot mol^{-1}] \tag{15}$$

and

$$V_m(\mathrm{CaO}) = \frac{M(\mathrm{CaO})}{\rho(\mathrm{CaO})} = \frac{56.1}{3.3} = 17.00\ [\mathrm{cm^3 \cdot mol^{-1}}] \tag{16}$$

with V_m the molar volume.

During the reaction, we have

$$\frac{V(t)}{V(t=0)} = 1 - \alpha\left[1 - \frac{V_m(\mathrm{CaO})}{V_m(\mathrm{CaCO_3})}\right] = 1 - 0.540\alpha \tag{17}$$

For a typical plane parallel sample holder, the sample height in the holder is related to the volume:

$$\frac{h(t)}{h(t=0)} = \frac{V(t)}{V(t=0)} \tag{18}$$

and

$$\Delta h = h(t{=}0) - h(t) = h(t{=}0)\left[1 - \frac{V(t)}{V(t=0)}\right] \tag{19}$$

with Δh the distance between sample holder surface and sample surface. Figure 4 shows the reduced mass change, the reduced volume change and the reduced sample displacement *vs*. the reaction extent α.

In the widely used Paar cell for high-temperature X-ray diffractometry, the sample holder has the dimensions 20×7×0.2 mm = length × width × depth. We have $h(\mathrm{t}=0) = 0.2$ mm. Substitution in Eqs (17), (19) and (14) gives

$$\Delta 2\Theta = -0.061\alpha \quad [°2\Theta] \tag{20}$$

with $R = 200$ mm and $\Theta = 10°$ ($2\Theta = 20°$).

From Bragg's equation (13), we obtain at $2\theta = 20°$:

$$\frac{\Delta d}{d} = \Delta\Theta\cot\Theta = 0.0030\alpha\ [1] \tag{21}$$

The error encountered during the decarboxylation of $\mathrm{CaCO_3}$ is shown in Fig. 5. It is linear over the whole range. It can be up to $3 \cdot 10^{-3}$ for $\alpha = 1$. This seems to be small, but it is large compared to typical expansion coefficients of inorganic materials which are of the order of

$$\frac{1}{d}\frac{\Delta d}{\Delta T} \approx 10^{-5}\,K^{-1} \tag{22}$$

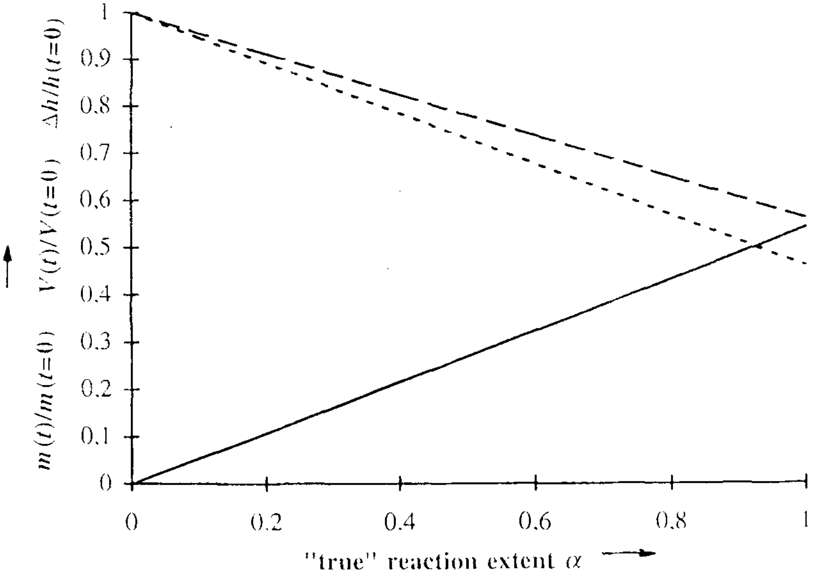

Fig. 4 Some important parameters of the sample during the decarboxylation of $CaCO_3$ plotted against the reaction extent α. We have the reduced sample mass $m(t)/m(t = 0)$ (dashed line), the reduced sample volume $V(t)/V(t = 0)$ (dotted line), and the reduced sample displacement from the top of the holder $\Delta h/h(t = 0)$ (solid line). The curves are characteristic for this reaction when carried out in a plane parallel sample holder

It is comparable to a thermal expansion in an interval of 300 K! This error would make it difficult to follow the lattice parameters of $CaCO_3$ and CaO during the reaction. It would be dangerous to draw conclusions from any values or discontinuities found.

It should be emphasized that the error displayed in Fig. 4 is the maximum error that may be encountered during the model reaction $CaCO_3 \rightarrow CaO+CO_2$. It may be the case that the sample is not shrinking according to the mass loss and density increase as calculated but rather retains a looser porous structure, as shown in Fig. 3c. In this case the sample surface is still as high as the sample holder surface ($\Delta h = 0$).

However, this leads to another error in powder diffractometry, known as the "specimen-transparency error" [16]. Not all X-rays are absorbed in the topmost layer, i.e., tangential to the goniometer circle. They are absorbed with an exponential decrease, therefore the effective sample surface is below the geometrical surface. This effect is stronger for low absorbing substances, i.e., with small μ_T^*. The formation of a porous structure reduces the mass absorption coefficient, which has the same effect as a lowering of the sample surface. The direction of the error is the same, only its magnitude is a little smaller as before.

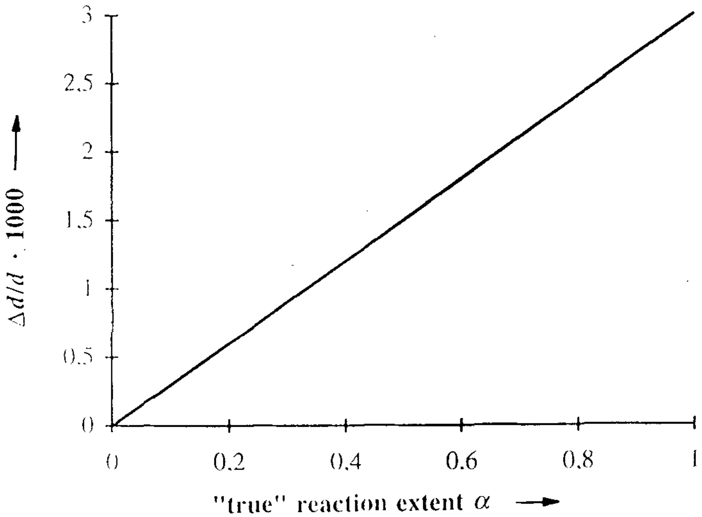

Fig. 5 The relative error made in the determination of the lattice constant during the decarboxylation of $CaCO_3$ when neglecting the volume change during the reaction. A complete volume decrease as in Fig. 3b is assumed. This curve is valid for this reaction, this sample holder and the set of parameters ($\Theta = 10°$, $R = 200$ mm) specified in the text

Note that the absolute sample displacement increases with increasing sample holder depth $h(t = 0)$ (Eq. (19)). For a thicker sample, the described error would be much higher.

To correct such a defocusing, it is recommended to add an inert standard to the sample and to correct the peak positions with this standard. The thermal expansion coefficient of the standard must be known to correct the temperature-resolved data. Recommended *d*-spacing standards are silicon, fluorophlogopite, tungsten, silver, quartz and diamond [16]. The thermal expansion coefficients for silicon in the interval of 300–1500 K can be found in [17].

Conclusions

It has been shown that incorrect treatment of X-ray diffractometric intensity data can lead to severe errors when interpreting the results. This can be especially dangerous when a kinetic evaluation is performed. The correct ways of dealing with X-ray data have been outlined and demonstrated on the decarboxylation of $CaCO_3$. After the correction of the mass absorption coefficient μ_T^* and the conversion of mass fractions into molar fractions, it is possible to compute the reaction extent.

A volume shrinking of a sample during a reaction or a phase transformation can lead to strong errors when lattice parameters are determined. This is due to a defocusing of the X-ray diffractometer. For the decarboxylation of $CaCO_3$, the error in lattice constant is comparable to a thermal expansion of a few hundred degrees. There is no easy way of correcting this error, therefore the addition of an internal standard with known lattice constants is recommended.

* * *

I thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. I gratefully thank Prof. A. Reller for generous support of my work.

References

1 M. Maciejewski and A. Reller, Thermochim. Acta, 110 (1987) 145.
2 M. Maciejewski, J. Thermal Anal., 33 (1988) 1269.
3 M. Maciejewski, J. Thermal Anal., 38 (1992) 51.
4 J. Šesták, J. Thermal Anal., 16 (1979) 503.
5 J. Šesták, J. Thermal Anal., 33 (1988) 1263.
6 W. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the solid state, Elsevier, Amsterdam 1980.
7 E. V. Boldyreva, J. Thermal Anal., 38 (1992) 89.
8 W. H. McClennen, R. M. Buchanan, N. S. Arnold, J. P. Dworzanski and H. L. C. Meuzelaaer, Anal. Chem., 65 (1993) 2819.
9 G. Székely, M. Nebuloni and L. F. Zerilli, Thermochim. Acta, 196 (1992) 511.
10 V. Balek, Thermochim. Acta, 192 (1991) 1.
11 M. Epple, J. Thermal Anal., 42 (1994) 559.
12 M. Epple and H. K. Cammenga, J. Thermal Anal., 38 (1992) 619.
13 M. Epple and H. K. Cammenga, Ber. Bunsenges. Phys. Chem., 96 (1992) 1774.
14 J. O. Hill, For better thermal analysis and calorimetry, International Confederation for Thermal Analysis and Calorimetry (ICTAC), 1991.
15 M. Epple, Thermochim. Acta, (1995) (in press).
16 D. L. Bish, J. E. Post (Eds.), Modern powder diffraction, Mineralogical Society of America, Washington DC 1989.
17 Y. Okada and Y. Tokumaru, J. Appl. Phys., 56 (1984) 314.

Zusammenfassung — Die möglichen Fehler durch eine fehlerhafte Auswertung von zeit- oder temperaturaufgelösten Röntgenmessungen (TXRD) werden dargestellt. Bei der Berechnung der Zusammensetzung einer Probe, z.B. für eine kinetische Auswertung, können erhebliche Fehler resultieren, wenn der Einfluß des sich ändernden Massenschwächungskoeffizienten nicht berücksichtigt wird. Wichtig ist auch die Umrechnung von Massenanteilen auf Stoffmengenanteile. Bei der Berechnung struktureller Größen sollte auf eine mögliche Volumenänderung der Probe geachtet werden. Die korrekte Auswertung und die Größenordnung der auftretenden Fehler werden am Beispiel der thermischen Decarboxylierung von Calciumcarbonat dargestellt.