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STUDY OF THE KINETICS OF THE MECHANISM OF SOLID-STATE REACTIONS AT INCREASING TEMPERATURES

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ABSTRACT

Possible reasons for the misinterpretation of non-isothermal kinetics are discussed. The importance of the correct selection for the assessment of the progress of the reaction and the acquisition of representative experimental data, as well as the effect of non-isothermal conditions and possible change of the equilibrium on the kinetic equation are stressed. Detailed attention is given to the probable mechanisms of individual cases of solid-state reactions as expressed in integral and/or differential forms of kinetic equations. Reactions controlled by the movement of phase boundaries, by simple nucleation, by nucleation followed by nuclei growth and by diffusion are discussed; a combined form of differential equation suggested for the preliminary appraisal of possible mechanisms is

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p$$

INTRODUCTION

The study of reaction kinetics in the solid state (and/or liquids) is mainly designed to gain information about the kinetic parameters and associated mechanisms of the process. In dynamic experiments with increasing temperature[1–4]

$$\frac{dT}{dt} = \Phi \quad \text{and} \quad t = \frac{T-T_0}{\Phi} \tag{1}$$

where Φ is the linear heating rate and T_0 the temperature of the equilibrium of conversion[6], the calculation of kinetic parameters is often simplified and may be based on the assumption that the course of the reaction can be described by the differential equation

$$\frac{d\alpha}{dt} = k'(T)\,f(\alpha) \tag{2}$$

where α is the degree of conversion, $d\alpha/dt$ the rate of reaction, $k'(T)$ the temperature dependent rate constant and f(α) a function* which represents the hypothetical model of the reaction mechanism. Apart from direct investigational methods[9,32,33], mathematical models based on hypothetical reaction mechanisms may be used[7,8,33–53].

The correlation between the reacted fraction (α) and time of reaction (t) is usually derived for isothermal studies and the variables are given in a complex form

$$\alpha = f(V, N, O, r, p, t\ldots)_{T=\text{const.}} \tag{3}$$

where

V = reacting volume of material
N = number of nuclei (or spots available for nucleation)
O = specific surface
r = geometric factor of particles (radius *etc.*)
p = partial pressure of the gaseous products

POSSIBLE SOURCES OF ERRORS AND MISINTERPRETATIONS IN NON-ISOTHERMAL KINETICS

a. Selection of a correct expression for the degree of reaction

Contrary to gases (or liquids), concentration is not a valid representative parameter for solid-state processes as it may vary through the sample[3]. Therefore, a nondimensional term, degree of conversion α, should be introduced.

The problem is, in what sense is the value of α a linear function of the physical property measured[6] and how does it represent the state of the system investigated. In basic thermoanalytical methods, such as thermogravimetry (and dilatometry) this function is defined as

$$\alpha = \frac{V_t - V_0}{V_\infty - V_0} = \frac{W_t}{W_\infty} \tag{4}$$

where V and W are weight (volume) and weight loss (volume contraction) of the sample, and indexes 0, t and ∞ indicate initial, instantaneous and final stages, respectively. Differential thermal analysis is still of questionable validity[31] because a representative value which would unambigously define the change in the system from the initial or from the final state is not yet available from a DTA peak.

b. Selection of the experimental condition for a representative experimental process model

All variable factors describing experimental conditions, such as grain size distribution, sample packing and geometry as well as the effect of dynamic environ-

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*f(α) is frequently oversimplified as $(1-\alpha)^n$ or α^m assuming analogy with homogeneous kinetics of gases[1–4], and setting n and m as orders of reaction. This simplification has, however, no general validity for solid-state reactions[5] but as an approximation it may be used to investigate the variation of apparent activation energy under different experimental conditions[29].

ment and vacuum, should be defined in terms of the equilibrium of the process[6] and be included in the function $f(\alpha)$ if they alter the reaction mechanism. Temperature deviation from a chosen temperature increase (*e.g.* due to heat of reaction in the sample[1,30]) should be minimized. Uniform and programmed temperature throughout the sample body is required for the successful kinetic investigation of solid state reactions[1]. Heat and mass transport should be facilitated as much as possible by a suitable experimental arrangement, unless they are true and valid rate controlling processes.

Two possible approaches when investigating solid-state processes can be distinguished. The physicochemical approach[7] is to separate and stress that process usually associated with the re-arrangement of molecules and ions when forming a new phase. Specially developed experimental conditions are applied (*e.g.* thin layers of solid samples in good contact with large heat reservoirs[1]) in order to obtain information about the nature of physical and/or chemical changes. On the other hand, the engineering approach[27] is used to analyse the experiments (employing large solid samples with well defined outer geometry) in terms of thermal and concentration gradients in order to obtain information about the practical application of the process.

c. *Admitting a continuous change of the equilibrium of the process during temperature increases*

Contrary to the invariant processes, where the equilibrium state of the system changes by a jump, in monovariant processes equilibrium can be a monotonous function of temperature within the temperature interval of the reaction. Therefore a non-isothermal degree of conversion λ should be introduced[6]

$$\lambda = \alpha\lambda_{eq} \tag{5}$$

where λ_{eq} is the propagation of the equilibrium. The ordinary rate of reaction $d\alpha/dt$ must then be replaced by the corrected rate of the process $d\xi/dt$[6]

$$\frac{d\xi}{dt} = \left(\frac{d\lambda}{dt} + \lambda\frac{d\ln\lambda_{eq}}{dT}\Phi\right)/\lambda_{eq} \tag{6}$$

Thus it is necessary to establish the dependence[6] of λ_{eq} on T.

d. *Construction of a kinetic equation of solid-state reactions under non-isothermal conditions*

There are some doubts[6,10–12,19,20] as to the validity of the currently used kinetic equation (Eqn. (2)) either when describing heterogeneous and/or solid-state reactions or when considering the non-isothermal character of processes.

It is the total concept of the specified rate constant ((Eqn. (2)), frequently expressed in the form of the Arrhenius equation,

$$k(T) = A\exp(-E/RT) \tag{7}$$

which has been successfully employed and derived for homogeneous kinetics. A is the frequency factor proportional to the number of successful collisions of the reacting molecules and E is the activation energy. Polanyi and Wigner[51] attempted a quantitative treatment of the rate of solid state reactions using $k(T)$ (Eqn. (7)). They assumed that the molecules which achieved the critical energy E could escape from the reactant surface (here A is the atomic frequency of vibration).

Generally the exponential character of the rate constant[23-26] for solid state reactions can be accepted, as all true solid state processes are activated processes[7]. The rate constant represents the impedance which the process must overcome to achieve the new thermodynamically favourable arrangement in the solid state. The exponent represents the statistical probability for the energy barrier E to be surpassed when the system undergoes an effort with sufficient activation energy (E). The pre-exponential factor A can then be correlated with the number of successful attempts. The missing term T^m for multiplying A (where $0 \leqslant m \leqslant 1$ is derived in different ways depending on the theoretical application of $k(T)$) can be neglected when working in narrow temperature intervals, and included in A (together with the initial weight and the molecular weight of the sample).

For a particular analysis of solid state reactions as applied to the thermal decomposition of carbonates, the activated complex theory has been employed[24]. A in Eqn. (7) is then proportional to the Maxwell distribution coefficient kT/h and the ratio Q^*/Q, where Q^* and Q are complete partition functions for the activated complex and reactant, respectively. The partition function can be expressed using the partial partition function for translation, rotation and vibration for each unit of the crystal lattice undergoing the change, with regard to their possible activities. A good agreement between experimentally calculated and numerically predicted rate constants for various types of decompositions has been found[24].

A recent publication[19] claims that the current state of knowledge of solid state kinetics is inadequate[7,32-53]. New assumptions are made, namely that heterogeneous reactions are not activated processes (with no activation energy) and that the only rate controlling process is heat exchange between the reacting mass and its surroundings.

Furthermore, it is suggested that the reaction can proceed only at a fixed (reaction) temperature T_R, given by the equilibrium of the process (where the free enthalpy $\Delta G = 0$). The corrected rate constant is then found to be proportional to the heating rate, transfer of heat (heat conductivity) and to the reciprocal value of the heat of reaction. Good agreement is found for several types of endothermic decomposition[19,20].

The objection is, however, that in this case the physical property chosen (*e.g.* weight) for measuring reaction advancement is controlled by a heat supply corresponding to the instantaneous thermodynamical need for the interface reaction equilibrium (T_R at $\Delta G = 0$). This becomes true for specific conditions of voluminous samples, where the progress of reaction is governed by the interface advancement (or crystal growth in certain cases), as will be considered in the next section. In other cases activated types of process which can proceed at temperatures higher than T_R

can also be accepted (where $\Delta G < 0$), but no proof is yet available for either of these assumptions (by measuring and distinguishing whether the reaction proceeds at T_R or above T_R).

Another source of doubt is the time–temperature dependence of α under non-isothermal conditions.

$$\alpha = \mathrm{f}(t, T(t)) \tag{8}$$

In accordance with established mathematical rules for partial derivation, Eqn. (8) can be rewritten as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial t}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t} \tag{9}$$

Some authors[12,19] claim that the formal isothermal kinetic equation is valid in the form

$$\left(\frac{\partial\alpha}{\partial t}\right)_T = k(T)\,\mathrm{f}(\alpha) \tag{10}$$

contrary to the current formulation of Eqn. (2). Using pure mathematical operations, the combination of Eqns. (9) and (10) results in the corrected non-isothermal rate constant $k'(T)$ in the form[6]

$$k'(T) = k(T)\left(1 + \frac{T-T_0}{T^2}\frac{E}{R}\right) \tag{11}$$

This correction is calculated to give ±50% in E for $(T-T_0) < 10$ and $E < 10^4$. Although it is difficult to imagine the physical meaning of the change of the degree of conversion with temperature when time is kept constant[11], particularly when temperature can change within a definite time interval, isochrones (t = const.) can be drawn[19]. This, in its way a mathematically correct approach needs more examination as there is little experimental evidence as well as logical justification[5].

There is still a confusing deviation in the activation energy values calculated from data derived from the first part of experimental results of the process. If probable experimental errors are neglected, the best mathematical approach seems to be the appreciation of a correction for the proximity to equilibrium[13,18]

$$k'(T) = k(T)(1 - \exp(-\Delta G/RT)) \tag{12}$$

where the change of free energy for the reaction (ΔG) approaches zero at the equilibrium temperature $T_0(\exp(-\Delta G/RT_0) \to 1)$ and is unchanged for stages distant from equilibrium ($\Delta G \ll 0$).

This correction has a logical justification in the obvious "activation energy" diagram, ΔG *vs.* reaction travel, and can also be derived by means of irreversible thermodynamics. The expression was originally derived for transformations passing through the vapour phase[13], and satisfactorily applied to describe heterogeneous kinetics.

It must be admitted that the theoretical concept of $k'(T)$ for solid state reactions studied under non-isothermal conditions is still not satisfactorily resolved, but it is difficult to believe that a new concept will be introduced. The proportionality constant ($K \equiv$ integral form, $k \equiv$ derivative form) in the next section will, however, be used without a closely defined meaning.

e. *Physical meaning of evaluated kinetic parameters*

Many theories have been advanced[7,8,21,22,38] in order to give a true meaning to the pre-exponential constant A (see Eqn. (2)). Generally it can be said that A can include many constants describing the initial state of the sample, such as three-dimensional shape factors of initial particles, molecular mass, density, stoichiometric factors of chemical reaction, active surface and number of lattice imperfections, *etc.*, as well as factors arising from the surface adsorption of gas, and pressure.

The activation energy E can be understood only in relation to the rate controlling processes. For example, in the case of diffusion, E can be associated with the activation energy of intrinsic diffusion as well as for substitutional reactions. Proportionality between $k(T)$ and the specific electronic conductivity can be established by the activation energy of electrical conductivity. Also, for nucleation and crystal growth the value of E is composed of activation energies of mass supply (diffusion) and factors arising from the thermodynamical potential of nucleation and/or crystal growth, *etc.*

f. *Construction of a hypothetical mathematical description of the reaction mechanism*

A formal equation in general use (simiiar to Eqn. (2)) and applicable to solid-state reactions should represent the relation between $d\alpha/dt$ and α. It sometimes includes a term $f(t)$ as well. This type of differential equation implies pure mathematical fitting of experimental data and may be treated in two ways:

1. As a pure mathematical fitting of a polynom to the experimental curve, the expression

$$f(\alpha) = A_0 + A_1\alpha + A_2\alpha^2 + \dots\dots + A_n\alpha^n \tag{13}$$

is usually employed in computer calculations of mathematical derivations (process rates)[28–30], without considering the specific reaction mechanism. Also, the use of the term "reaction order"[3] is included, having a certain physical and engineering application.

2. By using a certain logical model to form the function $f(\alpha)$ in accordance with the suggested reaction mechanism.

This equation includes the basic geometrical and physicochemical aspects of processes. A detailed analysis of this problem for classifying final equations in a simplified way is the aim of this article and will be dealt with in the following section (all thermodynamically directed aspects discussed in this section were given in detail in a previous article "Kinetics with regard to the thermodynamics of processes studied by use of non-isothermal techniques"[6]).

MATHEMATICAL DESCRIPTION OF POSSIBLE MECHANISMS IN SOLID-STATE PROCESSES

The reaction mechanism can be expressed in two ways. The ordinary formulation α *vs.* t as employed for basic isothermal concepts (see Eqn. (3))[7-9,32-50] is here mathematically transferred into the relation $\mathrm{d}\alpha/\mathrm{d}t$ *vs.* α in accordance with the requirement given by the differential Eqn. (2)[3,4,10]. The final and simplified forms of formal kinetic equations are listed below for individual types of mechanism. The left-hand side presents the equations frequently called the integrated form[15-18] and provided with function $g(\alpha)$. These functions [14-18] were satisfactorily employed in the only known method for the estimation of reaction mechanisms from dynamic TG traces by using monograms[17,18]. The right-hand side gives the equivalent forms of the function $f(\alpha)$.

a. Phase-boundary controlled processes

Surface nucleation takes place extremely rapidly and the total process is governed by movement of the resulting interface* towards the center[7,39].

A. One-dimensional movement (and some cases of evaporation)[52]

$$\alpha = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^0 = \text{constant} \tag{14}$$

B. Two-dimensional movement (for cylinder or prism)

$$1-(1-\alpha)^{1/2} = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^{1/2} \tag{15}$$

C. A sphere reacting from all surfaces inwards (three-dimensional movement)

$$1-(1-\alpha)^{1/3} = Kt; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^{2/3} \tag{16}$$

b. Reactions controlled by nucleation

A. Nucleation according to the power law[7,8]

$$\alpha = Kt^p; \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^m \tag{17}$$

where $m < 1$ and $p = 1, 2, 3, 4$ according to the spherical symmetry[36] of nuclei.

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*The rate controlling process might be the chemical reaction on this interface as given by Eqns. (14), (15), (16) or the mass and/or heat transport to or from this surface, such as diffusion or heat exchange[19] as a special case of a non-activated process following the equation[19,20]:

$$1-(1-\alpha)^{1/3} = K_0 \frac{\Phi}{\Delta H} t^2$$

This represents volatile products during the endothermal decomposition of a spherical sample where K_0 is the linear constant and ΔH is the heat of the reaction.

B. Nucleation according to exponential law[7,40]

$$\alpha = 1-\exp(-Kt^p); \quad \frac{d\alpha}{dt} = k\alpha^n(1-\alpha)^m \tag{18}$$

where n lies between $1/2$ and 1 and m between 0.774 and 0.556 corresponding to integer numbers of $p = 2, 3, 4$. For both m and $n = 1/2$, the rate of reaction was found to be proportional to the difference between interfaces of reacting solids[36]. For further reaction progress see Eqns. (20) and (21).

c. Process is governed by nucleation followed by the bulk growth of nuclei

(Nucleation proceeds according to the exponential law, see Eqn. (18)).

A. Induction stage[7,41,43]

$$\alpha = Kt^p; \quad \frac{d\alpha}{dt} = k\alpha^n \tag{19}$$

where $p \cong 4$ and $n \cong 3/4$. This equation is also suitable for the description of the linear rate of nuclei growth when the rate of nucleation is negligible[36].

B. Two-dimensional growth of nuclei[7,43] (Avrami equation)

$$-\ln(1-\alpha) = Kt^2; \quad \frac{d\alpha}{dt} = k(1-\alpha)(-\ln(1-\alpha))^{1/2} \tag{20}$$

C. Three-dimensional growth of nuclei[7,8,43] (Avrami equation)

$$-\ln(1-\alpha) = Kt^3; \quad \frac{d\alpha}{dt} = k(1-\alpha)(-\ln(1-\alpha))^{2/3} \tag{21}$$

D. Later stages (unimolecular decay law)[41]

$$-\ln(1-\alpha) = Kt; \quad \frac{d\alpha}{dt} = k(1-\alpha) \tag{22}$$

or random nucleation with one nucleus on the individual particle[17,32]. This form of the equation may also describe some cases of the decomposition and/or volatilization of pure condensed phase systems in which the reaction occurs homogeneously[36] and without dilution of the reactant by reaction products.

[E. Interaction of nucleation frequency (for $p > 4$ increasing and for $3 \leqslant p \leqslant 4$ decreasing) and time[42]

$$-\ln(1-\alpha) = Kt^p; \quad \frac{d\alpha}{dt} = k(1-\alpha)(-\ln(1-\alpha))^{p-1/p} \tag{23}$$

where $(p-1)/p$ is between $2/3$ and $3/4$. For $p = 0.63$ this equation may also be used to describe bimolecular reactions[36]. Mathematically, this is the appropriate form of the differential expressing Eqns. (18) and (31).]

d. Process is controlled by nucleation followed by the linear growth of nuclei

A. Chain growth of nuclei including the possibility of their branching[7,44]

$$\alpha = K\exp(-K't); \quad -\frac{d\alpha}{dt} = k\alpha \tag{24}$$

$\left(\text{also explosive reactions where time has a large power, } \frac{d\alpha}{dt} = k\alpha^n \text{ for } n \gg 1^{44,53,54}\right)$

B. Branching nuclei interacting during their growth[7,45]

$$\ln\frac{\alpha}{1-\alpha} = Kt; \quad \frac{d\alpha}{dt} = k\alpha(1-\alpha) \tag{25}$$

C. Later stages of A and B[7,45]

$$\ln\frac{\alpha}{1-\alpha} = K\log t; \quad \frac{d\alpha}{dt} = k\alpha^n(1-\alpha)^m \tag{26}$$

where $n < 1$ and $m > 1$.

e. Diffusion-controlled reactions

A. One-dimensional transport process with constant diffusion coefficient (parabolic law)[32-35]

$$\alpha^2 = Kt; \quad \frac{d\alpha}{dt} = k\alpha^{-1} \tag{27}$$

A similar equation, $d\alpha/dt = k\alpha^{-n}$, may also be valid for some cases of sintering where $0 < n < 1$, or possibly in the form of Eqns. (30) and (31)[9].

B. Two-dimensional transport process (*e.g.* for a cylinder with no volume change during the reaction[46])

$$(1-\alpha)\ln(1-\alpha)+\alpha = Kt; \quad \frac{d\alpha}{dt} = k(-\ln(1-\alpha))^{-1} \tag{28}$$

C. Three-dimensional transport process in a sphere* (Jander's equation[32-34,47])

$$(1-(1-\alpha)^{1/3})^2 = Kt; \quad \frac{d\alpha}{dt} = k'(1-\alpha)^{1/3}((1-\alpha)^{-1/3}-1)^{-1}$$

$$\cong k(1-\alpha)^{1/3}(-\ln(1-\alpha))^{-1} \tag{29}$$

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*These integral equations are difficult to simplify into a suitable differential form and thus an approximation is necessary:

$$(1-\alpha)^{-1/3} \cong 1+(1/3)\alpha+(4/18)\alpha^2+(21/162)\alpha^3+\ldots\ldots$$

$$\ln(1-\alpha) \cong -(\alpha+(1/2)\alpha^2+(1/3)\alpha^3+(1/4)\alpha^4+\ldots\ldots)$$

The Ginstling and Brounshtein equation[33,48,49]

$$1-2/3\alpha-(1-\alpha)^{2/3}=Kt;\quad \frac{d\alpha}{dt}=k'((1-\alpha)^{-1/3}-1)^{-1}$$

$$\cong k(-\ln(1-\alpha))^{-1} \tag{30}$$

[D. Growth of spherical particles during their precipitation determined by diffusion[50] and expressed by an approximate form of the differential equation[36]

$$-\ln(1-\alpha)=Kt^{p};\quad \frac{d\alpha}{dt}=k\alpha^{n}(1-\alpha)^{m} \tag{31}$$

where $p = 3/2$, 2, 5/2, 3 depending on interface reaction and particle size and geometry[50]. Some other authors give p a value below 0.5 in the diffusion region[36].]

DISCUSSION

A consideration of all cases of the mechanisms mentioned above with regard to the function f(α) in the differential Eqn (2) seems to indicate that it is possible to express this function in a more analytical form (there has been no attempt to give a complete enumeration). The most convenient approximation can be considered to be as follows:

$$\frac{d\alpha}{dt}=k(1-\alpha)^{n}\alpha^{m}(-\ln(1-\alpha))^{p} \tag{32}$$

thus rendering a proper combination of exponent-factors n, m and p and a mathematical description of the majority of possible mechanisms.

If the relationship

$$((1-\alpha)^{-1/3}-1)=B_{\alpha}(-\ln(1-\alpha))$$

is assumed, it is possible to establish the tendency of B_{α}. The value of B_{α} was computed as a constant using 5 terms of the series written above by means of IBM/360 for α from 0.1 (step 0.1) to 0.9

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
B_{α}	0.339	0.346	0.354	0.363	0.373	0.384	0.396	0.409	0.423

The maximum deviation from the average value for B is about ±10%. This is quite suitable having regard to the accuracy required for the experimental data and the activation energy. Thus the average value of B ($\cong$0.376) may be included in the pre-exponential factor of k, see Eqns. (29) and (30). The above series of B_{α} may also be adopted in the actual evaluation.

Combination of

n	m	p	is suitable for:
○	○	○	Phase boundary reaction (linear Eqn. (14))
×	○	○	Phase boundary reaction (Eqns. (15), (16)) Unimolecular decay law (Eqn. (22))
○	×	○	Nucleation (Eqns. (17), (19)), linear growth of nuclei (Eqn. (24)), linear diffusion (Eqn. (27))
○	○	×	Diffusion (Eqns. (28), (30))
×	×	○	Nucleation (Eqns. (18), (25)), latter stages of linear growth of nuclei (Eqns. (25), (26)), diffusion (Eqn. (31))
×	○	×	Growth of nuclei (Eqns. (20), (21), (23)), diffusion (Eqn. (30))
○	×	×	Unjustified as yet
×	×	×	Any complicated case, unjustified as yet

This equation appears to be suitable for the algorithmization of the preliminary estimation of the probable reaction mechanisms either when fitting experimental data $d\alpha/dt$ and α into different combinations of two exponent factors of Eqn. (32) in order to get a constant value for k, or by direct computation of the combination of two factors (*e.g.* by matrix evaluation). The suitability of such a treatment can be justified only by the evaluation of known experimental data. This discussion touches only upon theoretical points of view.

This procedure, however, cannot give the direct answer in the search for a true reaction mechanism. The overlapping of the values of the exponent-factors, as well as the expected difficulties with the numerical solution of Eqn. (32) will provide only a rough idea of a spectrum of possible reaction mechanisms. Therefore a complementary direct investigation of the process by means of X-ray diffraction and/or microscopy becomes necessary. This should be included in all kinetic investigations.

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