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THERMAL EFFECT OF OSCILLATING SOLID STATE REACTIONS

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ABSTRACT

Solid state reactions with an intermediate show oscillating behaviour (ref. 1, 2). The dependence of heat evolution during reaction has been derived for isothermal and dynamic conditions using the relaxation kinetic model (ref. 3) and an Arrhenius rate constants extrapolation. Simulation of ideal heat evolution curves show effects to be taken in account evaluating quantitatively DTA or DSC signals.

INTRODUCTION

The prevailing part of solid state reactions is not simple but proceeds through one or more crystallochemical intermediates. The question on principles of phase composition development during reactions of this type has often been given in the past, but not answered by theory till now.

One of the most simple cases is the synthesis of a solid - with a single intermediate, according to

$$A_s + B_s \xrightarrow{/A_2B_s/} AB_s \qquad (1)$$

THEORY

It has recently been postulated (ref. 1, 2) that reactions of the type above show oscillating character, appearing in strongly damped amplitudes of the rate of products forming during reaction.

When the initial state of the system is defined by stoichiometric composition $/n_{Ao} = n_{Bo} = 1/$ the amounts of products will depend on the conversions degree /U/ of starting substances :

$$n_{AB} = 2\,U_B - U_A \qquad (2)$$

$$n_{A_2B} = U_A - U_B \qquad (3)$$

The total reaction proceeds in general through four steps

$$A + B = AB \qquad \Delta H_1^o \quad /x/ \qquad (4)$$

$$2A + B = A_2B \qquad \Delta H_2^o \quad /y/ \qquad (5)$$

$$A + AB = A_2B \qquad \Delta H_3^o \quad /z/ \qquad (6)$$

$$A_2B + B = 2\,AB \qquad \Delta H_4^o \quad /u/ \qquad (7)$$

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according to the scheme

$$\begin{tikzcd} & AB \arrow[dr, "z"] & & \\ A + B \arrow[ur, "x"] \arrow[rr, "y"'] & & A_2B \arrow[r, "u"] & AB \end{tikzcd} \qquad (8)$$

where /x,y,z,u/ are extents $(\Delta n_i/\nu_i)$ of simple reactions (4) - (7), and ΔH_i^o their standard enthalpy changes, (ν_i - stoichiometric coefficient).

From (1), (2) and (4) - (7) follows :

$$d\, n_{AB} = dx - dz + 2du = 2dU_B - dU_A \qquad (9)$$

$$d\, n_{A_2B} = dy + dz - du = dU_A - dU_B \qquad (10)$$

and

$$\Delta H_3^o = \Delta H_2^o - \Delta H_1^o \qquad (11)$$

$$\Delta H_4^o = 2\,\Delta H_1^o - \Delta H_2^o \qquad (12)$$

Thus the standard enthalpy change of the whole system during reaction will then be

$$\Delta H^o = \Delta H_1^o dx + \Delta H_2^o dy + \Delta H_3^o dz + \Delta H_4^o du \qquad (13)$$

By substitution of (9) (10) (11) (12) into (13), derivation and rearraning we get

$$\frac{d\,\Delta H^o}{dt} = /2\,\Delta H_1^o - \Delta H_2^o/\,\frac{dU_B}{dt} + /\,\Delta H_2^o - \Delta H_1^o/\,\frac{dU_A}{dt} \qquad (14)$$

The consumption of each starting component /j/ might be expressed by its conversion /U/ (ref. 3)

$$U_j = \sum_{i=1}^{p_j} X_{ji}\left[1 - \exp /- r_{ji}\, t/\right] \qquad (15)$$

where p=the number of different reactivities $/r_{ji}/$, X_{ji}=the molar fraction of the reactivity /i/, and t=the reaction time.

By derivation of (15) we get

$$\frac{dU_j}{dt} = \sum_{i=1}^{pj} X_{ji} \cdot r_{ji} \cdot \exp /- r_{ji}\, t/ \qquad (16)$$

Thus the thermal effect of an isothermal /ideal/ DSC run will be given by substitution of (16) into (14).

Supposing that reactivities depend on temperature according to the Arrhenius low

$$r_{ji} = r_{jio} \exp /- \frac{E}{R.T}/ \qquad (17)$$

and a linear heating rate

$$T = at + T_o \qquad (18)$$

we get by substitution of (18) and (17) into (15) and derivation

$$\frac{dU_j}{dt} = \sum_{i=1}^{p_j} X_{ji} r_{jio} \left(1 + \frac{a.b.t}{/at+T_o/^2}\right) \exp\left(\frac{-b}{at+T_o}\right) \exp\left[-r_{jio} t.\exp\frac{-b}{at+T_o}\right] \qquad (19)$$

where b = E/R.

By substitution of (19) for both A and B into (14) we will get the heat evolution during reaction (1) under dynamic conditions.

EVALUATION

Experimental values of starting components consumption in reaction of $CaCO_3$ with pure natural quartz (ref. 4) at 1573 K in a mixture of air and water vapour /9:1/ could be correlated by a two term /p_j=2/ relaxation kinetic model according to relation (15). Parameters of the relation were computed by the Simplex method from experimental data and are given in Table 1. The reactivities /r_{jio}/ were derived from (17) with an estimation of $E = 25\ 104\ J.mol^{-1}$. The standard enthalpy changes corresponding to (4) and (5) are :

$\Delta H_1^o = -\ 32\ 500\ J.mol^{-1}$ and $\Delta H_2^o = -\ 61\ 534\ J.mol^{-1}$ (ref. 5).

TABLE 1.

Reactivities r_{ji} and r_{jio} /min^{-1}/ and their fractions /X_{ji}/ in the reaction of CaO /C/ and SiO_2 /S/ at 1573 K.

	X_1	X_2	r_1	r_2	r_{1o}	r_{2o}
CaO	0,707	0,293	0,19	0,0160	8,36	0,7270
SiO_2	0,509	0,491	0,22	0,0014	9,97	0,0634

The heat evolution during reaction

$$CaO + SiO_2 \xrightarrow{/2CaO\ .\ SiO_2/} CaO\ .\ SiO_2$$

at conditions given above - has been computed according to the procedure given in THEORY.

With $dQ = -\ d\,\Delta H^o \sim \Delta T$, relation (14) describes the dependence of heat evolution on time, i.e. it simulates an idealized isothermal DSC or DTA curve /Fig. 1 a/. Computed results show, that the TA signal falls practically to zero value when the SiO_2 conversion degree /U_S/ is only about 0,5.

Similary the heat evolution was computed in dependence on temperature according to (19) and (14) for dynamic conditions with linear temperature raise /$a = 20\ K\ min^{-1}$, $T_o = 300\ K$/ See Fig. 1 b.

It is evident that the heat evolution curve might show a shoulder or, under some conditions, a double peak.

From the study follows, that the progress of solid state reactions of the type studied cannot be derived from thermoanalytic curves in the usual simple way.

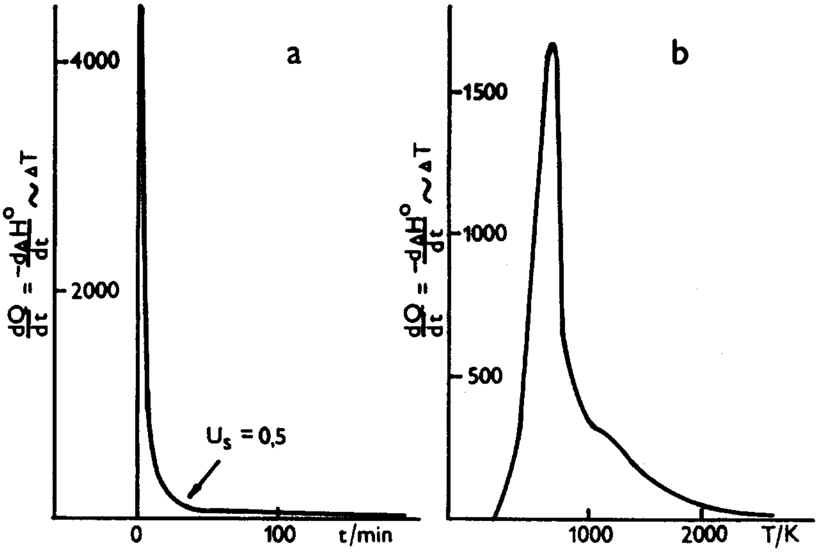

Fig. 1. Computed isothermal /1573 K/ /a/, and dynamic /b/ DSC curves of the reaction mixture C + S /1:1 molar/.

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