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Use of the Quartz Crystal Microbalance for Kinetic Studies of Thermal Decomposition of Solids

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A quartz crystal microbalance has been proposed for studies on the temperature dependence of the linear rate of a reaction interface advance in topochemical reactions of the thermal decomposition of solids. A quartz crystal microbalance has been used in investigations of the $CuSO_4 \cdot 5H_2O$ dehydration. The data agree fairly well with those available in the literature. Advantages and disadvantages of the method proposed are discussed.

Introduction

At present the temperature dependence of the rate of a reaction interface advance, $V(T)$, in topochemical reactions of thermal decomposition of solids,

$$A(s) \rightleftarrows B(s) + C(g), \qquad (1)$$

is usually studied on powders (*1*). Reactions (1) proceed, as a rule, through formation and growth of nuclei. However, since nucleation is a random process the indeterminate effects of the total area of the reaction interface acquires primary importance. The problem was first solved by Garner and Tanner (*2*) who prevented the nucleation stage by activating the initial reactant faces. They rubbed the faces of a $CuSO_4 \cdot 5H_2O$ single crystal with the dehydration product. As a result, $CuSO_4 \cdot 5H_2O$ dehydration started over the entire activated surface which led (with sufficient accuracy) to formation of a planar product–reactant interface. Garner and Tanner's idea (*2*) was then developed by Fichte and Flanagan (*3*): to study $V(T)$ along a single direction, they artificially coated appropriate crystal surfaces with glue to impede gaseous product release. In this case, the reaction interface did move in the preset direction. An analogous result can be obtained with a sample shaped as a thin plate. Here the contribution from the side surfaces to the overall reaction rate is negligible (*4*). The temperature dependence of the interface advance rate $V(T)$ in samples prepared in the above manner (*2–4*) can be investigated as follows: $V(T_1)$ is first measured at a certain temperature T_1; then the thermostat temperature is changed to T_2, $V(T_2)$ is then measured, after thermal equilibrium between the sample and the thermostat is established, etc. (*5*). If the rate of advance of the reactant–product interface does not depend on the product layer thickness, this method permits isothermal investigations of $V(T)$ to

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be carried out over a wide temperature range in the same sample. Unfortunately, this method of studying thermal decomposition reactions (1) has not found wide use, principally, because of serious disadvantages (*6, 7*) of the balance methods that have been employed. Indeed, investigators are often confronted by the dilemma that a decrease in pressure in the reaction vessel, required to reduce the reverse reaction (which is especially important for reversible reactions (*8*)), worsens the reactant–thermostat heat exchange and hence randomly changes the reaction zone temperature. Analogously, a rise in pressure inside the reaction vessel, required to improve the heat exchange, increases the reverse reaction contribution. As a result, the most current $V(T)$ studies involve photomicrography of nuclei (*10*). This technique, however, is too laborious to enjoy wide use.

We believe that the above method of investigating thermal decomposition reactions (*2–5*) can be utilized provided mass-loss measurements are replaced by studies of the temperature dependence of the gaseous product flux $j(T)$. If ρ_0 is the density of the substance in the initial reactant that is removed during thermolysis, then in the vicinity of the plane reactant–product interface,

$$j(T) = \rho_0 V(T). \tag{2}$$

The available methods of $j(T)$ measurements (*11*) are highly sensitive and, what is more, free from the limitations of the balance methods (*6, 7*). A quartz crystal microbalance (*12*) has other general advantages (*11*). It can be easily constructed and operated and it is the most sensitive of the methods available, being almost unaffected by mechanical shocks and external vibrations.

In the present paper a quartz crystal microbalance is proposed for investigations of the rate of advance of a reaction interface as a function of temperature, $V(T)$ (see Eq. (2)) in thermal decomposition reactions (1), under the above experimental conditions (*2–5*). This technique is illustrated for the case of the copper sulfate pentahydrate dehydration.

A Quartz Crystal Microbalance

Quartz crystals oscillating at their resonant frequency are commonly used in electronics for frequency stabilization. The same crystals are usually used to measure the thickness of deposited films (*12*). The physical basis of the method is that a film of a material deposited on a quartz crystal affects the resonant frequency of the latter. In first approximation the frequency shift Δf is determined by the film thickness d_i and the film density ρ_f by (*12*)

$$\Delta f \cong \frac{2\rho_f d_i f_0 f_i}{\rho_q v_q} \tag{3}$$

where $\rho_q = 2.648\ \mathrm{g \cdot cm^{-3}}$ is quartz density, $v_q = 3.336 \times 10^5\ \mathrm{cm \cdot sec^{-1}}$ is the velocity of shear wave propagation in quartz. The resonant frequences with and without the film are f_i and f_o, respectively. This property of a quartz crystal has been sufficiently used to investigate condensation coefficients (*13*) and adsorption isotherms (*14, 15*) of gases, oxidation kinetics of aluminum (*16–19*) and iron (*20*) films, PbI_2 photolysis (*21*), silver sulfidization, and iodization (*18, 22*), and cobalt sublimation (*23*).

The setup for $V(T)$ studies in thermal decomposition reactions (1) is shown schematically in Fig. 1. It utilizes a quartz crystal as a detector of the reaction product flux $j(T)$. The initial single crystal reactant in the form of a thin disk is placed on a thermostatically controlled support in a high-vacuum chamber. The thermal contact between the sample and support is improved by an indium–gallium eutectic. The product–reactant interface is rendered planar by activating the outer surface of the crystal

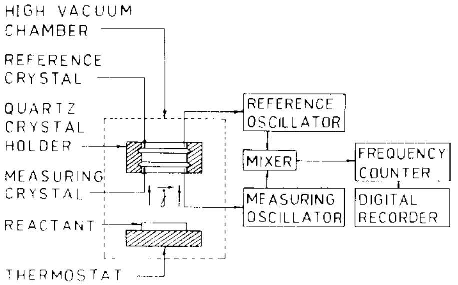

FIG. 1. Apparatus for rate measurements of thermal decomposition of solids schematic.

with fine abrasive (*2*). The measuring quartz crystal (f_0 = 6 MHz, AT-cut, ϕ = 1.2 cm) is fastened in a specially designed holder some 2 cm above the sample. After evacuation of the high-vacuum chamber to the limiting pressure (the dynamic vacuum, less than 4×10^{-5} Pa, was maintained during all experimental runs), the quartz crystals are cooled to the boiling-point of liquid nitrogen and kept at this temperature during the whole experiment. The quartz crystal resonant frequency (both measuring and reference ones) versus temperature characteristics were determined in advance (*24*); quartz crystals with the same characteristics were used. On reaching the cooled quartz crystal, a portion of gaseous molecules—reaction products—condenses, thus affecting the resonant frequency of the measuring quartz crystal (This method can evidently be applied only to studies of reactions whose gaseous products condense to solid phase at the boiling-point of liquid nitrogen, e.g., CO_2, NH_3, H_2O.) If the molecular flux of the gaseous reaction product $j(T)$ is constant, the mass of the substance that has condensed on the quartz measurement crystal within a time $\Delta t = t_j - t_i$ is

$$\Delta m = S \cdot j(T) \cdot k \cdot (t_j - t_i) \qquad (4)$$

or, taking into account Eq. (2),

$$\Delta m = S \cdot V(T) \cdot \rho_0 \cdot k \cdot (t_j - t_i) \qquad (5)$$

where S is the electrode area, k is the empirical coefficient (see below). On the other hand,

$$\Delta m = S \cdot \rho_f \cdot (d_j - d_i) \qquad (6)$$

where d_j and d_i are the film thicknesses of the condensed reaction product on the measuring quartz crystal at times t_j and t_i, respectively. Thus, Eqs. (5) and (6) yield

$$V(T) = \frac{\rho_f}{\rho_0 \cdot k} \cdot \left(\frac{dj - d_i}{t_j - t_i}\right). \qquad (7)$$

It has been shown (*24*) that

$$d_i = \frac{v_f}{2 \cdot \pi \cdot f_i} \cdot \tan^{-1}\left\{\frac{\rho_q \cdot v_q}{\rho_f \cdot v_f} \cdot \tan\left[\pi \cdot \left(\frac{f_0 - f_i}{f_0}\right)\right]\right\} \qquad (8)$$

where v_f is the velocity of shear wave propagation in the film deposited on the quartz crystal. If the frequency shift of the measuring quartz is small, Eqs. (7) and (8) yield

$$V(T) \cong \frac{\rho_q \cdot v_q}{2 \cdot \rho_0 \cdot k \cdot f_i \cdot f_j} \cdot \left(\frac{f_i - f_j}{t_j - t_i}\right) \qquad (9)$$

The applicability of Eqs. (8) and (9) is discussed below.

The residual atmosphere in the high-vacuum chamber can be taken into account by use of a reference quartz crystal (Fig. 1). Simple, yet reliable, electric circuits generators (both measuring and reference ones) are described in Refs. (*24*, *25*). In our case we have used the circuit proposed by Ashworth and Shacklette (*25*).

Calibration of the Quartz Crystal Microbalance

The coefficient k in Eq. (7) depends on the geometry of the quartz crystal holder, the distance between crystal holder and reactant, the geometry of the reactant, and the condensation coefficient of the gaseous product flux on the measuring quartz crystal which is cooled to the boiling-point of liquid nitrogen. For a particular gaseous product (in our case it is H_2O) and for the standard geometry of setup units, mentioned above, the k remains constant.

The coefficient k can be determined empirically as follows: a sample of standard geometry prepared in the above manner is first weighed to determine the mass, m_1, that escapes after full decomposition of the reagent. If all the substance is assumed to condense on the measuring quartz crystal, the film thickness is given by

$$d_1 = \frac{m_1}{\rho_f \cdot S} \tag{10}$$

Since some of the gaseous product deposit elsewhere or escape and since the condensation coefficient in general is not equal to 1 (*11, 13*), the film thickness will be $d_2 < d_1$. Since the sample decomposes completely, the value of d_2 can be calculated (Eq. (8)) by the frequency shift measured experimentally. Hence,

$$k = d_2/d_1 \tag{11}$$

In our case the quartz crystal microbalance was calibrated by the dehydration reaction

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O + 4H_2O \tag{12}$$

The film thickness d_2 was calculated by Eq. (8) using $\rho_f = 0.96$ g · cm^{-3}, $v_f = 1.909 \times 10^5$ cm · sec^{-1} (*26*). Measurements carried out with three samples of standard geometry (see below) have shown that $k = (0.178 \pm 0.002)$. For any other kind of gaseous product the coefficient k must be determined independently.

$CuSO_4 \cdot 5H_2O$ Dehydration

Copper sulfate pentahydrate dehydration (12) is one of few reactions of thermal solid decomposition allowing one either to circumvent or to minimize the above-mentioned difficulties during the investigation (*2–9*). Hence, it is expected that the $CuSO_4 \cdot 5H_2O$ dehydration kinetics studied with a quartz crystal microbalance will indicate the reliability of the kinetic parameters obtained by our method.

$CuSO_4 \cdot 5H_2O$ single crystals were grown from a saturated water solution by evaporation at room temperature. The crystals obtained, free from visible growth imperfections (microscopic control), were used to cut out 0.1-cm-thick disks, 0.6 cm in diameter. To eliminate the nucleation stage, one of the faces was rubbed with fine abrasive; the opposite face and the side surfaces were covered with an indium–gallium eutectic. The In–Ga eutectic performed two functions: First, it eliminated the reaction on the side surface (as did the watertight glue in Ref. (*3*)); second, it ensured thermal contact between the sample and the thermostatically controlled support which is extremely important for endothermic reactions in high vacuum (*9*). The sample was then placed inside the high-vacuum chamber on the thermostatically controlled support (Fig. 1). The sample was cooled to $T = 258$ K to prevent dehydration during evacuation of the system up to the limiting pressure $P \sim 4 \times 10^{-5}$ Pa. Then the quartz crystals were cooled to the boiling-point of liquid nitrogen.

The reaction (12) has been found (*9*) to slow down as the solid product layer $CuSO_4 \cdot H_2O$ grows. Therefore, $V(T)$ studies in any sample must be preceded by investigations of the rate of the reaction interface advance as a function of the product layer thickness. To this end, the sample was decomposed for 320 min at $T = 303$ K (Fig. 2). The instantaneous rate of the reaction interface advance was calculated by both the exact Eq. (8) (Fig. 2, ●) and the approximate Eq. (9) (Fig. 2, ▲). In the calculations we used $\rho_f = 0.96$ g · cm^{-3}, $v_f = 1.909 \times 10^5$ cm · sec^{-1} (*26*). Figure 2 shows the approximate relation, Eq. (9) to be valid, as expected, at small frequency shifts of the measuring quartz crystal. It follows also from Fig. 2 (●) that after the slow initial

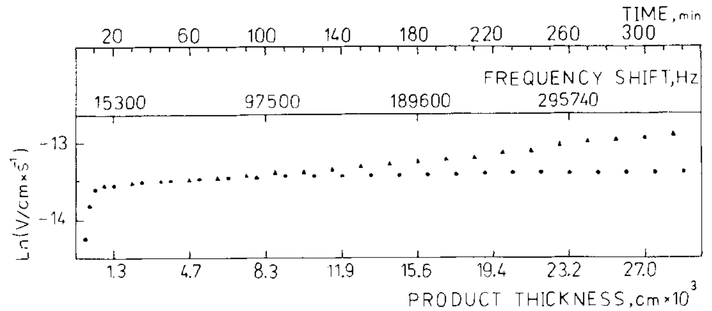

FIG. 2. Plots of the linear rate of a reaction interface advance vs the product layer thickness for $CuSO_4 \cdot 5H_2O$ at $T = 303$ K. (●) Exact Eq. (8), (▲) approximate Eq. (9).

increase the V values reach a "plateau" and then become practically independent of the solid product layer thickness. We carried out the investigation to a product's thickness of up to 2.7×10^{-2} cm, sufficient for the one experimental run. The partly decomposed sample was then cleaved, and the cleavage surface was investigated with an optical microscope. The product layer thickness corresponded to that calculated, and the reactant–product interface was found to have a plane geometry and was parallel to the initial face (110). Thus, studies on the rate of the reaction interface advance as a function of the product layer $CuSO_4 \cdot H_2O$ thickness at a constant temperature supply information necessary for $V(T)$ investigations in this one sample.

As the next step of our investigations every newly prepared sample was first decomposed at $T = 303$ K until the V values reached the "plateau" (Fig. 2). Thereafter the frequency shifts were measured versus time at various temperatures of the thermostat (Fig. 3). The data obtained were used to calculate $V(T)$ by Eqs. (7) and (8). Figure 4 depicts the calculated results in the Arrhenius coordinates. Under the assumption that the interface advance rate $V(T)$ is

$$V(T) = \delta \cdot \nu \cdot \exp(-E/RT) \qquad (13)$$

(where δ is the distance between neighboring water molecules in the lattice), the method of the least squares yields the following kinetic parameters: $\nu = (1.8 \pm 0.5) \times 10^{14}$ sec^{-1}, $E = (17.8 \pm 0.2)$ kcal/mole (for $\delta = 5 \times 10^{-8}$ cm).

Smith and Topley (9) have shown that for $273 < T < 316$ K the rate constant of reaction (12) is

$$\log K = 12.112 - 3982/T, \qquad (14)$$

where K is in [mg · cm^{-2} · min^{-1}]. Simple recalculations of the above data then yield $E = 18.21$ kcal/mole, $\nu = 6.5 \times 10^{14}$ sec^{-1}.

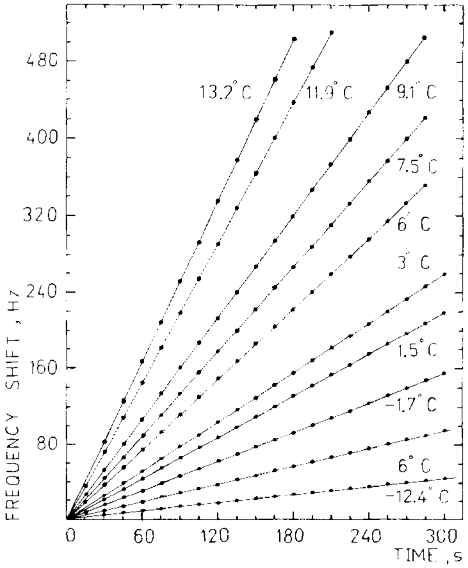

FIG. 3. Characteristic kinetic curves (frequency shift–time) for $CuSO_4 \cdot 5H_2O$.

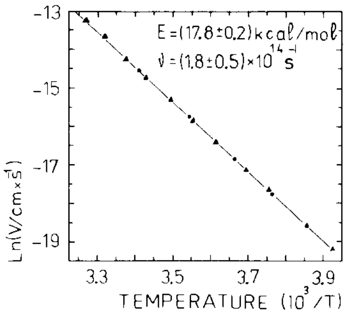

FIG. 4. Temperature dependence of the linear rate of a reaction interface advance for $CuSO_4 \cdot 5H_2O$ dehydration (Arrhenius coordinates). The kinetic parameters ν and E are calculated by Eq. (13) for $\delta = 5 \times 10^{-8}$ cm: (●) and (▲) correspond to different samples.

Thus, the substantial agreement of our results with those published by Smith and Topley (*9*) has established the reliability of the kinetic parameters obtained by our method.

Discussion

The above approach to studies on the temperature dependence of the rate of the reaction interface advance $V(T)$ in topochemical reactions (1), combined with the ways of preparing samples mentioned (*2–4*), seems to possess the following advantages:

(1) Since in experiments on the thermal decomposition of solids in vacuum the sample is placed on a thermostatically controlled support with a good thermal contact (Fig. 1), the self-cooling in the reaction zone can be reduced to a minimum.

(2) The activation of the initial face results in a planar and hence well determined and constant in time configuration of a product–reactant interface. As the reaction proceeds, the interface moves into the bulk reactant parallel to the initial face. This advance of the interface in a single direction permits $V(T)$ studies along various crystallographic directions to be carried out.

(3) Due to the high sensitivity of the quartz crystal to the flux $j(T)$ (*13, 23*), the time of measurement of a single V value at a certain temperature T does not exceed 5 min (Fig. 3). This fact is especially important for low-temperature measurements when the mass-loss measurements or nuclei photomicrography are either time-consuming or inapplicable.

(4) If the interface advance rate is independent of the solid product B(s) layer thickness (see (1)), our technique permits isothermal investigations of $V(T)$ in a single sample over a wide temperature range during several hours.

The reliability of experimental data is largely determined by correct calibration of the quartz crystal microbalance employed. In our case the calibration (see above) evidently depends upon the applicability of Eq. (8). Hence, an independent calibration is required which can be realized, e.g., by comparing the $V(T)$ data obtained by photomicrography of nuclei with those taken by quartz crystal microbalances. We have carried out similar investigations of KNa $C_4H_4O_6 \cdot 4H_2O$ dehydration. The coefficient k proves to be the same within the experimental error, which fact seems to confirm the reliability of Eq. (8).

The other limitation of the method considered here is obviously its failure to work in an atmosphere with controlled pressure of gaseous reaction products, since the high-vacuum chamber must be continuously evacuated.

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