

$\frac{1}{T}$ HEATING PROGRAM IN REACTION KINETIC STUDIES

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The paper deals with the practical realization of a hyperbolic temperature program.

In the kinetical interpretation of measurements made under dynamic conditions, the change in temperature is treated in terms of the Arrhenius equation [1].

The integral derived from the general kinetic differential equation can be resolved in finite form according to Zsakó [2] in cases where a hyperbolic temperature program is used, as follows:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = -\frac{Z}{b} \int_{\infty}^{\frac{1}{T}} e^{-\frac{E}{RT}} d\left(\frac{1}{T}\right) = \frac{ZR}{bE} e^{-\frac{E}{RT}} \quad (1)$$

where:

α = degree of transformation

g, f = symbols for functions

Z = Arrhenius pre-exponential factor

R = gas constant = 1.987 cal. mole⁻¹ deg⁻¹

T = absolute temperature (°K)

b = constant which depends on the experimental conditions.

The aim of the present work is the practical realization of a $\frac{1}{T}$ heating program.

In the case of a dynamic heating program the temperature of the furnace can be given as follows:

$$T = T_0 + f(t) \quad (2)$$

where:

T = temperature in °K

T_0 = temperature at time $t = 0$

$f(t)$ = temperature vs. time function determined by the heating program.

Our purpose has been to apply a heating program in which the reciprocal of the temperature changes linearly with time, i.e.

$$\frac{1}{T} = a - bt \quad (3)$$

The negative sign follows from physical considerations.

The constants a and b in Eq. (3) can be calculated from the initial and final temperatures.

$$\text{At } t = 0, \quad T = T_0; \quad (4)$$

$$\text{and at } t = t_{\max}, \quad T = T_{\max}$$

from which

$$a = \frac{1}{T_0}; \quad b = \frac{1}{t_{\max}} \left(\frac{1}{T_0} - \frac{1}{T_{\max}} \right) \quad (5)$$

The values of T_{\max} and t_{\max} cannot be chosen arbitrarily as they depend on the parameters of the furnace.

From Eqs (2) and (3)

$$T_0 + f(t) = \frac{1}{a - bt} \quad (6)$$

and from Eqs (4) and (5)

$$f(t) = T_0 \frac{t}{A t_{\max} - t} \quad (7)$$

where

$$A = \frac{T_{\max}}{T_{\max} - T_0}$$

The derivative of the function $f(t)$ with respect to time provides the rate of heating.

$$\frac{\partial f(t)}{\partial t} = q(t) = T_0 \frac{A t_{\max}}{(A t_{\max} - t)^2} \quad (8)$$

In the case of the derivatograph [3] the rate of heating is determined by the angular speed (ω) of the disc wedged on the shaft of a toroidal transformer. Accordingly,

$$q(t) = k\omega(t) \quad (9)$$

where $k = \text{constant}$, its dimension being $\text{degree} \cdot \text{sec}^{-1}$. k can be calculated as follows:

$$k = \frac{T_{\max} - T_0}{2\pi} \quad (10)$$

2π is the maximum angular displacement of the disc attached to the toroidal transformer. From Eqs (8) and (9)

$$\omega(t) = \frac{T_0}{k} \frac{At_{\max}}{(At_{\max} - t)^2} \quad (11)$$

The toroidal transformer is driven by a spindle by means of a wire coiled on the disc. Since the peripheral speeds of the spindle and disc are the same,

$$\omega_0(t) = \frac{d}{d_0} \omega(t) \quad (12)$$

where

ω_0 = angular speed of the spindle

d_0 = diameter of the spindle

d = diameter of the disc

Hence

$$\omega(t) = \frac{d}{d_0} \frac{T_0}{k} \frac{At_{\max}}{(At_{\max} - t)^2} \quad (13)$$

From Eqs (2) and (7) it follows that

$$T = T_0 \left(1 + \frac{t}{At_{\max} - t} \right) \quad (14)$$

The values of $\omega(t)$ calculated by means of Eq. (13) and the theoretical temperatures obtained from Eq. (14) are presented in Table 1. t_{\max} can be calculated from Eq. (8) if the maximum heating rate allowed by the applied furnace is known.

Table 1

Time, sec	Temperature, °K	$\omega_0(t) \cdot 10^{-3}$ rad sec ⁻¹ d $d_0 = 0.42$
500	323	0.820
1000	352	0.972
1500	387	1.185
2000	430	1.463
2500	483	1.842
3000	552	2.410
3500	642	3.255
4000	770	4.675
4500	960	7.400
5000	1275	12.880

With the derivatograph ω_0 cannot be varied continuously and can only assume discrete values; therefore the function $\omega_0(t)$ defined by Eq. (13) was approached in steps.

The values of ω_0 for various speeds of the motor driving the slide contact of the toroidal transformer are given in Table 2.

Table 2

Number of program position given by the derivatograph	ω , rad sec ⁻¹
25	14.95
50	7.44
100	3.74
200	1.87
400	0.93
800	0.47

As the relationship between the angular displacement of the slide contact of the toroidal transformer and the heating voltage is linear in the case of electronic control, the programming of the heating voltage is determined by the integral with respect to time of the function defined by Eq. (11).

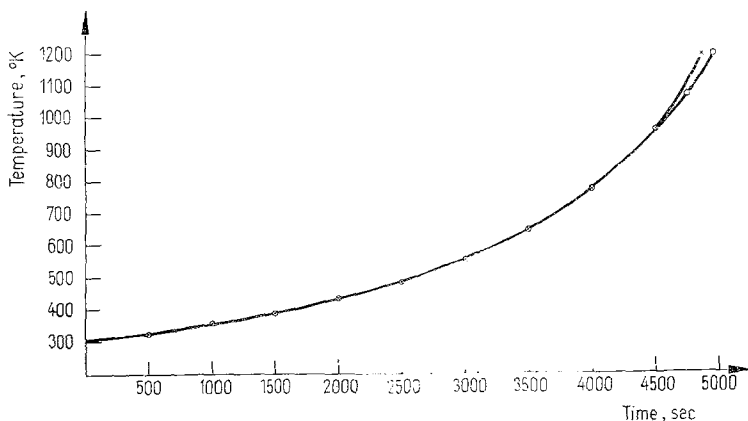


Fig. 1. Theoretical curve: \times ; experimental curve: \circ

Fig. 1 demonstrates the calculated theoretical and the experimental $\frac{1}{T}$ heating curves.

In Fig. 2 are the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of calcium oxalate monohydrate $[\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}]$ in the case of

$\frac{1}{T}$ heating. The particle size of the investigated sample was 0.045 mm. The decomposition reaction took place on the surface of a multiplate sample holder [4].

The investigation of the kinetic parameters obtained by the application of a hyperbolic heating program is in progress.

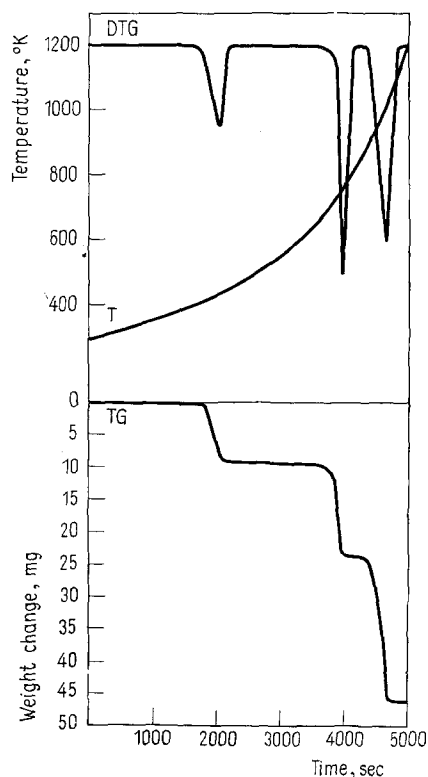


Fig. 2. Decomposition of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$ in the case of a hyperbolic heating program

References

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