LABORATORY TECHNIQUES AND METHODS

Periodic Thermal Analysis

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When a reaction takes place in the sample within a range of the periodicaly varying temperature some quantities characterizing the temperature variation of the sample change and from the shape of these temperature variations (periodic thermal analysis curves) the character of the investigated process may be estimated.

The principle of proposed periodic thermal analysis method (PTA) is based on the recording of relatively fast periodic temperature changes of the studied sample about an average value which may be rapidly changed to a great extent and put into an interval where the process under investigation takes place in the sample.

A heating device must, therefore, have a small temperature inertia. For this reason, a sample has been placed either on or in the junction of a thermocouple heated by means of high-frequency current, which has been amplitude-modulated by a low-frequency signal. In this case, the amount of sample must be small in order that the temperature difference between the sample and the junction might be neglected.

The first part of this study deals with the PTA application to the equilibrium temperature (T_e) determination in heterogeneous systems provided that the number of present phases remains constant. In the second part the possibilities of using this method for the study of some processes in which the number of phases in system changes will be discussed.

Simultaneous heating and temperature measuring with a sample on thermocouple junction heated by alternating current was used by *Ordway* [1] and other authors [2—4]. DTA of small sample amounts (as small as 1 μg) placed in thermocouple junction was developped by *Mazières* [5—7].

Equipmental

Practical examination of the suggested PTA method was carried out by means of an equipment, the block diagram of which is represented in Fig. 1.

High-frequency signal generated by the oscillator *1* is modulated by means of an amplitude-modulator *3* and modified to suitable amplitude by low-frequency modulation voltage supplied by a modulation frequency supply *2*. After amplification in a selective power amplifier *4* the amplitude-modulated high-frequency signal passes through an adaptation transformer and filter of the type „high pass filter" *5* into measuring head with proper thermocouple *6*. The limiting frequency of high-pass filter is chosen in a manner that this filter should not represent a short circuit for the d.c. component and low-frequency spectrum of thermocouple voltage.
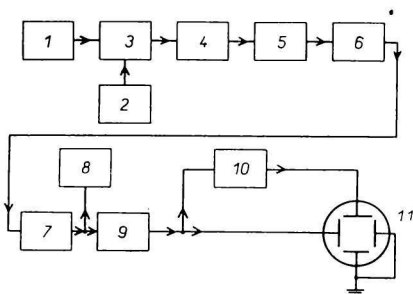
Fig. 1. Block diagram of the equipment used for PTA.

After filtering the high-frequency components of thermocouple voltage by using „low pass filter" 7, the measurement of d.c. component of thermocouple voltage, that means the average temperature, is performed in a block 8. The block 9 represents an amplifier of the time-variable component of thermocouple voltage, whereas the block 10 is a differential amplifier. On the oscilloscope 11 the relation

$$-\frac{dT}{d\tau} = f_1(T) \qquad (1)$$

can be observed. It is also possible to eliminate the differential amplifier and to convey the temperature-proportional signal to the vertical input of oscilloscope while the voltage of time base with a convenient frequency must be brought to the horizontal input. Thus a relationship of the type $T = f_2(\tau)$ can be registered, T being the thermocouple or sample temperature and τ being time.

Instead of the oscilloscope *11*, a suitable recorder can be used.

The reaction $KNO_3(s) \rightleftharpoons KNO_3(l)$ (m.p. 337°C) was chosen as a model reaction. Sample amounts in the range 8 to 35 μg were placed on the junction of thermocouple $PtRh_{10} - Au_{60}Pd_{30}Pt_{10}$ (pallaplat of the firm Heraeus, wire diameter 0.3 mm). The heating amplitude-modulated high-frequency current was supplied into the thermocouple by massive leads. The molten KNO_3 wetted the whole surface of the thermocouple junction.

As a modulation voltage supply, the low-frequency generator was used. The difficulties due to a broad frequency spectrum of rectangular modulation voltage compelled us to use only a simple harmonic signal. It follows from a theoretical analysis that the amplitude of temperature changes decreases with the increasing frequency of modulation signal. Regarding the sensitivity of this equipment the maximum modulation frequency of 10 Hz was used.

Discussion

1. Investigation of systems with constant number of phases

When the reaction under investigation can run in both directions, a suitable choice of experimental conditions (heating input, modulation signal frequency etc.) may cause periodic alternating shifts of the equilibrium state in either direction without disappearance of any phase present in the system. After the completion of a modulation-signal period, the system comes back into the original state. The values of

some parameters characterizing this „steady state with reaction" are different from those corresponding to „steady state without reaction". The temperature T_e lies between the maximum and minimum temperature of the sample.

In this case, the determination of T_e is not distorted by any nucleation processes. If the periods of temperature-changes are short and their amplitudes low enough the change of T_e effected by simultaneous or consecutive processes in the sample (for instance sintering or growth of grains etc.) is suppressed to a great extent.

Considering the importance of the reliable values of T_e, the possibility of PTA application to their determination will be discussed.

1.1. Theoretical

In the following considerations, the dependence of the relative over-all rate of heterogeneous reactions in systems with constant number of phases on the difference between sample temperature T_v and T_e, as stated above [8], has been used:

$$\frac{\mathrm{d}f^*}{\mathrm{d}\tau} \doteq A(T_v - T_e).\tag{2}$$

This approximate relation holds under following conditions:

a) The difference $(T_v - T_e)$ has to be small.

b) The activities of substances taking part in the reaction have to be approximately constant.

c) The change of interfacial surface has to be small.

These three conditions are fulfilled if the period of temperature changes during PTA is short and their amplitude low enough. The third condition is fulfilled also in that case when the interfacial surface is approximately equal to the surface of the sensing element used for the investigation of a process (e.g. boiling point measurement of the liquid covering the sensing element in a thin layer).

If the temperature drop between the sample and the sensing element (thermocouple junction) may be neglected ($T_v \doteq T_j = T$), the time change of sample temperature is given by the equation

$$N(\tau) \doteq mc\frac{\mathrm{d}T}{\mathrm{d}\tau} + \chi(T - T_o) + \xi(T^4 - T_o^4) + \Delta h_r \cdot A(T - T_e).\tag{3}$$

$N(\tau)$ — energy input into thermocouple junction,

$mc = m_v c_v + m_j c_j$ — heat capacity of the sensing element with sample,

m_v and m_j — the masses of the sample and sensing element, resp.,

c_v and c_j — the specific heats of the sample and sensing element, resp.,

χ — coefficient of heat transport by both thermal convection from the whole surface of sensing element with sample and thermal conduction by thermocouple wires,

T_o — effective temperature of surroundings,

ξ — coefficient of radiant heat transmission from the whole surface-area of sensing element with sample,

Δh_r — enthalpy increase during the reaction under investigation, calculated for the amount of sample.

If the temperature amplitude is small enough, a temperature T^* may be chosen, its value being conform to the approximate equation (4)

$$T^4 = [T^* + (T - T^*)]^4 = (T^* + \Delta T)^4 \doteq 4T^{*3}\,T - 3T^{*4}. \tag{4}$$

By inserting from (4) into (3) and rearrangement, we get the expression

$$\frac{dT}{d\tau} + T\,\frac{\chi + 4\xi T^{*3} + \Delta h_r \cdot A}{mc} - \frac{\chi T_0 + \xi(3T^{*4} + T_0^4) + \Delta h_r \cdot AT_e}{mc} - \frac{N(\tau)}{mc} \doteq 0, \tag{5a}$$

resp.

$$\frac{dT}{d\tau} + T\,\frac{L}{K} + \frac{M}{K} - \frac{N(\tau)}{K} \doteq 0, \tag{5b}$$

where

$$K = mc, \tag{6a}$$
$$L = \chi + 4\xi T^{*3} + \Delta h_r \cdot A, \tag{6b}$$
$$M = -[\chi T_0 + \xi(3T^{*4} + T_0^4) + \Delta h_r \cdot AT_e]. \tag{6c}$$

The solution of differential equations (5) is dependent on the time characteristic of the energy input $N(\tau)$.

1.1.1. Heating current is amplitude-modulated by a signal with rectangular oscillations

a) A period λ of modulation signal is formed by two generally unequal time intervals $\beta \cdot \lambda$ and $(1 - \beta)\lambda$ (Fig. 2) (β is the relative division of this period).

Quantities corresponding to the first or second interval of the period λ are denoted by the index $i = 1$ and $i = 2$, respectively.

The energy input into the thermocouple junction remains constant during the part i of a period λ so that the equation $(5b)$ can be integrated after rearrangement:

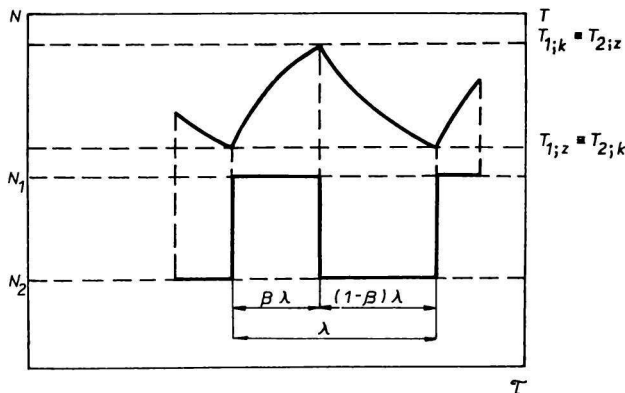$$\frac{dT_i}{T_i + \dfrac{M - N_i}{L}} \doteq -\frac{L}{K}\,d\tau_i. \tag{7}$$

Fig. 2. Diagram of the time course of energy input into sensing element (N) and of the sensing element temperature (T).

By integrating (7) we get equation

$$\ln \left(T_i + \frac{M - N_i}{L} \right) \doteq - \frac{L}{K} \tau_i + C \tag{8}$$

and after finding the antilogarithm

$$T_i + \frac{M - N_i}{L} \doteq C' \exp \left(- \frac{L}{K} \tau_i \right). \tag{9}$$

T_i equals $T_{i;z}$ in the time $\tau_i = 0$ (Fig. 2) so that

$$C' \doteq T_{i;z} + \frac{M - N_i}{L}. \tag{10}$$

After substituting from (10) into (9) and rearranging we get

$$T_i \doteq T_{i;z} \exp \left(- \frac{L}{K} \tau_i \right) + \frac{N_i - M}{L} \left[1 - \exp \left(- \frac{L}{K} \tau_i \right) \right]. \tag{11}$$

A steady temperature course of the sample is attained under following conditions

$$T_{1;k} = T_{2;z}, \tag{12a}$$
$$T_{2;k} = T_{1;z} \tag{12b}$$

and

$$A \int_0^{\beta\lambda} (T_1 - T_e) \, d\tau_1 + A \int_0^{(1-\beta)\lambda} (T_2 - T_e) \, d\tau_2 \doteq 0. \tag{12c}$$

$T_{i;k}$ is the temperature of the sample at the end of the part i of the period λ.

b) After substituting from (11) into (12a) and (12b), resp. and after rearranging, we get expressions

$$T_{1;z} \doteq \frac{N_2 - M}{L} + \frac{N_1 - N_2}{L} \cdot \frac{1 - \exp \left(\dfrac{L}{K} \beta\lambda \right)}{1 - \exp \left(\dfrac{L}{K} \lambda \right)} \tag{13a}$$

and

$$T_{2;z} \doteq \frac{N_1 - M}{L} - \frac{N_1 - N_2}{L} \cdot \frac{1 - \exp \left[\dfrac{L}{K} (1 - \beta)\lambda \right]}{1 - \exp \left(\dfrac{L}{K} \lambda \right)}. \tag{13b}$$

It follows from equation (12c)

$$T_e \doteq \frac{1}{\lambda} \int_0^{\lambda} T \, d\tau = \bar{T}. \tag{14}$$

By the evaluation of measured time-temperature dependence, it is thus possible either to calculate the values of K, L, and M using the expression (*11*) or the value of T_e by means of equation (*14*). (In case of relatively small values of temperature change it is possible to put $T^* \doteq \overline{T}$.)

1.1.2. Energy input changes continuously

a) Energy input into thermocouple junction changes according to the equation

$$N(\tau) = \frac{U^2}{R} = \frac{1}{R}[B(1 + \alpha \cos \nu\tau) \cos \omega\tau]^2. \tag{15}$$

B — amplitude of h.f. current voltage,
$\omega = 2\pi f_\omega$ — angular frequency of heating current,
αB — amplitude of modulation current,
α — modulation depth,
$\nu = 2\pi f_\nu$ — angular frequency of modulation current,
R — resistance of thermocouple junction.

By inserting from (*15*) into (*5b*), we get the expression

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} + T \frac{L}{K} + \frac{M}{K} - \frac{\frac{1}{R}[B(1 + \alpha \cos \nu\tau) \cos \omega\tau]^2}{K} \doteq 0. \tag{16}$$

This expression is a common inhomogeneous linear differential equation of first order

$$y' + Py + Q \doteq 0; \tag{17a}$$

$$P = \frac{L}{K}, \tag{17b}$$

$$Q = \frac{M - \frac{1}{R}[B(1 + \alpha \cos \nu\tau) \cos \omega\tau]^2}{K}. \tag{17c}$$

General solution of (*17a*) is the equation

$$y \doteq C \exp\left(-\int P \, \mathrm{d}x\right) - \exp\left(-\int P \, \mathrm{d}x\right) \cdot \int Q \exp\left(\int P \, \mathrm{d}x\right) \mathrm{d}x. \tag{18}$$

After substituting from (*17b*) and (*17c*) into (*18*) and integrating, we get the expression

$$T \doteq C \exp\left(-\frac{L}{K}\tau\right) - \frac{M}{L} + \frac{B^2\left(1 + \dfrac{\alpha^2}{2}\right)}{2RL} + F(\tau), \tag{19}$$

where $F(\tau)$ is a trigonometric time function. Since the relation $f_\omega \gg f_\nu$ holds in the described arrangement, the following approximate equations are, therefore, valid

$$2\omega + \nu \doteq 2\omega,$$
$$2\omega - \nu \doteq 2\omega,$$
$$2\omega + 2\nu \doteq 2\omega,$$
$$2\omega - 2\nu \doteq 2\omega. \tag{20}$$

By inserting from (20) into F (τ), this expression turns into a simpler form

$$F(\tau) \doteq \frac{B^2(1+\alpha)^2}{2RK\left(\dfrac{L^2}{K^2}+4\omega^2\right)} \cdot \cos(2\omega\tau - \varphi_1) +$$

$$+ \frac{B^2\alpha^2 \cos(2\nu\tau - \varphi_2)}{4RK\left(\dfrac{L^2}{K^2}+4\nu^2\right)} + \frac{B^2\alpha}{RK\left(\dfrac{L^2}{K^2}+\nu^2\right)} \cdot \cos(\nu\tau - \varphi_3), \tag{21}$$

$$\operatorname{tg}\varphi_1 = \frac{2\omega \cdot K}{L}, \tag{22a}$$

$$\operatorname{tg}\varphi_2 = \frac{2\nu \cdot K}{L}, \tag{22b}$$

$$\operatorname{tg}\varphi_3 = \frac{\nu \cdot K}{L}. \tag{22c}$$

A steady state is attained if the following two conditions are fulfilled $\left(\dfrac{1}{f_\nu}=\lambda\right)$:

$$T_\tau = T_{\tau+\lambda} \tag{23}$$

and

$$\int_\tau^{\tau+\lambda} A(T - T_e)\,\mathrm{d}\tau \doteq 0. \tag{24}$$

By inserting from (19) into (23), we get expression

$$C \exp\left(-\frac{L}{K}\tau\right) - \frac{M}{L} + \frac{B^2\left(1+\dfrac{\alpha^2}{2}\right)}{2RL} + F(\tau) \doteq C \exp\left[-\frac{L}{K}(\tau+\lambda)\right] \cdots$$

$$- \frac{M}{L} + \frac{B^2\left(1+\dfrac{\alpha^2}{2}\right)}{2RL} + F(\tau+\lambda). \tag{25}$$

If the term with a coefficient $\cos(2\omega\tau - \varphi_1)$ is neglected in F (τ) owing to the large value of ω or if it is assumed that f_ω is equal to integer multiple of f_ν, the equation (19) is fulfilled on condition that

$$C \doteq 0. \tag{26}$$

After substituting from (26), the equation (19) turns into equation of ,,steady state of given arrangement"

$$T \doteq \frac{B^2\left(1 + \dfrac{\alpha^2}{2}\right)}{2RL} - \frac{M}{L} + F(\tau) = \bar{T} + F(\tau), \tag{27a}$$

$$\bar{T} \doteq \frac{1}{\lambda} \int_{\tau}^{\tau+\lambda} T\, d\tau. \tag{27b}$$

$\bar{T}$ — average temperature.

By means of a differentiated expression (27a), the minimum and maximum value of T may be calculated.

b) By inserting from (27a) into (24), we get the expression

$$\int_{\tau}^{\tau+\lambda}\left[\frac{B^2\left(1 + \dfrac{\alpha^2}{2}\right)}{2RL} - \frac{M}{L} + F(\tau) - T_e\right] d\tau =$$

$$= \left[\frac{B^2\left(1 + \dfrac{\alpha^2}{2}\right)}{2RL} - \frac{M}{L} - T_e\right]\lambda \doteq 0 \tag{28a}$$

and

$$T_e \doteq \frac{B^2\left(1 + \dfrac{\alpha^2}{2}\right)}{2RL} - \frac{M}{L} = \bar{T}. \tag{28b}$$

The equilibrium temperature, therefore, equals the average value of temperature T.

On the basis of equation (21), the conditions suitable for reducing the unfavourable influence of the term with coefficient $\cos(2\nu\tau - \varphi_2)$ on T or time derivative of T can be calculated. The value of α must be small and if the value of L/K is small too, a high value of frequency ν is advantageous.

If the influence of second harmonic components of frequencies f_ν and f_ω in (21) on the course of T is neglected in the first approximation, the amplitude of temperature change is given by the expression

$$B_T \doteq \frac{B^2\alpha}{RK\left(\dfrac{L^2}{K^2} + \nu^2\right)}. \tag{29}$$

c) The required average temperature of thermocouple junction with sample can be adjusted under given experimental conditions either by the change of amplitude B or by the change of modulation depth (α).

If the values M and L or M_0 and L_0, resp. corresponding to the steady state of periodic temperature changes of the sample in which the investigated reaction either runs or does not run, are inserted into expression for T (27a), the following expressions can be deduced with respect to (28b)

$$B = B_0, \quad (R, \nu, \alpha, \bar{T}\ldots), \tag{30a}$$

and

$$\alpha = \alpha_0, \quad (R, \nu, B, \bar{T}\ldots). \tag{30b}$$

The approximate value of a amplitude ratio ($\varkappa$) of steady periodic temperature changes in the sample in which the investigated process either runs or does not run, can be calculated by means of equations (29) and (30):

$$\varkappa = \frac{B_T}{B_{T;0}} \doteq \frac{L_0^2 + \nu^2 K^2}{L^2 + \nu^2 K^2} \quad (\bar{T}). \tag{31}$$

The minimum value of amplitude ratio for the periodic temperature changes of the sample in which the studied reaction either does or does not take place serves as a criterion of reliability for the steady state determination or $\bar{T} \equiv T_e$ determination under given conditions.

In Fig. 3 the plots representing the dependence of the temperature change amplitude in thermocouple junction without a sample on $\bar{t}$ are given.
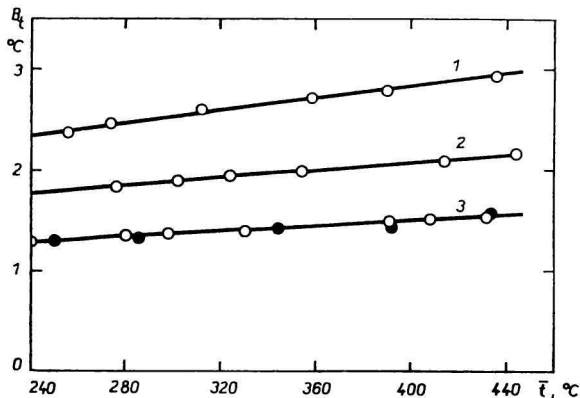
Fig. 3. Dependence of the temperature change amplitude (B_t) of thermocouple junction without sample on the mean value of its temperature ($\bar{t}$).
1. $f_\nu = 5$ Hz, $\alpha = 50$ p.c.; 2. $f_\nu = 7$ Hz, $\alpha = 50$ p.c.; 3. ○ $f_\nu = 10$ Hz, $\alpha = 50$ p.c.; 3. ● $f_r = 5$ Hz, $\alpha = 20.4$ p.c.

The plots showing the dependence of the temperature change amplitude in thermocouple junction with a sample (KNO_3) on $\bar{t}$ are presented in Fig. 4.

In this case the studied reaction was melting and solidifying of KNO_3, resp. The geometrical arrangement and the rather small amount of sample (20 ± 3 µg) fulfils approximately the conditions under which the equation (2) is valid.

If the above modulation parameters are used, there are always both phases — melt and crystals — present in the sample. The minimum temperature change amplitude in the thermocouple junction with KNO_3 corresponds to $\bar{T} = T_{m.p.} = 610°K$ (m.p. 337°C).

d) If the geometrical arrangement and the amount of sample fulfil the relations
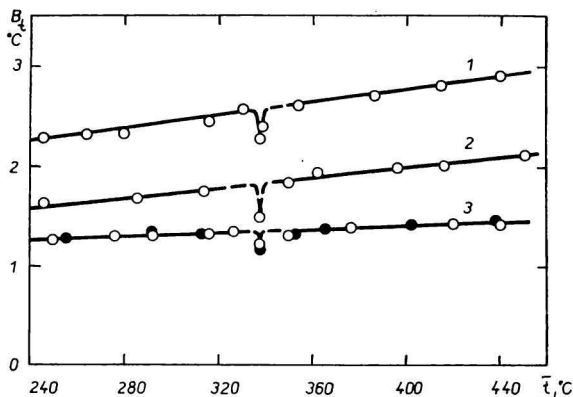
$$mc \doteq m_j c_j \gg m_v c_v \tag{32}$$

Fig. 4. Dependence of the temperature change amplitude (B_t) of thermocouple junction with KNO_3 ($m = 20 \pm 3$ μg) on the mean value of its temperature ($\bar{t}$).
1. $f_r = 5$ Hz, $\alpha = 50$ p.c.; *2.* $f_r = 7$ Hz, $\alpha = 50$ p.c.; *3.* $\bigcirc$ $f_r = 10$ Hz, $\alpha = 50$ p.c.;
3. $\bullet$ $f_r = 5$ Hz, $\alpha = 23.4$ p.c.

and

$$P_v \doteq P_j \doteq \text{const} \cdot m_j^{2/3} \doteq \text{const} \cdot m^{2/3} \tag{33}$$

(P_j being the surface of sensing element), all terms of L and L_0 are approximately proportional to $m^{2/3}$. In this case the equation (*31*) turns into an approximate relationship

$$\varkappa \doteq \frac{m^{4/3}\,I_0 + v^2 m^2 c^2}{m^{4/3}I + v^2 m^2 c^2} = \frac{I_0 + (vm^{1/3})^2\,c^2}{I + (vm^{1/3})^2\,c^2}\,, \tag{34}$$

where I_0 and I are constants.

That means that the value of $\varkappa$ does not change if the expression $vm^{1/3}$ remains constant. An increase of modulation frequency, advantageous for putting down the unfavourable effect of simultaneous and consecutive processes on the reproducibility and possibility of reaching the equilibrium state of the investigated reaction, is possible only in case of reducing an important dimension of the sensing element.

e) By evaluating the time course of sample temperature, the approximate values of constants K, L, and M may be calculated using the equations (*22c*), (*27a*), (*28b*), and (*29*).

2. Systems with varying number of phases during PTA

When the amount of sample and frequency of modulation signal are small and the temperature amplitude and reaction rate high enough, the studied process runs in corresponding direction to the end during a part of the period. The reaction course may be influenced by a homogeneous or heterogeneous nucleation and thus it can not be described by the equation (*2*). In this case, the inflexion points corresponding to initial and final phases of reactions in respective direction appear on PTA curves

during both parts of period. Their presence in PTA curves can be observed only with difficulties. They are, however, much more distinct with curves describing relation (*1*).

The dependence of $dT/d\tau$ on T has been put forward as one of possible evaluations of TA by *Pilojan* [9]. This dependence has been recorded during fast temperature changes in the range of 100°C by using an oscilloscope [10].
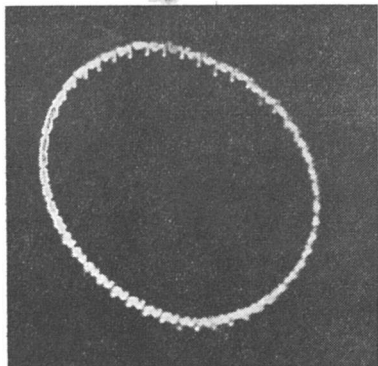

Fig. 5. Oscillogram of the plot (*1*) (*t*-curve of DPTA) for the thermocouple junction without sample (f$_\nu$ = 1 Hz; α = 20 p.c.; $\bar{t}$ = 337°C; B_t = ±10°C).
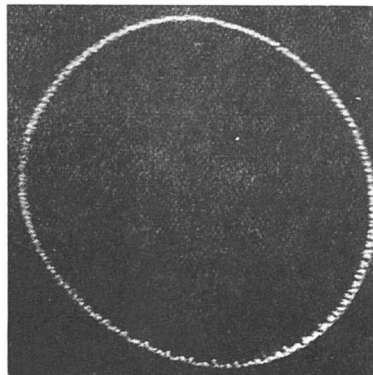
Fig. 6. Oscillogram of the *t*-curve of DPTA for the thermocouple junction without sample (f$_\nu$ = 1 Hz; α = 25 p.c.; $\bar{t}$ = 337°C; B_t = ±12.8°C).

In Fig. 5 the function (*1*) for a thermocouple without sample at the modulation depth α = 20 p.c. and the temperature $\bar{t}$ = 337°C is presented. The temperature amplitude is ±10°C around the average temperature with modulation frequency f$_\nu$ = 1 Hz. Fig. 6 presents the same curve for the thermocouple without sample at α = 25 p.c. and $\bar{t}$ = 337°C. The temperature amplitude is ±12.75°C with a modulation frequency f$_\nu$ = 1 Hz.

The upper part of these curves represents the cooling and the lower part the heating of the thermocouple. In case of a sinusoidal signal, the plot of equation (*1*) would be a circle. From a theoretical analysis follows that the deviations from a circle are due to the distortion by the second harmonic component in equation (*21*).

The ripple effect of the curves corresponding to the equation (*1*) is due to noise and high-frequency interference which plays an important part especially in the derivative circuit *10* (Fig. 1).

In Fig. 7 the function (*1*) is recorded for the modulation frequency f$_\nu$ = 1 Hz, modulation depth α = 20 p.c. and amount of KNO_3 m = 30 ± 3 μg. The average temperature is 337°C and temperature amplitude ±9°C.

The function is recorded for the modulation depth α = 30 p.c. and corresponding temperature amplitude ±14°C in Fig. 8.

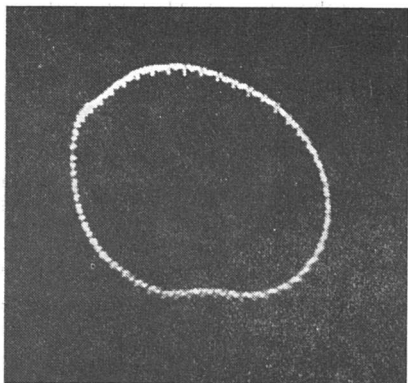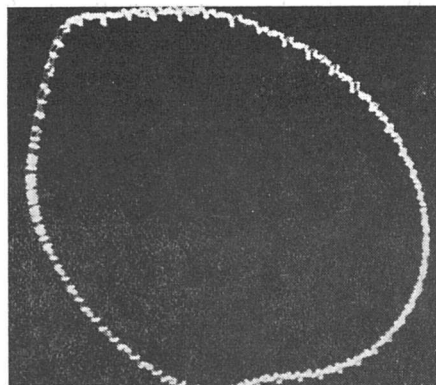Fig. 9 has been obtained with 8 μg KNO_3 and the modulation depth α = 25 p.c. The temperature amplitude is ±12.5°C.

Fig. 7. Oscillogram of the *t*-curve of DPTA for the thermocouple junction with KNO$_3$ ($m = 30 \pm 3$ µg; f$_r = 1$ Hz; $\alpha = 20$ p.c.; $\bar{t} = 337°$C; $B_t = \pm 9°$C).

Fig. 8. Oscillogram of the *t*-curve of DPTA for the thermocouple junction with KNO$_3$ ($m = 30 \pm 3$ µg; f$_r = 1$ Hz; $\alpha = 30$ p.c.; $\bar{t} = 337°$C; $B_t = \pm 14°$C).

The curves in Fig. 10 and 11 represent the corresponding functions $-dT/d\tau = f_1 (T)$ and $T = f (\tau)$ for 35 µg KNO$_3$ and modulation depth $\alpha = 25$ p.c. The temperature change is $\pm 12°$C. The heating of sample corresponds to the lower part of the curve in Fig. 10 and to the ascending part of the curve in Fig. 11. The comparision of both
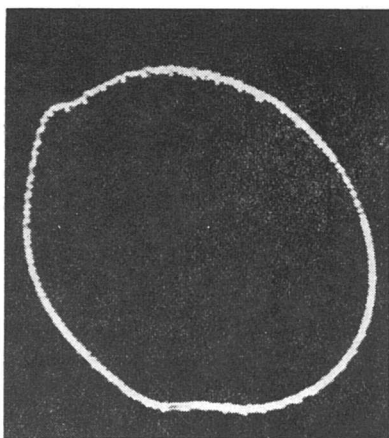

Fig. 9. Oscillogram of the *t*-curve of DPTA for the thermocouple junction with KNO$_3$ ($m = 8 \pm 3$ µg; f$_r = 1$ Hz; $\alpha = 25$ p.c.; $\bar{t} = 337°$C; $B_t = \pm 12.5°$C).
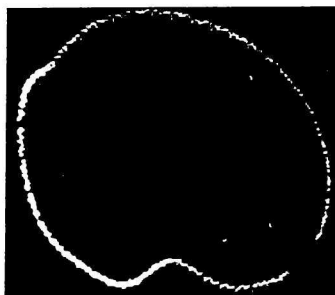
Fig. 10. Oscillogram of the *t*-curve of DPTA for the thermocouple junction with KNO$_3$ ($m = 35 \pm 3$ µg; f$_r = 1$ Hz; $\alpha = 25$ p.c.; $\bar{t} = 337°$C; $B_t = \pm 12°$C).

curves shows that the recording of the derivative function is much more suitable for the purposes of identification because the bends of the curve in Fig. 10 are much more distinct than those of the curve in Fig. 11.
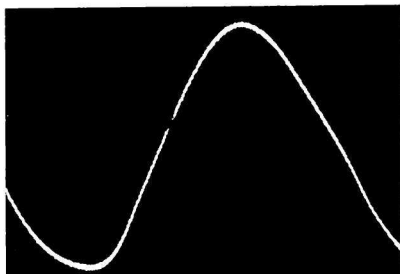

Fig. 11. Oscillogram of the PTA curve for the thermocouple junction with KNO_3. (The values of all quantities are the same as in Fig. 10.)
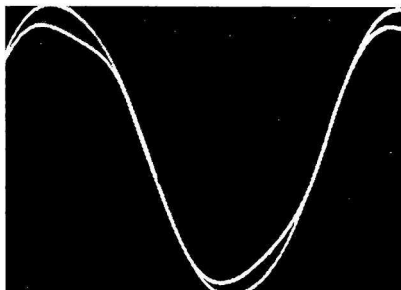

Fig. 12. Oscillogram of PTA curves for the thermocouple junction both without and with sample.

The possibilities of determining the relationship between Δh_r and the shape change of PTA curves in a system where the number of phases changes during PTA will be discussed in the subsequent paper. The temperature-time courses of thermocouples both without and with a sample of 50 μg KNO_3 are presented in Fig. 12.

Conclusion

The main advantages of PTA appear to be:

1. The possibility of determining the value of T_e that is not distorted by nucleation processes. The temperature range within which T_e may lie depends on the choice of a single thermocouple.

2. The use of relatively small amounts of sample.

3. The applicability for analytical purposes.

4. The promptitude of method.

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