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by

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On The Dehydration Of Borax

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SUMMARY

Dehydration of borax has been investigated by differential thermal and thermogravimetric analyses.

It was found that the dehydration of borax occurred mostly in the temperature range 115 – 238 °C. Therofore, low density and powdered anhydrous borax may be produced in a convenient reactor system by heating borax decahydrate.

Dehydration of borax at 245 °C in a small rotary kiln was represented by the first order reaction log (b–m) = — kt + C where m is the quantity of water eliminated at time t, and b is the quantity of initial water. The rate constant k of the reaction was 8.5×10^{-4} min^{-1}.

I. INTRODUCTION

Crystalline borax, $Na_2B_4O_7.10H_2O$; contains 47.2 % water. It is predicted that 8 moles of water of crystallization of borax can be eliminated easily but that the remaining two moles of water are strongly attached to the structure (I). Thus, the dehydration of water of crystallization which amounts to nearly a half of the weight of borax yields anhydrous borax, $Na_2B_4O_7$, and decreases the transport fees considerably with respect to the B_2O_3 component. On the other hand, anhydrous borax is particularly used as a raw material in many industrial fields such as ceramics, kilns, sodium perborate manufacturing, grinding wheels, enamels, borosilicate glasses.

A considerable number of attempts has therefore been made to develop new methods for the manufacture of anhydrous borax. These methods, in each of which the decahydrate is used as raw matherial because of its availability and cheapness, may be categorized into three main groups as follows.

a) Azeotropic distillation

The granulated or crushed borax is suspended in a suitable organic solvent or in a mixture of solvents which are immiscible with water. The suspension is stirred and heated to the boiling point. The vapours are condensed, the water removed and the organic solvent recovered. The remaining solid is centrifuged, washed with a low-boiling organic solvent and dried. This process is not yet suitable for industrial purposes because of the low yield and the relatively high heat input needed. For example, in an azeotropic distillation using xylene, 2130 cal of heat were necessary to eliminate each gram of water although only 834.4 cal were needed in an ordinary drying process (2).

b) Dehydration in a fluidized bed

The borax decahydrate can be transformed into anhydrous borax in a fluidized bed reactor. Some workers obtained a powdered form of anhydrous borax with this technique by gradual and multi-stage heating with a final stage at about 220-700°C. This method is still being developed (3).

c) Melting

This technique is used extensively in industry to make high density and crystalline anhydrous borax. In the process, borax is partially dehydrated at low temperatures in a rotary kiln (calcination), thus the melting and entire removal of water are facilitated. Borax is then fed into a specially designed fusion furnace where it is heated to its melting point at about 767°C. The water of orystallization is completely eliminated in this furnace. Molten borax flows out of the furnace into molding machines to be cooled. Slow cooling promotes crystal formation but instantaneous cooling gives an amorphous glass. In spite of the production of high density anhydrous burax, there are difficulties in the process, such as in the handling of molten materials which prevents the proper and easy running of the process.

2. THEORETICAL BACKGROUND

a) Thermal decomposition reactions

The dehydration of borax can be described as the thermal decomposition of a solid substance. This type of reaction is generally formulated as,

$$A_{solid} \xrightarrow{heat} B_{solid} + C_{gas} \tag{1}$$

The first step in the study of thermal decomposition reaction kinetics is the determination of a curve representing the decomposed fraction as a function of time (4). Typical curves obtained from the thermal decomposition reactions are shown in Figure 1. In general they are sigmoid indicating autocatalytic reactions. There are three sections in each of them ; a) an induction period showing the beginning of reaction, b) an acceleratory period

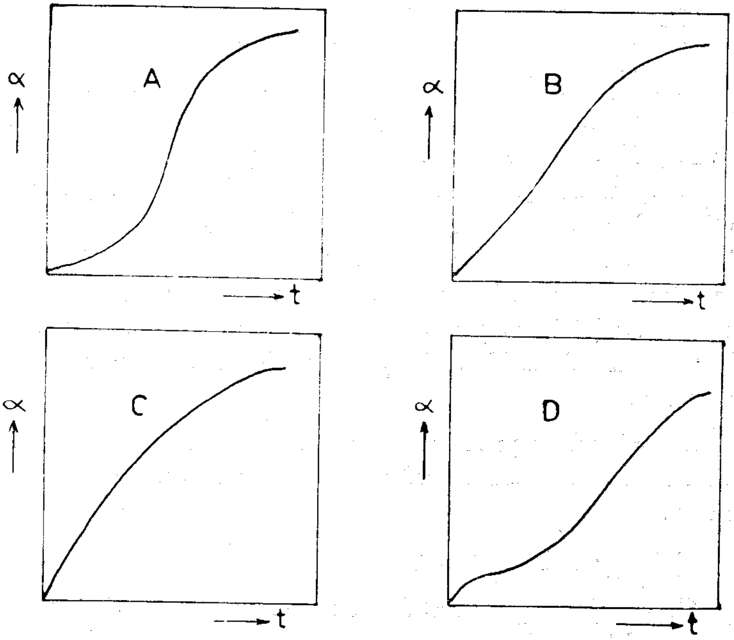

Figure.1- Typical curves of thermal decomposition reactions representing the main reaction, c) a fial decay period indicating the end of reaction.

In theory, the reaction (1) takes place in two steps corresponding to the formation and growth of nuclei.

The starting of the reaction involves the formation of phase B at special points in the lattice of A. The first formed fragments of B, fixed firmly in a surrounding phase of A, may retain the molecular volume and lattice of A. This first stage of the reaction is called "Nucleation". Decomposition starts when local fluctuations in the lattice of A provide the activation energy required for the formation of B. The nuclei are supposed to appear at definite localized spots where the activation energy is least. The number of nuclei formed in a given time will thus depend upon the number of these potential nucleus forming sites as well as on the mean activation energy. Jacobs and Tompkins (5) and Bag dassarian (6) have found theoretical expressions giving the number of formed nuclei as a function of time.

Initially the formed nuclei are of two sizes, small and large. The small nuclei are generally unstable and may reverse back to the pahase A. While large nuclei appearing as a new phase tend to grow and posses a different molecular volume and lattice to that of the surrounding phase A. This stage is called "Growth of nuclei". From microscopie observations, it is predicted that once nuclei attain visible size they grow at a constant rate. Bright and Garner (7) have photographed the nuclei formed during the dehydration of $CuSO_4 . 5 H_2O$ crystals and determinated the growth rate.

After nucleus formation and the growth of nuclei, further reaction occurs at the interface between the two solid phases A and B.

b) Dehydration of borax

Two major experimental studies of the kinetics of the dehydration of borax have been published. In the first, Murgulescu and Segal (8) studied single borax crystals by means of an automatic balance which provided continuous measurement of weight loss throughout dehydration. They concluded that the transformation of the decahydrate to the pentahydrate at 50-60 °C in a nitrogen atmosphere was in accordance with the following equation

$$\log \frac{m}{b-m} = k\,t + C \qquad (2)$$

where m was the water eliminated at time t, b the initial water, k and C are constants.

In the second study, Thomas and Soustelle (9) investigated the same reaction as the previous workers also using borax crystals but in the temperature range between 19,1–46,5 °C and at 2×10^{-3} mm Hg pressure. Their experimental results verified that the dehydration was restricted by interfacial reactions on the crystal surfaces. Their equation giving the decomposition rate was

$$\frac{dm}{dt} = 6\,k\,(1 - kt) \qquad (3)$$

3. EXPERIMENTAL

Dehydration of borax by exposure to air without heating was first investigated. Later, differential thermal and thermogravimetric analyses were performed and finally, dehydration was carried out in a small rotary kiln. Technically pure, refined borax manufactured by Etibank Borax and Boric Acid Factories (Bandırma) was used for all the experimental work.

3.1. Determinations of water of crystallization

Determinations of water of crystallization have been carried out by heating samples in a muffle-furnace MR–170 for 6 hours at about 900 °C.

3.2. Differential thermal analyses

Al_2O_3 cells, one filled with the sample, the other with standard kaolin were heated at 10 °C/min. PtRh-Pt thermocouples were used.

3.3. Thermogravimetric analyses

Borax particles of 0.04 mm diameter previously stored in the open air at room temperature were heated at 5 °C and 10 °C/min.

3.4. Dehydration in a rotary kiln

The most important part of the apparatus consisted of a small, cast iron rotary kiln 30 cm in lenght, of 2 cm internal diameter and 2 mm wall thickness. It was connected by a metal support to two bearings so that both ends of the kiln could be rotated at known rates by a motor associated with gears fitted to the outside of the kiln. The kiln was provided with a screwed cover for the addition and withdrawal of samples and also with two sets of 4 mm wide lifting baffles. The kiln was insulated with 10 mm thick asbestos.

The kiln was heated by air previously passed over an electrical haater. Inlet and outlet temperatures were measured by thermocouples. The kiln was connected to a dust collector, a wet gazometer and a vacuum pump.

4. RESULTS

Differential thermal and thermogravimetric analyses are shown in Figure 2, 3 and 4. The quantities of water removed during the thermogravimetric analyses are shown in Table 1. Figure 5 shows the curve of dehydration in the rotary kiln.

TABLE. 1

The quantities of water removed during the thermogravimetric analyses

	Dehydrated water (moles)	
Temperature (°C)	at 5 °C/min	at 10 °C/min
100	0.17	0.65
150	2.14	1.74
200	2.62	3.13
250	3.00	3.71
300	3.37	4.24
350	3.74	4.62
450	4.13	5.16

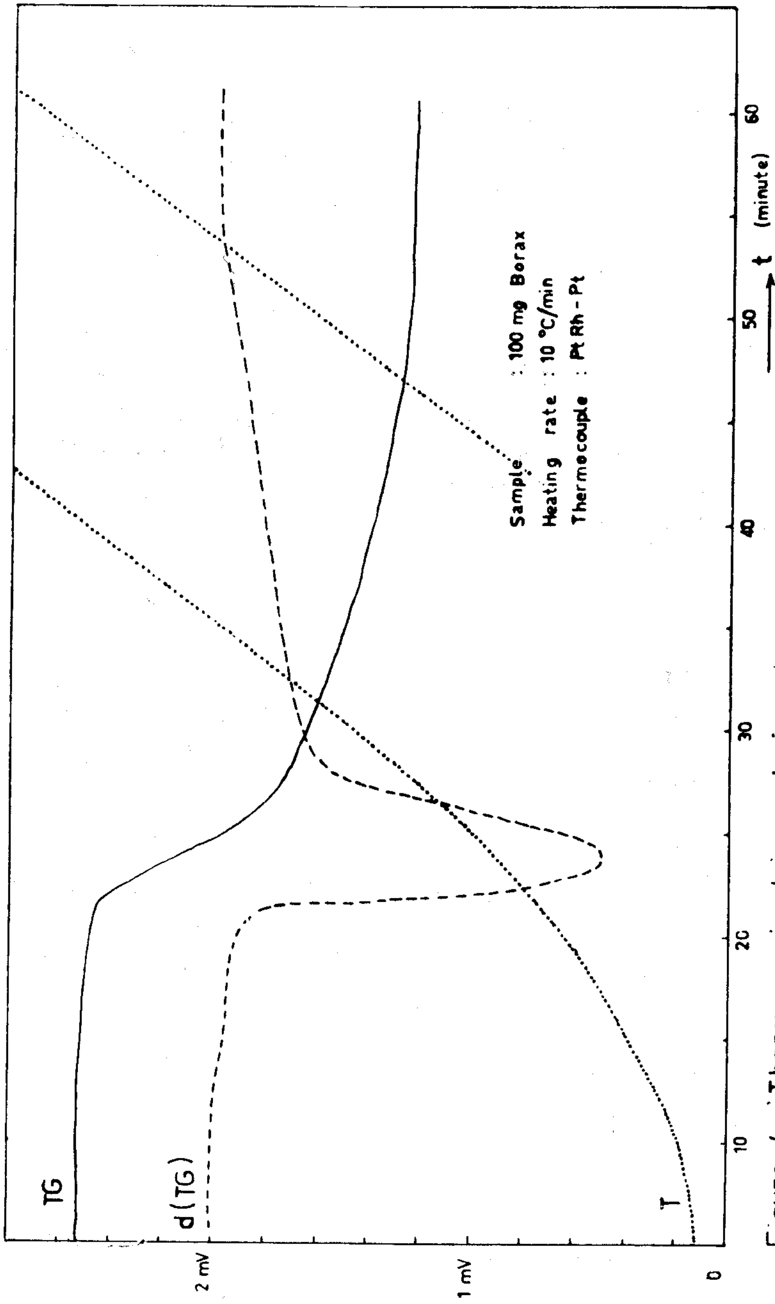

Figure. 4 - Thermogravimetric analysis

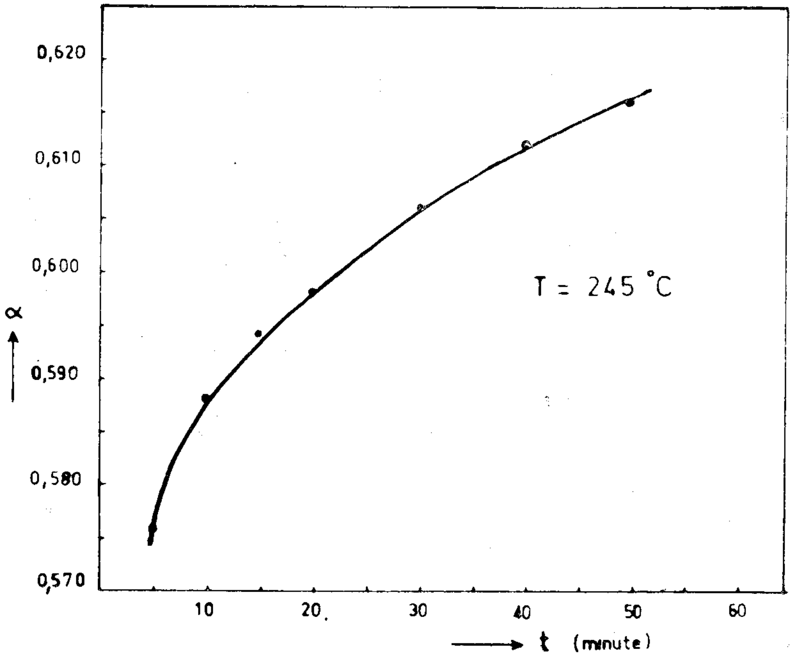

Figure 5-'Dehaydration curve in rotary kiln

5. DISCUSSION AND CONCLUSIONS

a) Determinations of water of crystallization showed that borax (decahydrated) left in the open air became converted to the pentahydrate.

b) Differential analyses showed a single endothermic peak starting of 115 °C, with a peak at 145 °C and finishing at 238 °C indicating that dehydration of borax occurred during this temperature range at atmospheric pressure. The thermogravimetric analyses showed that in fact dehydration was complete by 350–450 °C.

c) In accordance with these fundamental studies it was found that quantities of borax could be completely dehydrated by heating in the rotary kiln to about 350 °C.

d) The curve of dehydration at 245 °C has been replotted in Figure 6 showing that dehydration in the kiln was a first order reaction following the equation

$$\log (b - m) = - kt + C \tag{4}$$

where m is the water eliminated at time t and b is the amount of water initially present.

The rate constant k had the value 8.5×10^{-4} min^{-1} at 245 °C.

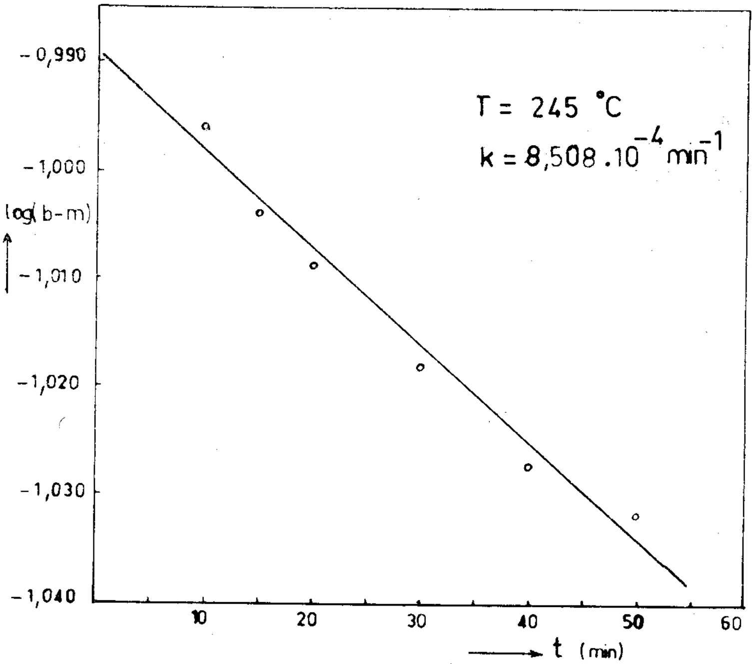

Figure . 6 _ Plot of the equation

$\log (b - m) = - k t + C$

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ÖZET

Boraksın susuzlaştırılması bu çalışmada diferansiyel termik ve termogravimetrik analiz yöntemleriyle incelenmiş ve bu tepkimenin çoğunlukla 115–238 °C aralığında gerçekleştiği görülmüştür. Ayrıca, düşük yoğunlukta ve pudra şeklinde susuz boraksın uygun bir reaktör sistemi içinde boraks dekahidratın ısıtılmasından elde edilebileceği sonucuna varılmıştır.

Boraksın 245 °C da küçük bir döner fırın içinde susuzlaştırılmasının; t anında uzaklaştırılan su miktarı m, başlangıçtaki su miktarı b olmak üzere, $\log(b-m) = -kt + C$ denklemi ile gösterilen birinci mertebeden bir tepkime olduğu bulunmuştur. Tepkimenin hız sabiti k, 8.5×10^{-4} dak^{-1} olarak hesaplanmıştır.

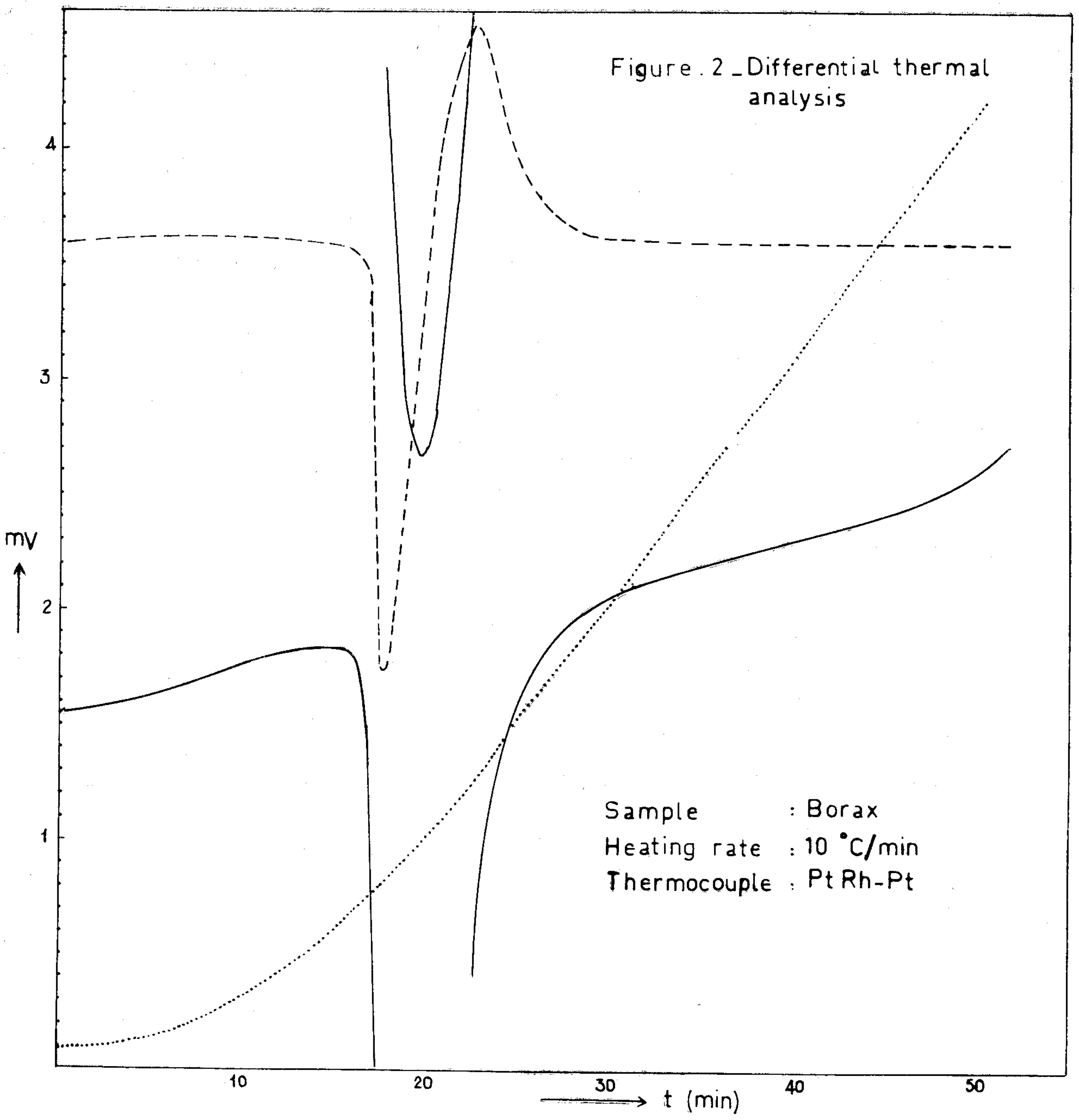

Figure. 2 _Differential thermal analysis

Sample : Borax
Heating rate : 10 °C/min
Thermocouple : Pt Rh-Pt

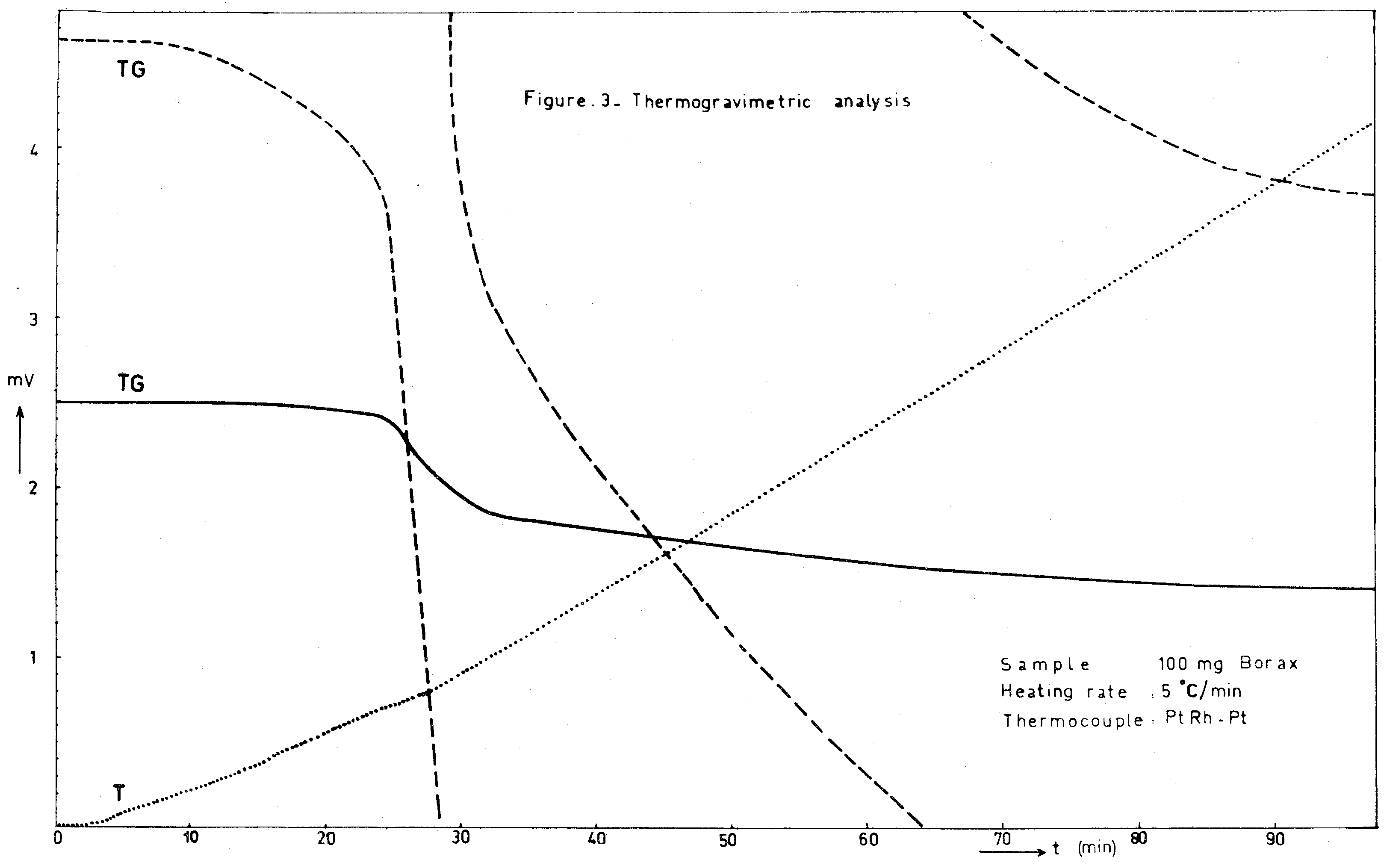

Figure . 3 - Thermogravimetric analysis

Sample 100 mg Borax
Heating rate : 5 °C/min
Thermocouple : Pt Rh - Pt

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