# DIFFERENTIAL THERMAL ANALYSIS OF SYNTHETIC MANGANESE DIOXIDES

BY N. S. KRISHNA PRASAD AND C. C. PATEL

(*Department of General Chemistry, Indian Institute of Science, Bangalore-3*)

## SUMMARY

Differential thermal analysis of synthetic and natural modifications of $MnO_2$ samples has been carried out using Pt-Pt (13% Rh) thermo-couples. It has been shown that the results obtained with Pt-Pt (Rh) thermo-couple are not reliable on account of the corrosion of Pt (Rh) alloy by the chemically prepared $MnO_2$. A method has been suggested for the application of corrections to overcome this difficulty in getting the thermal curves.

## I. INTRODUCTION

In recent years the method of differential thermal analysis has been employed for the study of various amorphous powders, rocks and minerals. This method in combination with X-ray diffraction has been applied by McMurdie and Golovato[1] for the identification of the several modifications of manganese dioxide, *viz.*, pyrolusite, $\gamma$-$MnO_2$, ramsdellite, cryptomelane and $\delta$-$MnO_2$. X-ray diffraction studies on both natural and chemically prepared samples of manganese dioxide by Cole, Wadsley and Walkley,[2] agree in general with those of McMurdie and Golovato[1] except in the case of $\gamma$-$MnO_2$ where three modifications are noticed. Differential thermal analysis and X-ray studies of the natural dioxides by Delano,[3] on the other hand, indicate only three modifications—pyrolusite, ramsdellite and $\alpha$-$MnO_2$. He opines that modifications such as $\gamma$ and $\delta$-$MnO_2$ are due to impure forms of the oxides. Kulp and Perfetti[4] have distinguished between the naturally occurring pyrolusite, ramsdellite, manganite and psilomelane by differential thermal analysis and X-ray diffraction. The results obtained by McMurdie and Golovato[1] and Kulp and Perfetti[4] for the naturally occurring crystalline forms of manganese dioxide are in good agreement.

During the course of differential thermal analysis of samples of synthetic manganese dioxide, it was noticed that the chromel-alumel thermocouples employed got easily corroded by the finely divided manganese dioxide at about 750° C. and resulted in the breakdown of the thermocouple. This difficulty did not arise with the naturally occurring ores. McMurdie and Golovato[1] noticed large differences in the nature of the differential curves particularly in the case of the artificially prepared oxides. Even the Pt-Pt (Rh) thermocouples were found to get corroded by the chemically prepared oxides. White[5] also noticed that prolonged use of the thermocouples led to changes in heat effect caused by contamination of the thermocouples. When the contaminated Pt-Pt (Rh) couples were tested by the present authors employing alumina powder in both the sockets of the sample holder of the differential thermal apparatus, highly erratic potentials were noticed.

From the foregoing, it is clear that the determination of the thermal curves for manganese dioxide has to be carried out employing uncorrodable couples or a suitable correction should be applied for the change of the voltage in the thermocouple due to corrosion.

## II. EXPERIMENTAL

### *Preparation of Samples*

(1) *Pyrolusite.*—Manganese nitrate was slowly decomposed at 150° C., till the evolution of nitrous fumes ceased. To oxidise any lower oxides formed, the product was heated in a current of oxygen at 450° C. for six hours. The substance was then washed with distilled water and finally dried at 60° C.

(2) $\gamma$-$MnO_2$.—This oxide was prepared by four different methods, as described below:—

(*a*) *Morozov and Kuznetsov's*[6] *Method.*—Manganous nitrate was heated in air at 300° C. The $MnO_2$ obtained was then converted to bixbyite ($Mn_2O_3$) by heating at 750° C. for three hours followed by reoxidation by chlorine in presence of 2% hydrochloric acid at 70°–80° C. for eight hours. The product was washed and dried at room temperature.

(*b*) Manganous sulphate was oxidised with potassium bromate in presence of sulphuric acid. The product was washed and dried at 60° C.

(*c*) *Glemser's*[7] *Method.*—An aqueous solution of manganous sulphate was oxidised in presence of a mixture of nitric acid and ammonium persulphate. The washed solid was dried at 60° C.

(*d*) *Electrolytic* $MnO_2$.—25% aqueous manganous sulphate was subjected to electrolytic oxidation at 65° C. in presence of sulphuric acid using platinum anode and graphite cathode, the current density at the anode being 0·25 amp./dm.$^2$ The anode was separated from the cathode by a porous porcelain diaphragm in order to avoid contamination with graphite particles. The product was washed and dried at 60° C.

(3) To a boiling solution of manganous sulphate, potassium permanganate solution was added drop by drop with stirring till the supernatant liquid became just pink. The manganese dioxide formed was washed free of sulphate and dried at room temperature.

(4) Commercial samples of manganese dioxide supplied by National Carbon Co., Ltd., Calcutta, and Estrella Batteries, Ltd., Bombay, were also subjected to thermal analysis to find out the nature of the oxides.

### *Analysis of the Samples*

The samples used were analysed for their 'total manganese' and 'dioxide' contents. 'Total manganese' was determined by Fischer's[8] modification of Volhard's method as recommended by Cohen and Little.[9] The 'dioxide' content was determined by oxalic acid method. The results of analysis are given in Table I.

TABLE I

| No. | Sample | % Mn | % $MnO_2$ |
|---|---|---|---|
| 1 | Chemical .. | 62·9 | 99·11 |
| 2*a* | Chemical .. | 61·9 | 95·4 |
| 2*b* | Chemical .. | 61·28 | 89·17 |
| 2*c* | Chemical .. | 57·99 | 86·9 |
| 2*d* | Electrolytic | 61·5 | 87·98 |
| 3 | Chemical .. | 59·1 | 84·63 |
| 4*a* | Commercial samples of Manganese dioxide | 56·84 | 83·49 |
| 4*b* | | 60·16 | 88·55 |
| 4*c* | | 53·33 | 75·61 |
| 4*d* | | 57·3 | 87·6 |

### *Apparatus for Thermal Analysis*

The apparatus employed for the determination of thermal curves was essentially the same as described by Norton[10] except for the fact that the furnace was mounted vertically and the differential temperature was recorded by noting the deflections on a scale with a high sensitive galvanometer. The sample holder consisted of a cylindrical 18–8 stainless steel block (1" in diameter and 1" in height) with two cups (5/16" in diameter and 5/8" in depth) capable of holding about 0·5–0·6 gm. of tightly packed alumina. The thermocouple holders could be introduced from below into these cups through a narrow passage drilled in the block. The sample holder was mounted on a vertical fire-clay tower over which the furnace could easily be slid. The E.M.F. of the differential temperature was measured with the galvanometer with a sensitivity of 13 mm. per 1° C. difference in temperature. Differential curves were obtained by heating the samples at a uniform rate of 10° C./minute by employing a 'variac' in the circuit. Ignited alumina was used as the inert material.

### *Standardisation of Thermocouples for Use with Chemically Prepared Manganese Dioxides*

In order to test the behaviour of Pt-Pt (Rh) thermocouple, the two cups were filled with ignited alumina after introducing the thermocouples at the centre. The differential temperature between the two samples was measured for every rise of 50° C. in the furnace temperature. The curve obtained is given in Fig. 1 (*a*) which indicates that the rate of heating of the two samples is quite uniform. In the next experiment, the alumina in one of the cups was replaced by the chemically prepared $MnO_2$ and the differential curve 1 (*b*) was obtained. After this experiment it was noticed that the Pt-Rh alloy wire had become slightly tarnished and this damage could not be corrected either by treatment with concentrated hydrochloric acid or by gentle abrasive action. In order to find whether the corrosion had any influence on the differential temperature, the two sample cups were cleaned and refilled with ignited alumina and the differential curve 1 (*c*) was taken. The comparison of curve 1 (*a*) with 1 (*c*) indicates that there is a good deal of change in the temperature recorded by the thermocouple due to corrosion of the thermocouple by the $MnO_2$. Reference to literature indicated that the other types of thermocouples are less suitable to be used with $MnO_2$, on account of greater corrosion with $MnO_2$ at higher temperatures. It was therefore decided to employ the Pt-Pt (Rh) couple with suitable corrections for the alteration of voltage due to corrosion, as described later.

In order to dissolve out the superficial contaminated layer, the thermocouple was heated with dilute nitric acid and its thermal behaviour studied with alumina in both the cups and the results obtained are given by curve 1 (*d*). Curve 1 (*e*) represents the behaviour of the thermocouple with alumina in both the cups after the bead and 2 mm. lengths of the thermocouple were cut off and the wires refused. Even when 2 mm. of the thermocouple wire was cut off, the behaviour was far from normal indicating thereby that the thermocouple was contaminated beyond 2 mm. length. Curve 1 (*f*) represents the behaviour of the thermocouple after 5 mm. of the corroded wire was cut off and re-fused with the platinum wire

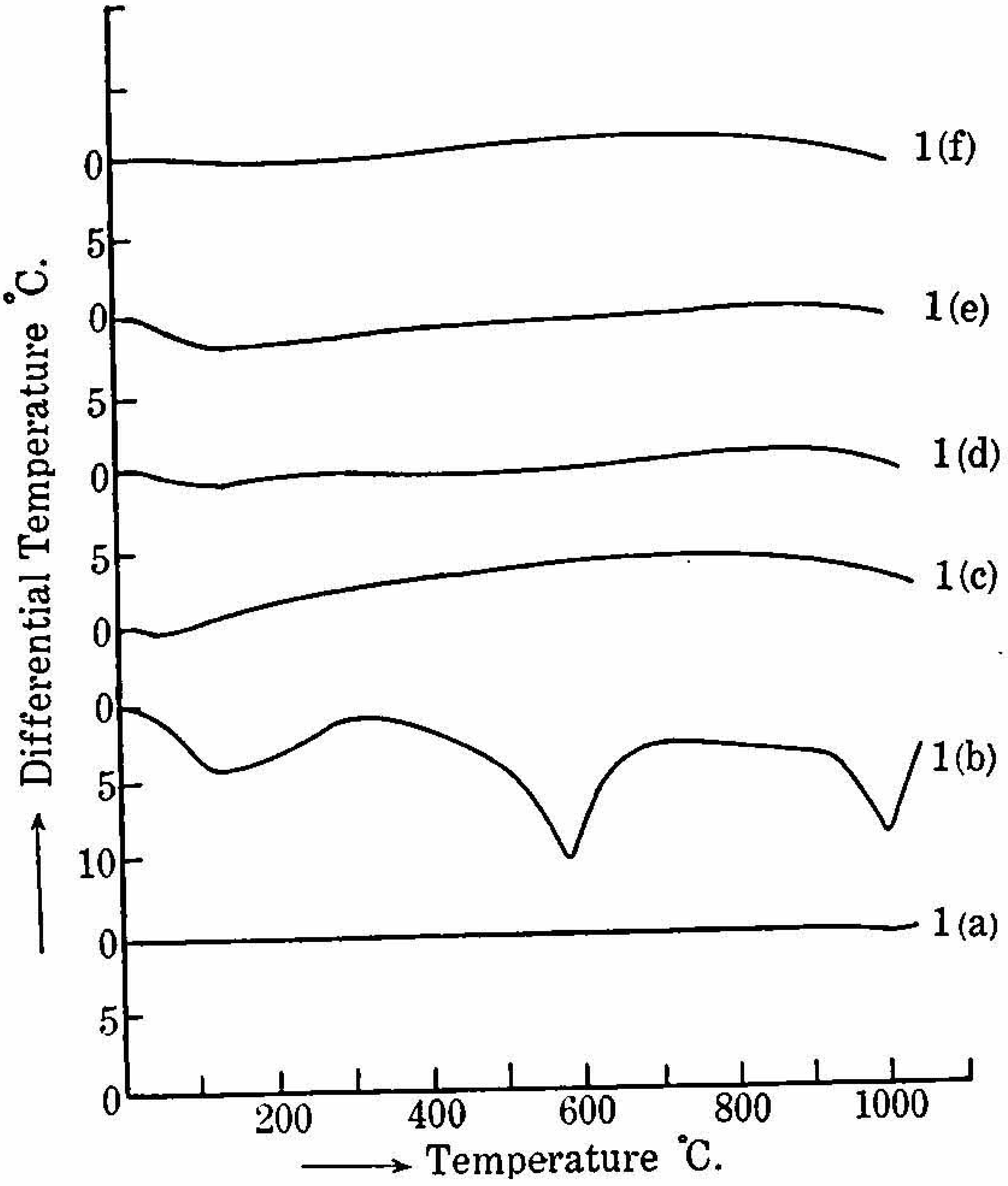

FIG. 1. Behaviour of Pt-Pt (Rh) thermocouple after use with chemical manganese dioxide.

1(*a*) Differential temperature for $Al_2O_3$—$Al_2O_3$

1(*b*) ,, ,, $Al_2O_3$—$MnO_2$ (Synthetic)

1(*c*) ,, ,, $Al_2O_3$—$Al_2O_3$ with the corroded couple of 1(*b*)

1(*d*) ,, ,, $Al_2O_3$—$Al_2O_3$ after the couple 1(*b*) was treated with ditute $HNO_3$.

1(*e*) Differential temperature for $Al_2O_3$—$Al_2O_3$ after cutting off 2 mm. from the tip of the couple 1(*b*).

1(*f*) Differential temperature for $Al_2O_3$—$Al_2O_3$ after cutting off 5 mm. from the tip of the couple 1(*c*).

and tried with the $Al_2O_3$ in both the sample holders. The results given above show considerable variation in temperatures indicated on account of the contamination of the thermocouple. The variation is of the order of 2° C. or 26 mm. galvanometer deflection. No single correction factor can therefore be applied as these variations are not uniform. Hence it is necessary that after doing the experiment with the chemically prepared $MnO_2$ sample, one should determine the thermal curve using alumina in both the sample cups. The corresponding corrections at each temperature could then be applied to all the differential thermal curves. As the choice of the thermo-

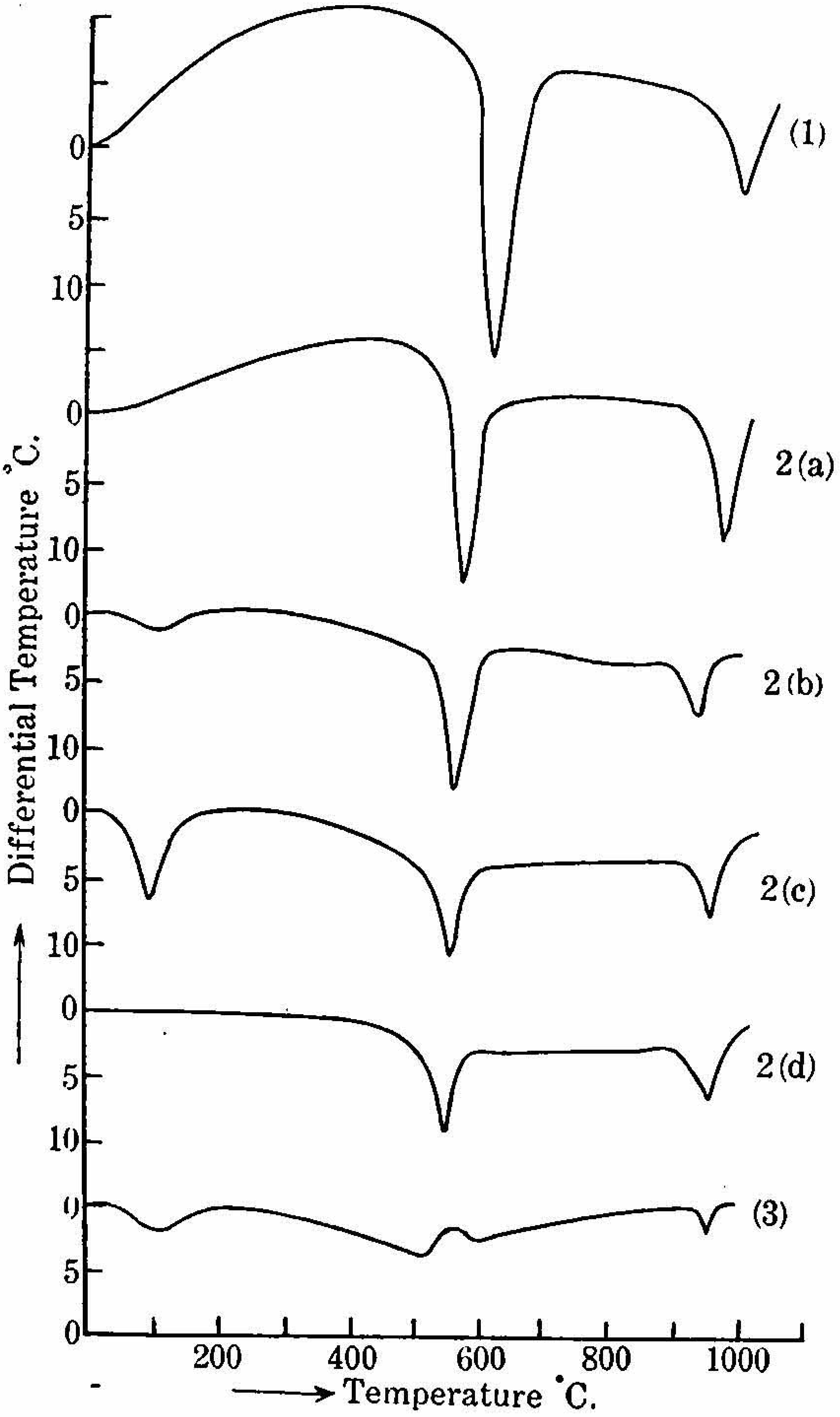

FIG. 2. Thermal curves for chemically prepared Manganese Dioxide Samples.

(1) Pyrolusite prepared from Mn $(NO_3)_2$
2(*a*) γ-$MnO_2$ ,, ,, Mn $(NO_3)_2$ by oxidation with chlorine
2(*b*) ,, ,, ,, Mn $SO_4$ ,, ,, $KBrO_3$
2(*c*) ,, ,, ,, ,, ,, ,, $(NH_4)_2$ $S_2O_8$
2(*d*) ,, ,, ,, ,, by electrolytic oxidation
3 $MnO_2$ ,, ,, Mn $SO_4$+$KMnO_4$

couples is limited, the correction factor as described above had to be employed in spite of the tediousness of the method. The curves given in Figs. 2 and 3 have all been drawn after application of the correction.

## III. RESULTS AND DISCUSSION

Differential thermal curves for the chemically prepared $MnO_2$ are given in Fig. 2. In expressing these results the differential temperatures have been plotted on the ordinate in place of the galvanometer readings as given by previous workers. Curve 1 (Fig. 2) indicates the behaviour of pyrolusite which gives two endothermic peaks at 620° C. and 990° C. The first endothermic depression is due to the formation of bixbyite ($Mn_2O_3$) and the second one is due to the formation of hausmanite ($Mn_3O_4$). These results are in conformity with those obtained by McMurdie and Golovato.[1] At the initial stages of the curve, however, there is a gradual exothermic change which is absent in the curve obtained by McMurdie and Golovato. Curve 2 (*a*) represents the behaviour of $\gamma$-$MnO_2$ prepared by heating Mn $(NO_3)_2$. In this case the transformations occur at 580° C. and 970° C. while in the case of pyrolusite the corresponding temperatures are 620° C. and 990° C. A gradual exothermic change at the initial stages of the curve could be noticed even in this curve. It is probable that the finely divided particles of the chemically prepared oxides may undergo sintering which gives rise to the initial exothermic change noticed. The curves 2 (*b*) and 2 (*c*) represent the behaviour of $\gamma$-$MnO_2$ prepared by chemical methods. In both the cases, a first endothermic depression is noticed at 100° C. due to dehydration. The other two depressions occur at about 560° C. and 950° C. These temperatures are also slightly lower than those obtained in curve 1. These differences from the thermal curves, therefore, can be employed to distinguish between $\gamma$-$MnO_2$ and chemically prepared pyrolusite. The behaviour of the $\gamma$-$MnO_2$ by electrolytic process is similar to that prepared by the chemical method, but for the absence of the depression at 100° C. The curves obtained by McMurdie and Golovato[1] for electrolytic $\gamma$-$MnO_2$ are widely variant from those noticed in the present investigation. In fact, there is a considerable variation in the two curves for the electrolytic $MnO_2$ prepared by McMurdie and Golovato by different methods. The large variation in their curves may partly be due to the presence of carbon in their samples. The erratic behaviour of the thermocouple employed without application of correction may also contribute to the divergence in the thermal curves obtained by them. As with their electrolytic preparations, there is a considerable deviation in the nature of the curves given for natural cryptomelanes. These authors have not given any curve for synthetic

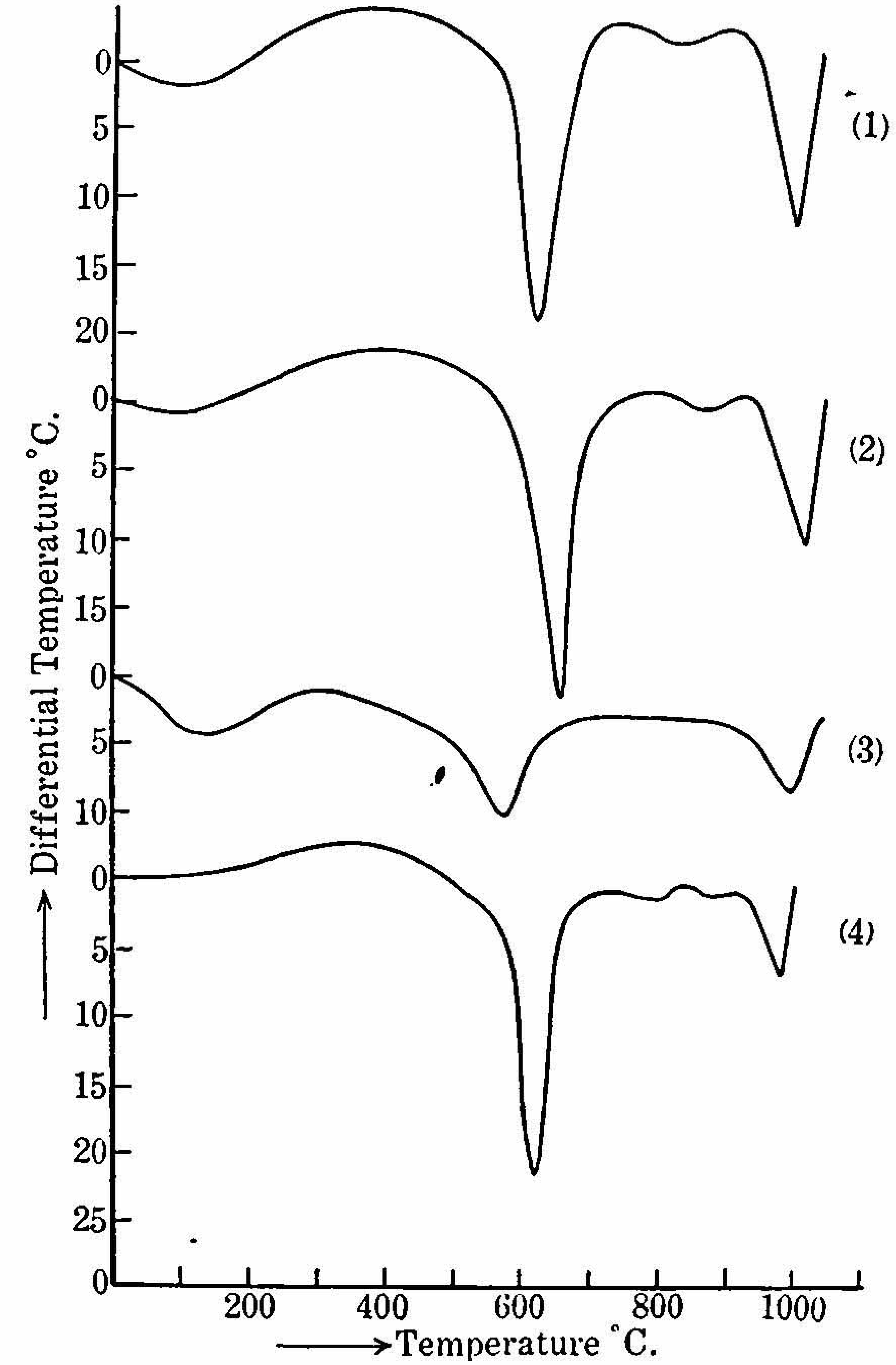

FIG. 3. Thermal curves for samples of Commercial Manganese Dioxide.
Curves 1,2,3 and 4 are the thermal curves for samples 4(*a*), 4(*b*), 4(*c*) and 4(*d*) respectively (Table I).

cryptomelane. The thermal curve obtained for the sample (3) with three endothermic depressions at 120°, 530° and 940° C. resembles that for cryptomelane, contrary to Cole, Wadsley and Walkley,[2] who identified the samples prepared by this method as $\gamma$-$MnO_2$. It is interesting to note in this connection that X-ray data for chemically prepared cryptomelane (Maxwell, Butler and Thirsk[11]) indicates a change in crystallinity at 200° C. and 500° C. while in the case of naturally occurring cryptomelane the change occurs between 600° C. and 800° C. depending upon the mode of occurrence of the sample.

Thermal curves for the natural and treated commercial samples of manganese dioxide are given in curves 1 and 2 in Fig. 3. In these curves there is an endothermic depression at about 100° C. indicating the loss of water. The other endothermic depressions occur at 620°–650° C. and at 1000° C. For natural pyrolusite the first endothermic change takes place between 650°–700° C. while for the $\gamma$-variety it occurs at about 600° C. The endothermic depressions at 100° C. and at 620°–650° C. can be taken to indicate that these two samples consist of mixtures of pyrolusite and $\gamma$-$MnO_2$. Curve (3) is for an activated variety of $MnO_2$ and has a prominent endothermic depression at 100° C. indicating thereby that the activated sample has a large percentage of $\gamma$-variety. This conclusion is supported further by the endothermic peak at 580° C. Curve (4) represents an F.S. quality sample of $MnO_2$ and seems to be mostly a pyrolusite. In conclusion, it can be stated that differential thermal analysis goes a long way in the identification of the various modifications of both natural and synthetic manganese dioxide samples.

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