Thermochimica Acta, 45 (1981) 279—292
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL DECOMPOSITION OF AQUEOUS MANGANESE NITRATE SOLUTIONS AND ANHYDROUS MANGANESE NITRATE. PART 2. HEATS OF REACTION

T.J.W. DE BRUIJN, G.M.J. DE RUITER, W.A. DE JONG and P.J. VAN DEN BERG

Delft University of Technology, Julianalaan 136, 2628 BL Delft (The Netherlands)

(Received 22 October 1980)

ABSTRACT

Differential thermal analysis of the thermal decomposition of aqueous manganese nitrate solutions in air and nitrogen shows three distinct endothermic heat effects. The first effect results from partial evaporation of water to a solution containing equimolar amounts of H_2O and $Mn(NO_3)_2$. The two subsequent decomposition steps produce MnO_2. The heat effect of each of the latter two steps depends on the sample weight but their sum remains constant at about 170 ± 14 kJ mole^{-1}.

Decomposition under vacuum of anhydrous $Mn(NO_3)_2$ shows only one heat effect of 155 ± 12 kJ mole^{-1}. DTA and X-ray analysis indicate that decomposition of a $Mn(NO_3)_2$ solution results in γ-MnO_2 and decomposition under vacuum of anhydrous $Mn(NO_3)_2$ results in γ-MnO_2 with large amounts of Mn_2O_3. A comparison between measured and calculated heats of reaction shows fair agreement.

INTRODUCTION

The thermal decomposition of aqueous manganese nitrate solutions is being studied as part of a project to obtain battery-grade MnO_2 from manganese dioxide ore via a manganese nitrate solution. In Part 1 of this series [1] the mechanism of the thermal decomposition has been discussed. It was found that on heating, an aqueous manganese nitrate solution loses weight in three steps:

(i) water evaporates to a solution containing equimolar amounts of water and $Mn(NO_3)_2$,

(ii) a decomposition step follows in which the residual water evolves and only part of the $Mn(NO_3)_2$ decomposes to MnO_2 due to acceleration of the $Mn(NO_3)_2$ decomposition by water vapour, and

(iii) decomposition of the remaining $Mn(NO_3)_2$ to MnO_2.

Chemical steps (ii) and (iii) will be called first and second decomposition step respectively, because the first thermal effect, evaporation, is a physical process. Below, results are reported of measurements of the heat of reaction of the two decomposition steps. Furthermore, the heat effects of the decomposition of anhydrous $Mn(NO_3)_2$ and of the reaction to Mn_2O_3 of products obtained by decomposing $Mn(NO_3)_2$ solutions and anhydrous $Mn(NO_3)_2$ were measured. The latter measurements were also performed with some battery-grade γ-MnO_2 reference samples. The experimental findings are compared with results calculated from thermodynamic data.

THERMODYNAMIC CALCULATION

General

The thermodynamic study reported below was confined to the reactions for which sufficient evidence had been found in our work on the mechanism of the decomposition of manganese nitrate solutions [1]. In other words, unlikely reactions such as the formation of manganese oxynitrate, $MnONO_3$ [2,3], were not included. The reactions considered are:
Evaporation of water from a solution of $Mn(NO_3)_2$ in 6 moles H_2O in steps of 1 mole H_2O each, finally resulting in anhydrous $Mn(NO_3)_2$:

$$\begin{array}{l} Mn(NO_3)_2 \text{ in } 6\ H_2O_{(l)} \rightarrow Mn(NO_3)_2 \text{ in } 5\ H_2O_{(l)} + H_2O_{(g)} \\ \quad\vdots \\ Mn(NO_3)_2 \text{ in } 1\ H_2O_{(l)} \rightarrow Mn(NO_3)_2 + H_2O_{(g)} \end{array} \tag{1}$$

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2\ NO_2 \tag{2}$$

$$Mn(NO_3)_2 \text{ in } 1\ H_2O_{(l)} \rightarrow MnO_2 + 2\ NO_2 + H_2O_{(g)} \tag{3}$$

$$Mn(NO_3)_2 \rightarrow MnO_2 + N_2O_4 \tag{4}$$

$$MnO_2 \rightarrow 1/2\ Mn_2O_3 + 1/4\ O_2 \tag{5}$$

Heats of reaction and free energy changes of the reactions were calculated. To that end, all relevant heats of formation and specific heat data were found from the literature or estimated. The heats of reaction at other temperatures than 298 K were calculated from

$$\Delta H_r^0 = \sum \Delta H_f^0 + \int_{298}^{T} \sum C_p^0 \, dT$$

Calculation of the free energy change of the reactions, ΔG_r^0, requires knowledge of the entropy change; this was calculated from

$$\Delta S_r^0 = \sum S_{298}^0 + \int_{298}^{T} \frac{\sum C_p^0}{T} \, dT$$

The free energy change of the reactions was obtained from

$$\Delta G_r^0 = \Delta H_r^0 - T\,\Delta S_r^0$$

and the equilibrium water vapour partial pressure for the various evaporation steps from

$$\Delta G_r^0 = -RT \ln p_{H_2O}$$

Data used

For several of the substances involved in the above reactions, one or more of the standard values of the enthalpy of formation, ΔH_f^0, entropy, S_{298}^0, and specific heat, $C_{p,298}^0$, had to be estimated by analogy from related data. This was done as outlined below.

The standard entropy, S_{298}^0, of crystalline $Mn(NO_3)_2$ was estimated by comparing S_{298}^0 values for several metal nitrates with S_{298}^0 values for chlorides and sulphates of the same metal, because entropy data for $MnCl_2$ and $MnSO_4$ are known whereas none are available for $Mn(NO_3)_2$. The difference in standard entropy between nitrates and chlorides, and between nitrates and sulphates is about 83.7 J mole^{-1} K^{-1}. This allowed the calculation of two values of S_{298}^0 for $Mn(NO_3)_2$, viz. 200.8 and 196.6 J mole^{-1} K^{-1}; the mean value, 198.7 J mole^{-1} K^{-1}, was used. This value is somewhat lower than Kelley's result, i.e. 205.0 J mole^{-1} K^{-1} [4].

Standard values for the specific heats of $Mn(NO_3)_2$ and its aqueous solutions are also unavailable. The $C_{p,298}^0$ values for only a few nitrates being known, the data of Kelley for Mg, Ca and Ba nitrates were used [4]. An estimate of the standard specific heat of $Mn(NO_3)_2$ was obtained by averaging the values for the above three nitrates. The result was 147.3 J mole^{-1} K^{-1}.

The temperature dependence of the specific heat of $Mn(NO_3)_2$ was also derived by averaging the values for the three nitrates (cf. Table 1).

The standard heats of formation, ΔH_f^0, of manganese nitrate in aqueous solutions with one and two moles H_2O per mole $Mn(NO_3)_2$ were derived by interpolation from the known values for crystalline $Mn(NO_3)_2$ and less concentrated $Mn(NO_3)_2$ solutions. ΔH_f^0 for the total solution is calculated by summation of ΔH_f^0 for $Mn(NO_3)_2$ in such a solution and ΔH_f^0 for H_2O for each mole of H_2O rpresent in the solution.

The standard entropy, S_{298}^0, for $Mn(NO_3)_2$ in an aqueous solution was found by interpolation from the known values for crystalline $Mn(NO_3)_2$ and an ideal aqueous solution of molality 1.

The standard specific heat of a manganese nitrate solution was estimated from the known $C_{p,298}^0$ value for $Mn(NO_3)_2 \cdot 6\,H_2O$, 613.8 J mole^{-1} K^{-1}, by subtracting 75.3 J mole^{-1} K^{-1} (i.e. $C_{p,298}^0$ for water) for each mole of water less in the solution.

The temperature dependence of C_p^0 for the manganese nitrate solution was calculated from those of the crystalline nitrate and $Mn(NO_3)_2 \cdot 6\,H_2O$ [4] by

TABLE 1

Equations for C_p^0 [4]

Substance	C_p^0 (J mole^{-1} K^{-1})
$Mg(NO_3)_2$	$44.7 + 298.1 \times 10^{-3}\,T + 7.5 \times 10^5\,T^{-2}$
$Ca(NO_3)_2$	$123.0 + 154.1 \times 10^{-3}\,T - 17.3 \times 10^5\,T^{-2}$
$Ba(NO_3)_2$	$125.8 + 149.5 \times 10^{-3}\,T - 16.8 \times 10^5\,T^{-2}$

the following equation

$$C_p^0[\mathrm{Mn(NO_3)_2 \text{ in } \mathit{x} \text{ mole } H_2O}]_T = \frac{x}{6}\, C_p^0[\mathrm{Mn(NO_3)_2 \text{ in } \mathit{x}\ H_2O}]_{298}$$

$$\times \frac{C_p^0[\mathrm{Mn(NO_3)_2 \cdot 6\ H_2O_{(l)}}]_T}{C_p^0[\mathrm{Mn(NO_3)_2 \cdot 6\ H_2O_{(l)}}]_{298}} + \frac{6-x}{6} \times C_p^0[\mathrm{Mn(NO_3)_2 \text{ in } \mathit{x}\ H_2O}]_{298}$$

$$\times \frac{C_p^0[\mathrm{Mn(NO_3)_2}]_T}{C_p^0[\mathrm{Mn(NO_3)_2}]_{298}} (0 \leqslant x \leqslant 6)$$

Values of ${}_{298}^{\ T}\!\int C_p^0\, \mathrm{d}T$ and ${}_{298}^{\ T}\!\int C_p^0/T\, \mathrm{d}T$ for NO_2 and N_2O_4 were obtained from tables given in ref. 5.

A survey of the data used in the thermodynamic calculations is shown in Tables 2 and 3; the temperature dependence of the specific heat of MnO_2, Mn_2O_3 and O_2 was derived from ref. 6.

Results

Free energies of reaction, ΔG_r^0, and ${}^{10}\log p_{H_2O}$ for the various stages of evaporation are shown in Figs. 1 and 2 as a function of temperature. Figure 3 contains ΔG_r^0 values as a function of temperature for the chemical reactions (2), (3), (4), and (5). Figure 4 shows the temperature dependence

TABLE 2

Thermodynamic data used in calculations [4—6]

Substance	ΔH_f^0 (kJ mole^{-1})	ΔG_f^0 (kJ mole^{-1})	S_{298}^0 (J mole^{-1} K^{-1})	$C_{p,298}^0$ (J mole^{-1} K^{-1})
$Mn(NO_3)_2 \cdot 6\ H_2O$ glassy	—2371.9			493.7
$Mn(NO_3)_2 \cdot 6\ H_2O_{(l)}$	—2331.6			613.8
$Mn(NO_3)_2$ in 6 H_2O	—616.6		210.9e	613.8 *
$Mn(NO_3)_2$ in 5 H_2O	—613.4		209.9e	538.5e *
$Mn(NO_3)_2$ in 4 H_2O	—608.9		208.5e	462.2e *
$Mn(NO_3)_2$ in 3 H_2O	—602.45		206.6e	387.9e *
$Mn(NO_3)_2$ in 2 H_2O	—594.5e		204.1e	312.5e *
$Mn(NO_3)_2$ in 1 H_2O	—585.5e		201.5e	237.2e *
$Mn(NO_3)_{2(c)}$	—576.26		198.7e	147.3e
$Mn(NO_3)_{2aq.m=1}$	—635.5	—451.0	216.6	
$MnO_{2(c)}$	—520.0	—465.2	53.1	54.1
$Mn_2O_{3(c)}$	—959.0	—881.2	110.5	107.7
$O_{2(g)}$	0.00	0.00	205.0	26.1
$NO_{2(g)}$	33.1	51.2	239.9	37.0
$N_2O_{4(g)}$	9.1	97.7	304.3	77.3
$H_2O_{(g)}$	—241.8	—228.6	188.7	33.6
$H_2O_{(l)}$	—285.9	—237.2	70.0	75.3

c = crystalline; l = liquid; g = gas. e = Estimated value; * = value for total solution; aq. *m* = 1 = ideal aqueous solution of molality 1.

TABLE 3

Equations for C_p^0 used in calculations

Substance	C_p^0 (J mole^{-1} K^{-1})
$Mn(NO_3)_2$ in 6 mole H_2O	$429.24 + 619.65 \times 10^{-3}T$
$Mn(NO_3)_2$ in 5 mole H_2O	$374.72 + 575.17 \times 10^{-3}T - 5.61 \times 10^5T^{-2}$
$Mn(NO_3)_2$ in 4 mole H_2O	$318.57 + 521.87 \times 10^{-3}T - 9.67 \times 10^5T^{-2}$
$Mn(NO_3)_2$ in 3 mole H_2O	$264.55 + 459.72 \times 10^{-3}T - 12.11 \times 10^5T^{-2}$
$Mn(NO_3)_2$ in 2 mole H_2O	$211.38 + 388.78 \times 10^{-3}T - 13.01 \times 10^5T^{-2}$
$Mn(NO_3)_2$ in 1 mole H_2O	$159.08 + 308.99 \times 10^{-3}T - 12.34 \times 10^5T^{-2}$
$Mn(NO_3)_{2(c)}$	$97.91 + 200.46 \times 10^{-3}T - 9.20 \times 10^5T^{-2}$
$MnO_{2(c)}$	$69.45 + 10.21 \times 10^{-3}T - 16.23 \times 10^5T^{-2}$
$Mn_2O_{3(c)}$	$103.47 + 35.06 \times 10^{-3}T - 13.51 \times 10^5T^{-2}$
$O_{2(g)}$	$34.60 + 1.079 \times 10^{-3}T - 7.853 \times 10^5T^{-2}$
$H_2O_{(l)}$	75.31

of the heat effects of the chemical reactions and of the evaporation of the last mole of H_2O.

EXPERIMENTAL

Equipment

Bureau de Liaison DTA equipment was used in all experiments. It contained two holders for platinum sample pans, one for the sample and the other for a reference substance, which deliver the DTA-signal, and a third holder for measuring the temperature in the equipment. Air or nitrogen

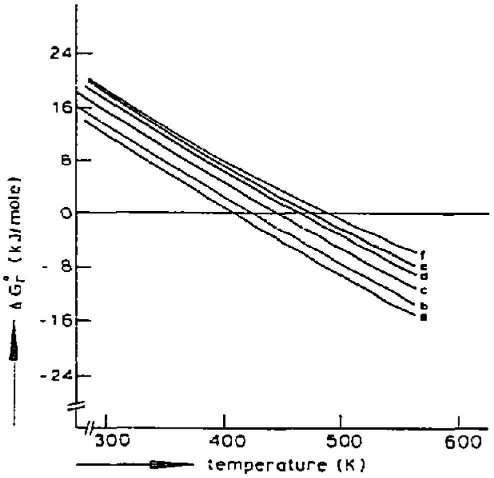

Fig. 1. ΔG_r^0 as a function of temperature for the evaporation of water from a solution of $Mn(NO_3)2$ in 6 H_2O in steps of 1 mole H_2O each.

Reactions: (a) $Mn(NO_3)_2$ in 6 mole $H_2O \rightarrow Mn(NO_3)_2$ in 5 mole $H_2O + H_2O_{(g)}$

(f) $Mn(NO_3)_2$ in 1 mole $H_2O \rightarrow Mn(NO_3)_{2(c)} + H_2O_{(g)}$

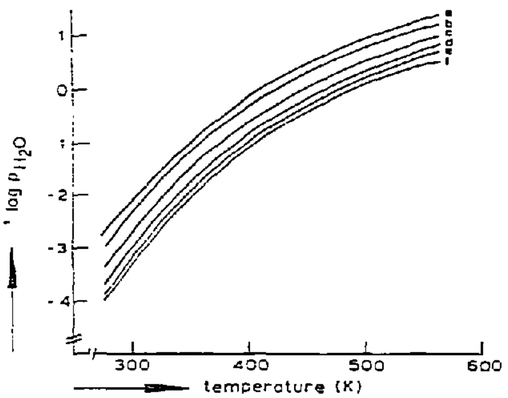

Fig. 2. $^{10}\log p_{H_2O}$ as a function of temperature for the evaporation of water from a solution of $Mn(NO_3)_2$ in 6 H_2O in steps of 1 mole H_2O each.
Reactions: (a) $Mn(NO_3)_2$ in 6 mole $H_2O \rightarrow Mn(NO_3)_2$ in 5 mole $H_2O + H_2O_{(g)}$
(f) $Mn(NO_3)_2$ in 1 mole $H_2O \rightarrow Mn(NO_3)_{2(c)} + H_2O_{(g)}$.

dried over molecular sieves was passed through the equipment; in some experiments the equipment was evacuated by a vacuum pump. In a few experiments a Dupont 910 differential scanning calorimeter flushed with N_2 gas dried over P_2O_5 was used.

Materials

An aqueous solution of reagent-grade manganese nitrate obtained from J.T. Baker Chemicals Corp. was used in the nitrate decomposition experiments. Analyses for Mn^{2+} and NO_3^- showed that the solution contained 52.1 wt.% $Mn(NO_3)_2$, 44.0 wt.% H_2O and 3.9 wt.% HNO_3.

In some experiments products obtained from decomposition of the nitrate solution were further decomposed to Mn_2O_3. The resulting heat effect was

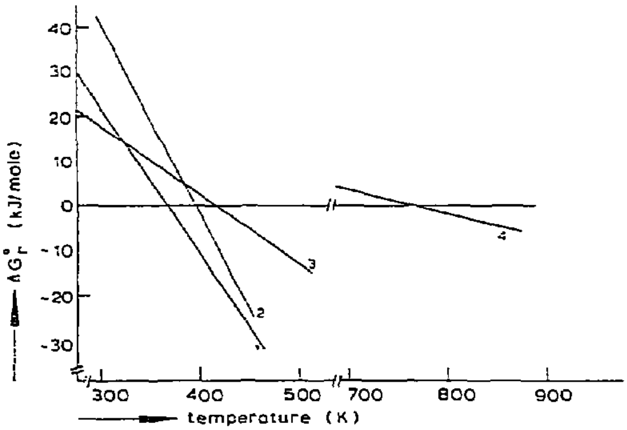

Fig. 3. ΔG_r^0 as a function of temperature for the following reactions: (1) $Mn(NO_3)_2 \rightarrow MnO_2 + 2\,NO_2$; (2) $Mn(NO_3)_2$ in 1 mole $H_2O \rightarrow MnO_2 + 2\,NO_2 + H_2O_{(g)}$; (3) $Mn(NO_3)_2 \rightarrow MnO_2 + N_2O_4$; (4) $MnO_2 \rightarrow 1/2\,Mn_2O_3 + 1/4\,O_2$.

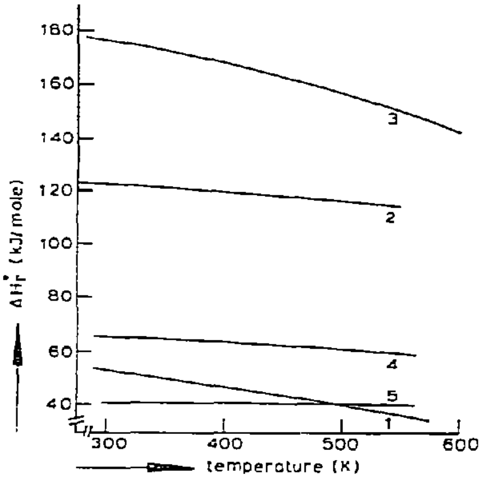

Fig. 4. Heat effects as a function of temperature for the following reactions: (1) $Mn(NO_3)_2$ in 1 mole $H_2O \rightarrow Mn(NO_3)_2 + H_2O_{(g)}$; (2) $Mn(NO_3)_2 \rightarrow MnO_2 + 2\ NO_2$; (3) $Mn(NO_3)_2$ in 1 mole $H_2O \rightarrow MnO_2 + 2\ NO_2 + H_2O_{(g)}$; (4) $Mn(NO_3)_2 \rightarrow MnO_2 + N_2O_4$; (5) $MnO_2 \rightarrow 1/2\ Mn_2O_3 + 1/4\ O_2$.

compared to the heat effect of the decomposition of standard γ- and β-MnO_2 samples, so-called International Common Samples (ICS). These IC samples, prepared mainly by battery manufacturers, are distributed by the IC Sample Office to serve as reference materials for the study, evaluation and comparison of various manganese oxides for battery use [8]. ICS Nos. 1, 2, 3 and 9 were selected as standards for γ-MnO_2 and ICS No. 6 for β-MnO_2. The γ-MnO_2 was prepared electrolytically and shows an X-ray diffraction diagram closely corresponding to the diagram for γ-MnO_2 given in ASTM index 14-644, whereas the diffraction pattern of ICS 6 corresponds to the pattern in ASTM index 12-716 [9], which applies to β-MnO_2s.

Procedures

Two procedures were used to study the decomposition of aqueous solutions and the decomposition of anhydrous $Mn(NO_3)_2$. The latter decomposition requires the removal of all water, which is accomplished under vacuum.

When decomposing manganese nitrate solution the procedure was as follows. After weighing the solution (1—25 mg), it was placed into the equipment as rapidly as possible. The apparatus was immediately closed and after adjustment of the air flow to 100 ml min^{-1} the sample holders were heated at 6°C min^{-1}, registering the temperature differences on a recorder. Some samples were decomposed in a nitrogen flow of 100 ml min^{-1}. Experiments in the DSC equipment were performed with a heating rate of 5°C min^{-1} and a nitrogen gas flow of 50 ml min^{-1}.

When studying the behaviour of anhydrous $Mn(NO_3)_2$, a sample of known weight was placed in the equipment, vacuum was applied ($\simeq$2.3 kPa) and the sample heated to 100—120°C at a rate of 6 or 12°C min^{-1}. A small air flow of 30 ml min^{-1} was maintained to sweep all water vapour from the equipment. The resulting anhydrous $Mn(NO_3)_2$ was decomposed by raising the

TABLE 4

Substances and data used for calibration of DTA equipment

Substance	Heat effect due to	Mean temp. T_m(° C)	Heat effect (kJ mole^{-1})
H_2O	Melting	2.0	6.0
Ga	Melting	31.0	5.6
In	Melting	161	3.3
Sn	Melting	238	7.2
$CdCO_3$	Decomposition	380	$\simeq$94.0
Ag_2O	Decomposition	420	$\simeq$26.6
K_2SO_4	Change of solid structure	590	8.1
$CaCo_3$	Decomposition	730	$\simeq$171.5

temperature to a maximum temperature between 300 and 400° C at a rate of 12° C min^{-1}, either without passing any gas through the apparatus at a pressure of $\simeq$0.5 kPa or with a small gas flow of 30 ml min^{-1} at $\simeq$2.3 kPa. The sample weight was varied between 1 and 10 mg. After each experiment the residue was weighed to measure the weight loss.

The decomposition of the IC samples or of products obtained by decomposing $Mn(NO_3)_2$ solutions was performed at 0.1 MPa by applying an air flow of 100 ml min^{-1} and a heating rate of 12° C min^{-1}. The sample weight of the IC samples was about 8 mg: the weight of the decomposition products varied, depending on the initial weight of the $Mn(NO_3)_2$ solution. The heat of the reaction, ΔH_r^0, was calculated from the resulting peaks by

$$\Delta H_r^0 = KA$$

with ΔH_r^0 = heat of reaction (kJ mole^{-1}), K = calibration factor (kJ/nonius unit), A = peak area (in nonius units). The peak area (A) was measured by means of a planimeter. K depends on the temperature and gas flow and is read from a calibration curve. The temperature at the centre of gravity of each peak (T_m) was taken as the mean temperature at which the reaction occurred.

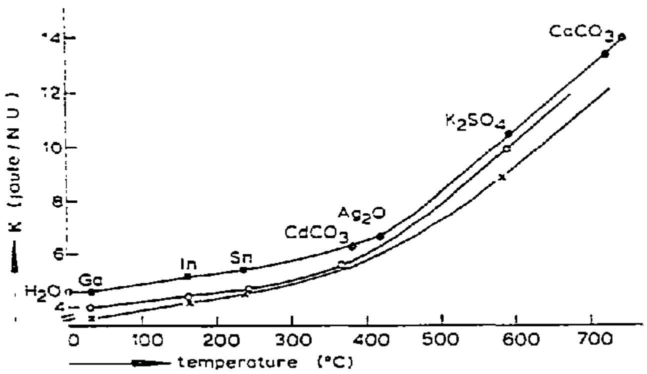

Fig. 5. Calibration curve for DTA experiments. ●, 100 ml min^{-1} air; ○, vacuum ($\simeq$2.3 kPa) + 30 ml min^{-1} air; ×, vacuum ($\simeq$0.5 kPa).

TABLE 5

Enthalpies as a function of temperature

Substance	ΔH_T^0 (J mole^{-1})
$CdCO_3$	$97\,069 + 19.00T - 36.44 \times 10^{-3}T^2$
Ag_2O	$30\,208 + 11.00T - 22.80 \times 10^{-3}T^2 - 2.18 \times 10^5T^{-1}$
$CaCO_3$	$177\,820 + 2.76T - 9.02 \times 10^{-3}T^2 - 0.17 \times 10^5T^{-1}$

Calibration

To calculate the heat effect of a reaction the calibration factor (K) must be known. It was established by measuring known heat effects and the resulting peak areas of some substances which are known to give reproducible results [10]. Some data on the substances used are listed in Table 4. For decomposition reactions the temperature, and thus the enthalpy, varies with the experimental conditions. The heat effect at the observed temperature was calculated using the equations given in Table 5 [10]. Figure 5 shows the resulting calibration curves for the three different experimental conditions used. The DSC equipment was calibrated with indium (m.p. 156°C) using a nitrogen flow of 50 ml min^{-1}.

RESULTS

A curve representative of the decomposition of aqueous $Mn(NO_3)_2$ solutions is shown in Fig. 6 in the form of a plot of ΔT vs. temperature. Three endothermal peaks are observed, in agreement with the weight losses observed in thermobalance experiments [1]. The first peak is caused by evaporation of water to a composition of the solution of approximately 1 mole of H_2O per mole of $Mn(NO_3)_2$ and the other two by decomposition of this con-

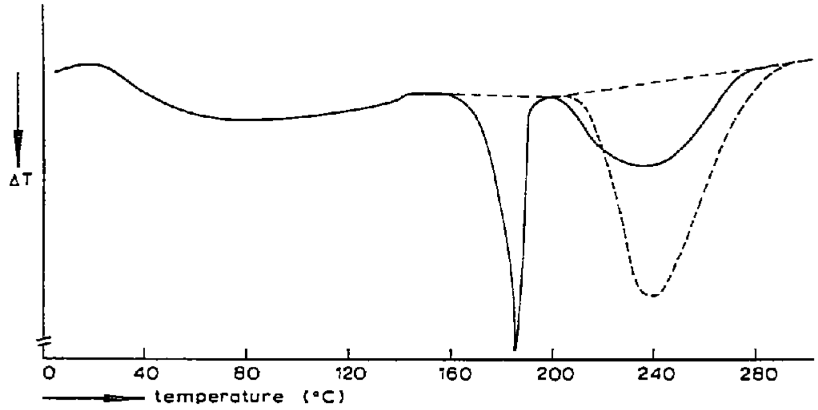

Fig. 6. Representative DTA curve for the decomposition of aqueous manganese nitrate solutions (————) and anhydrous manganese nitrate (— — —).

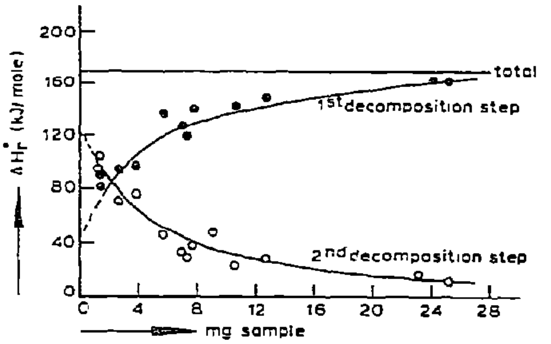

Fig. 7. Heat of reaction of both decomposition steps as a function of sample weight.

centrated solution to MnO_2 in two steps. Decomposition of anhydrous $Mn(NO_3)_2$, on the other hand, showed a single endothermic peak at a temperature at which the second decomposition step normally occurred when using aqueous solutions (T_m about 240°C) (Fig. 6).

Evaporation of water from the solution occurs from room temperature to about 120°C. A heating rate of 6°C min^{-1} or less had to be applied in order to separate the peak due to evaporation from the peak due to the first decomposition step. However, owing to the large temperature range over which water evaporated, a very broad low peak resulted; under such a peak a base line could not be drawn with sufficient accuracy. As a result, very large fluctuations occurred in the heat of reaction (up to 67 kJ $mole^{-1}$), and sufficiently reliable results for the evaporation cannot be given.

The decomposition depended on gas flow rate as well as on sample weight. At very low flow rates of 0—10 ml min^{-1} the peaks for the first and second decomposition steps completely coincided, only one peak being observed at a position where normally the first peak appears. An increase of the sample weight from 1 to 25 mg resulted in a comparable effect. As the sample weight is higher the heat effect of the first decomposition step increases, whereas that of the second decreases. However, the sum of the heat effects of the two steps remains virtually constant at 170 ± 14 kJ $mole^{-1}$ (Fig. 7).

TABLE 6

Data about the decomposition to Mn_2O_3 for several MnO_2 samples

Sample	Temp. decomposition started (°C)	T_m (°C)	ΔH_r^0 (kJ $mole^{-1}$)
ICS 1 (γ-MnO_2)	529	568	24.3
ICS 2 (γ-MnO_2)	523	562	24.1
ICS 3 (γ-MnO_2)	535	567	24.7
ICS 9 (γ-MnO_2)	526	565	23.3
ICS 6 (β-MnO_2)	631	650	39.0
Product (normal)	508	548	23.9
Product (vacuum)	508	530	10.7

Decomposition in nitrogen resulted in a combined heat effect of 174 ± 17 kJ mole^{-1} for the two decomposition steps. This agrees well with results from some exploratory experiments performed in the DSC equipment, also under nitrogen, which resulted in a mean total heat effect of about 165 kJ mole^{-1}. Such a change of atmosphere apparently has no or only a very small influence of the magnitude of the heat effect. The heat effect of decomposition of anhydrous $Mn(NO_3)_2$ was 155 ± 12 kJ mole^{-1}.

X-ray diffraction patterns of some of the DTA products obtained by decomposing the solution showed lines which corresponded well with the pattern of the standard γ-MnO_2 samples (ICS Nos. 1, 2, 3 and 9). In some patterns the strongest line of Mn_2O_3 was faintly visible. X-Ray diffraction photographs of products of the decomposition of anhydrous $Mn(NO_3)_2$ revealed the presence of much more Mn_2O_3 besides γ-MnO_2.

Other experiments also showed that an appreciable percentage of Mn_2O_3 must be present in the product prepared by decomposing anhydrous $Mn(NO_3)_2$. This follows from the heat effects determined on product and reference samples, as shown in Table 6. The heats of reaction given in the Table refer to decomposition to Mn_2O_3 in an air flow of 100 ml min^{-1}. The weight of the aqueous $Mn(NO_3)_2$ sample did not affect the heat of decomposition to Mn_2O_3 of the MnO_2 formed as the primary product.

DISCUSSION

From thermobalance experiments it is known that an equimolar solution of water and $Mn(NO_3)_2$ can be obtained relatively easily. Further removal of water is very difficult, although a reasonable evaporation rate can still be obtained by applying vacuum [1,11].

When the results given in Fig. 2 are considered, it is seen that these experimental facts tie in with the results of the thermodynamic calculations: if the partial pressure of water above a solution of manganese nitrate is low enough water evaporates until anhydrous $Mn(NO_3)_2$ is obtained.

It is concluded from Fig. 3 that decomposition to MnO_2 and NO_2 is thermodynamically more likely than decomposition to MnO_2 and N_2O_4; the temperature at which ΔG_r^0 is zero for the decomposition to NO_2 being $\simeq$95°C as against $\simeq$140°C for decomposition to N_2O_4. In this connection it should be borne in mind that the thermodynamic data apply to the formation of β-MnO_2. However, from X-ray data it was concluded that γ-MnO_2 was formed in the two-step decomposition. The difference in the heat of reaction, ΔH_r^0, between the decomposition of γ-MnO_2 to Mn_2O_3 and that of β-MnO_2 to Mn_2O_3 is estimated as 15 kJ mole^{-1}. This value can be deduced from the heats of reaction obtained for the IC samples (Table 6). Because ΔH_r^0 for the decomposition of β-MnO_2 does not change much with temperature, the difference in ΔH_r^0 between γ-MnO_2 and β-MnO_2 is also believed not to vary much with temperature. If the entropy for γ-MnO_2 is not much higher than the entropy for β-MnO_2, the free energy change for decomposition of $Mn(NO_3)_2$ to γ-MnO_2 will be higher than for decomposition to β-MnO_2 by at most 15 kJ mole^{-1}. This implies that the lines in Fig. 3 will shift to higher temperatures. As a consequence, the temperature at which $\Delta G_r^0 = 0$ shifts by at most 40°C to about 135°C (line 1); the corresponding temperature for line 3 increases by at most 100°C to about 230°C. This agrees with results obtained by Lundquist [12], who found β-MnO_2 as the product of decomposition of $Mn(NO_3)_2$ solution at low temperatures (as low as 100°C), whereas rapid decomposition at $\simeq$210 and 360°C resulted in what he called "gamma—rho MnO_2".

From the thermodynamic data given in Fig. 4 the heat effect of the decomposition of a solution and of anhydrous $Mn(NO_3)_2$ are estimated and compared to measured values. Suppose one decomposes a sample consisting of 8.5 mg 61.5 wt.% $Mn(NO_3)_2$ solution as used in ref. 1. T_m is 185°C and from Fig. 6 in ref. 1 it follows that the weight loss up to the second step is about 55%. Since 53% of the $Mn(NO_3)_2$ would decompose in the first decomposition step, the heat effect for this step would equal the sum of the heat effect for removal of 1 mole of water and 53% of the heat effect for $Mn(NO_3)_2$ decomposition, i.e. 106.4 kJ mole^{-1} in all. In the second step the remaining 47% of the $Mn(NO_3)_2$ would decompose at T_m = 230°C, resulting in $\Delta H_r^0 = 54.8$ kJ mole^{-1}. The total heat effect is thus expected to be 161.2 kJ mole^{-1} plus an additional 15 kJ mole^{-1} for the difference between γ- and β-MnO_2, i.e. approximately 176 kJ mole^{-1} for the overall decomposition of a solution of 1 mole of $Mn(NO_3)_2$ in 1 mole H_2O to γ-MnO_2 and 2 NO_2. This agrees quite satisfactorily with the measured value of 170 ± 14 kJ mole^{-1}.

For the decomposition in vacuum, the formation of Mn_2O_3 besides γ-MnO_2 has to be taken into account. It is supposed that the structure of the γ-MnO_2 of the IC samples is identical to the structure of the γ-MnO_2 present in the product obtained on decomposition of the anhydrous $Mn(NO_3)_2$. By comparing the heat effects of the decomposition to Mn_2O_3 ($\simeq$24.0 and 10.7 kJ mole^{-1}, respectively; Table 6) the amount of Mn_2O_3 present in the product was estimated at 55%. Now the heat effect of the decomposition of anhydrous $Mn(NO_3)_2$ can be estimated. For T_m = 240°C, ΔH_r^0 amounts to 116.2 (to β-MnO_2) + 0.55 × 40.3 (β-$MnO_2 \rightarrow Mn_2O_3$) + 0.45 × 15 ($\beta$-$MnO_2 \rightarrow \gamma$-$MnO_2$) = 145.1 kJ mole^{-1}, as compared to the measured value of 155 ± 12

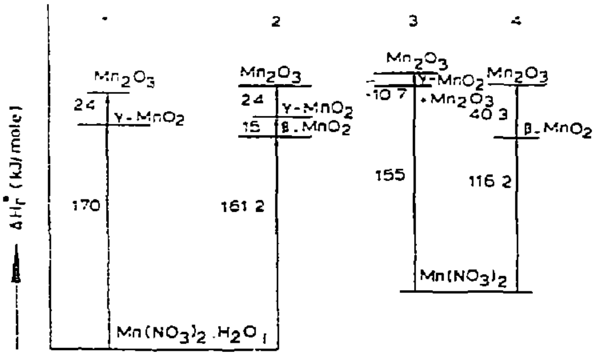

Fig. 8. Measured and calculated heats of reaction for the decomposition of an aqueous $Mn(NO_3)_2$ solution and anhydrous $Mn(NO_3)_2$. 1 and 3, Measured heats of reaction; 2 and 4, calculated heats of reaction; measured on IC samples.

kJ mole^{-1}. The measured results agree reasonably well with the estimated values; both are shown in Fig. 8.

The effects of sample weight and the low gas flow rate on the heat of reaction of the first and second steps (see Fig. 7) are due to the presence of water (vapour) and are in very good agreement with thermogravimetric results obtained in ref. 1. The phenomena are caused by water vapour which accelerates the decomposition of anhydrous $Mn(NO_3)_2$ and lowers the temperature at which the reaction occurs. The longer the residence time of the water vapour above or in the sample, the more $Mn(NO_3)_2$ decomposes at low temperatures, thus in the first step.

If the heat effects of both decomposition steps (Fig. 7) are extrapolated to zero sample weight, the heat effect of the first step amounts to 40—50 kJ mole^{-1} and that of the second step to 120—130 kJ mole^{-1}. According to ref. 1, a sample with negligible weight will lose only water in the first step, whereas in the second step all $Mn(NO_3)_2$ decomposes. At 180° C the theoretical heat effect of evaporation of the last mole of H_2O is 43 kJ mole^{-1}. The calculated heat effect of the $Mn(NO_3)_2$ decomposition to γ-MnO_2 at 230° C is 131 kJ mole^{-1}; 116 kJ mole^{-1} to β-MnO_2 plus 15 kJ mole^{-1} for the difference between γ- and β-MnO_2. These values agree well with the measured values.

As explained in ref. 1, water (vapour) probably changes the nature of the bonding of the nitrate groups in the anhydrous $Mn(NO_3)_2$, facilitating and accelerating the decomposition. Chemiluminescence measurements showed that the off-gas of the first as well as the second step consists of almost exclusively NO_2 or N_2O_4 [1]. The measurements did not reveal which of the two gases is primarily formed. However, the measured heat effect of the decomposition of anhydrous $Mn(NO_3)_2$, 155 ± 12 kJ mole^{-1}, agrees fairly well with the calculated heat effect of about 145 kJ mole^{-1} for decomposition to γ-MnO_2, 2 NO_2 and some Mn_2O_3 and O_2. The theoretical heat effect for decomposition to γ-MnO_2 and N_2O_4, on the other hand, amounts to only $\simeq$76 kJ mole^{-1}. This probably implies that NO_2 is the primary gaseous product.

CONCLUSIONS

The mechanism of the thermal decomposition of aqueous manganese nitrate solutions postulated in ref. 1 is confirmed. Water (vapour) enhances the decomposition of anhydrous $Mn(NO_3)_2$ and causes the decomposition of part of the $Mn(NO_3)_2$ at relatively low temperatures (first decomposition step).

The heat effect of the first decomposition step increases with sample weight, whereas at the same time that of the second step decreases. This effect is due to the accelerating effect of H_2O vapour on the $Mn(NO_3)_2$ decomposition. The total heat effect remains constant at about 170 ± 14 kJ mole^{-1}.

Decomposition of an aqueous $Mn(NO_3)_2$ solution results in γ-MnO_2. The heat effect of subsequent decomposition to Mn_2O_3 is equal to that found for standard γ-MnO_2 samples, viz. 24.0 kJ mole^{-1}.

Decomposition of anhydrous $Mn(NO_3)_2$ in vacuum results in a large amount of Mn_2O_3 as well as γ-MnO_2. The heat effect is relatively high: 155 ± 12 kJ mole^{-1}.

NO_2 is probably the primary gaseous product of all decompositions.

The heat effect measured for the decomposition of β-MnO_2 to Mn_2O_3 is 15 kJ mole^{-1} higher than for decomposition of γ-MnO_2 to Mn_2O_3, viz. 39.0 kJ mole^{-1}.

The measured heat effects agree fairly well with estimates of the heats of reaction from thermodynamic data.

REFERENCES

1 T.J.W. de Bruijn, W.A. de Jong and P.J. van den Berg, Thermochim. Acta, 45 (1981) 265.
2 P.K. Gallagher, F. Schrey and B. Prescott, Thermochim. Acta, 2 (1971) 405.
3 P.K. Gallagher and D.W. Johnson, Thermochim. Acta, 2 (1971) 413.
4 K.K. Kelley, U.S. Bur. Mines Rep. Invest., 3776 (1944).
5 D.R. Stull and H. Prophet (Eds.), JANAF Thermochemical Tables, NSRDS-NBS 37, Natl. Bur. Stand., 2nd edn., 1971.
6 R.C. Weast (Ed.), Handbook of Chemistry and Physics, Chemical Rubber Co., 52nd edn., 1971—1972.
7 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schuman, Natl. Bur. Stand. (U.S.), Tech. Note 270-4, (1969).
8 A. Kozawa and R.A. Powers, in A. Kozawa and R.J. Brodd (Eds.), Manganese Dioxide Symposium, Cleveland, 1975, Vol. 1.
9 X-Ray Powder Data File by American Society for Testing and Material or by Joint Committe on Powder Diffraction Standards.
10 G. Hakvoort, Thesis, Delft University of Technology, 1978, Ch. 5.
11 D. Weigel, B. Imelik and M. Prettre, Bull. Soc. Chim. Fr., (1964) 836.
12 R.V. Lundquist, U.S. Bur. Mines Rep. Invest., 5347 (1957).