Simultaneous TG, DTG and DTA Studies on Manganese Oxides

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Using a derivatograph, the temperatures and heats of decomposition of MnO_2 and Mn_2O_3 as well as the temperature and heat of transformation of Mn_3O_4 have been studied. Using CaCO_3 as standard, the heat of decomposition of MnO_2 to Mn_2O_3 has been determined to be 25.56 ± 1.67 kJ/mol of MnO_2 , and that of decomposition of Mn_2O_3 to Mn_3O_4 to be 15.94 ± 2.09 kJ/mol of Mn_2O_3 . The temperatures of decomposition of MnO_2 and Mn_2O_3 to lower oxides, namely, Mn_2O_3 and Mn_3O_4 respectively, have been found to be 843 ± 5 K and 1263 ± 5 K respectively under atmospheric conditions. It has been confirmed that Mn_3O_4 undergoes a crystalline transformation during cooling at 1453 ± 5 K with 4.35 ± 0.04 kJ/mol of Mn_3O_4 as the heat of transformation.

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I. Introduction

The system Mn-O is of considerable economic importance. In addition to the role of manganese as an alloying element in steel and non-ferrous alloys, it is a vital element, used for control of sulphur in steel-making and also the most commonly and widely used deoxidiser for molten steel. The oxide, so formed, constitutes a part of the slag, and this in turn may have a serious fluxing effect on the furnace refractories. Non-metallic uses of manganese ores in dry batteries and chemical compounds, in glass to neutralise the effect of iron and as a colouring agent in ceramics have also stimulated considerable interest in the Mn-O system. In recent years, the intermediate oxides, Mn_2O_3 and Mn_3O_4 , have also gained commercial importance. Consequently it is of interest to determine if either of these oxides can be obtained in relatively pure form as a decomposition product of manganese dioxide. The different needs of manganese have therefore caused a great deal of attention to be devoted to its effective utilisation and improved recovery from its ores and slags. For a scientific investigation of all these problems, a knowledge of the system Mn-O is necessary.

Data reported in the literature on the temperature and heats of decomposition of different

manganese oxides, as obtained by different investigators are summarised in Table 1, which clearly shows an appreciable variation in these values. It is also seen that in most of these investigations, separate and independent studies for the temperatures and heats of decomposition have been carried out. Therefore, it was thought desirable to check the reliability of the data reported using a derivatograph which can simultaneously obtain DTA, DTG, TG and T curves and thus permit a simultaneous determination of both the temperatures and heats of decomposition of different manganese oxides under a given set of experimental conditions.

II. Experimental

For the present investigation, a derivatograph described by Paulik *et al.*⁽¹⁰⁾ has been used. Figure 1 shows its construction and principle of operation. It records the TG curve photographically. A light signal indicating the deflection of the balance is projected onto photo-sensitive paper. On one end of the beam a coil is hung which moves (when the beam moves) in a homogeneous field set-up by permanent magnets. The light signal from a galvanometer connected to the ends of the coil records the DTG curve on the photo-sensitive paper. At the same time the derivatograph also operates as a DTA instrument. The sample and inert reference substance are contained in platinum crucibles of a special shape, and counter-connected thermocouples are placed in the

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Table 1 Heat and temperature of decomposition of manganese oxides.

Source	Method used for investigation	Heat of decomposition in kJ/mol of reactant		Temperature of decomposition (K)	
		$\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$	$\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$	$\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$	$\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$
Wicks and Block ⁽¹⁾	Calorimetric	41.0 $\pm$ 5.0	—	—	—
Meyer and Rotgers ⁽²⁾	Equilibrium	60.46	23.22	803	1213
Kapustinsky and Bayushkina ⁽³⁾	Equilibrium	32.93	—	—	—
Otto ⁽⁴⁾⁽⁵⁾	Equilibrium	39.58	28.70	697	1144
Honda and Sone ⁽⁶⁾	Magnetic susceptibility	—	—	808	1206
McMurdie and Golovato ⁽⁷⁾	Differential thermal analysis	—	—	943	1243
Matsushima and Thoburn ⁽⁸⁾	Differential thermal analysis	26.99 $\pm$ 1.67	17.61 $\pm$ 2.93	835	1200
Kulp and Perfetti ⁽⁹⁾	Differential thermal analysis	—	—	853~943	1278
Present work	Differential thermal analysis	25.56 $\pm$ 1.67	15.94 $\pm$ 2.09	843 $\pm$ 5	1263 $\pm$ 5

1. Crucible for the sample, 2. Crucible for the inert substance, 3. Porcelain tube, 4. Electric furnace, 5. Thermocouple, 6. Balance, 7. Optical slit, 8. Lamp, 9. Coil, 10. Permanent magnet, 11. Galvanometer, 12. Photographic paper.

Fig. 1 Schematic sketch showing the principle of the derivatograph. ① Crucible for the sample, ② Crucible for the inert substance, ③ Porcelain tube, ④ Electric furnace, ⑤ Thermocouple, ⑥ Balance, ⑦ Optical slit, ⑧ Lamp, ⑨ Coil, ⑩ Permanent magnet, ⑪ Galvanometer, ⑫ Photographic paper.

re-entrants in the bottom of the crucibles. A galvanometer in the thermocouple circuit measures the temperature difference between the sample and the reference substance (DTA curve), while another connected to the sample

thermocouple indicates the temperature of the sample (T curve). The instrument carries a voltage stabiliser unit and a temperature controlling device. It permits accurate control of temperature to ± 5 K and accurate weighing to ± 1.0 mg. For getting a derivatogram, first the photographic paper on the recording drum was ruled for 6 min after adjusting the position of the recorder to the maximum temperature desired. Then after the zero adjustment with

Fig. 2 Typical DTA, DTG and T curves for decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (mass: 0.750 g).

the empty platinum crucible, the crucible was filled with the moisture-free sample to the same volume as the alumina powder reference material in the other platinum crucible and weighed to ± 1.0 mg. The furnace was put in position, room temperature adjusted and heating programme (0.1 K/s or $6^\circ\text{C}/\text{min}$) set. The actual experiment was then started.

For experimental studies, micro-analytical reagent grade MnO_2 was used and the lower oxides of manganese, namely, Mn_2O_3 and Mn_3O_4 were produced by decomposing this MnO_2 at 1153 and 1373 K respectively for 172.8 ks (48 h) in each case. For calculation of heat change per unit area under DTA peak, analytical reagent grade calcium oxalate was used. The samples used in the test had particle size in the range 74 to 52 μm .

III. Results and Discussions

The derivatogram obtained for the decomposition of calcium oxalate is shown in Fig. 2. Peaks in the DTA curves above the base line are exothermic peaks and those below this base line, endothermic peaks. The first endothermic peak under DTA in this figure corresponds to the decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ to CaC_2O_4 and the second to the decomposition of CaCO_3 to CaO and CO_2 . Using standard data⁽¹¹⁾ on the heat of decomposition of CaCO_3 at 1173 K—the decomposition temperature of CaCO_3 as obtained from the DTA and T curves of Fig. 2, and also from a knowledge of the mass of CaCO_3 present in the sample of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ used for plotting this derivatogram and the area under the second endothermic peak of the DTA curve in Fig. 2, the heat change per unit area under DTA curve has been calculated and found to be 0.7058 J. This data has been subsequently used for calculation of the heat changes in the decomposition of different manganese oxides.

The derivatogram obtained for the decomposition of MnO_2 to Mn_2O_3 and then to Mn_3O_4 using the same sample is shown in Fig. 3. Area of the DTA curve under the first endothermic peak in this figure represents the heat of decomposition of MnO_2 to Mn_2O_3 and that under the second endothermic peak

corresponds to the heat of decomposition of Mn_2O_3 to Mn_3O_4 . From a knowledge of the heat change per unit area obtained from the above referred calibration run using calcium carbonate, the heats of decomposition of MnO_2 to Mn_2O_3 and of Mn_2O_3 to Mn_3O_4 have been calculated and presented in Table 1. It is seen from this table that the results of the present investigation on heat of decomposition are in close agreement with only the results of Matsushima and Thoburn⁽⁸⁾. It may be mentioned here that the values obtained by equilibrium technique have to be relied upon with some reservations because equilibrium is likely to take unduly long time. Moreover, effect of stoichiometry cannot be neglected. The actual chemical formula of manganese dioxide used in the present investigation was found to be $\text{MnO}_{1.96}$.

The derivatogram obtained for the determination of temperatures and heat changes of structural transformation in Mn_3O_4 on heating and cooling are shown in Fig. 4. The first

Fig. 3 Typical DTA, DTG, TG and T curves for decomposition of MnO_2 to Mn_2O_3 and then to Mn_3O_4 (mass: 4.00 g).

Table 2 Temperature and heat of structural transformation in Mn_3O_4 .

Source	Temperature (K)	Heat of transformation (kJ/mol of Mn_3O_4)
Southard and Moore ⁽¹²⁾	1445 $\pm$ 40	—
McMurdie and Golovato ⁽⁷⁾	1443 (upon heating)	—
	1373 (upon cooling)	—
Kelley ⁽¹³⁾	1445	20.9 $\pm$ 1.26
Van Hook and Keith ⁽¹⁴⁾	1433 $\pm$ 5	—
Present work	1473 $\pm$ 5 (upon heating)	5.73 $\pm$ 1.26
	1453 $\pm$ 5 (upon cooling)	4.35 $\pm$ 0.04

Fig. 4 Typical DTA, DTG, TG and T curves for structural transformation in Mn_3O_4 (mass: 4.00 g).

endothermic peak in the DTA curve of this figure is due to the sudden decomposition of some residual Mn_2O_3 which might have been present in the sample of Mn_3O_4 . The next two DTA endothermic peaks indicate the heat changes of structural transformation in Mn_3O_4 during heating, while the other two exothermic DTA peaks refer to the heat changes of the structural transformation in Mn_3O_4 during cooling. The average value of heat of structural transformation in Mn_3O_4 has been found to be 5.73 ± 1.26 kJ/mol of Mn_3O_4 at 1473 ± 5 K

during heating and 4.35 ± 0.04 kJ/mol of Mn_3O_4 at 1453 ± 5 K during cooling. These results are reported in Table 2 for a comparison with data reported in literature. It is seen from this table that while the temperature of structural transformation in Mn_3O_4 is in close agreement with the reported value in literature, the heat of structural transformation in Mn_3O_4 obtained in the present investigation is appreciably different than the data reported by Kelley⁽¹³⁾, which is the only data available in the literature.

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REFERENCES

- (1) C. E. Wicks and F. E. Block: U.S. Bur. Mines Bull., No. 605 (1963).
- (2) R. J. Meyer and K. Rotgers: Z. Anorg. Chem., **57** (1908), 104.
- (3) A. F. Kapustinsky and K. S. Bayushkina: J. Phys. Chem., **11** (1938), 77.
- (4) E. M. Otto: J. Electrochem. Soc., **111** (1964), 89.
- (5) E. M. Otto: *ibid.*, **112** (1965), 98.
- (6) K. Honda and T. Sone: Sci. Rep., Tohoku Imp. Univ., **3** (1914), 139.
- (7) H. F. McMurdie and E. Golovato: J. Res. Natl. Bur. Std., **41** (1948), 589.
- (8) T. Matsushima and W. J. Thoburn: Canad. J. Chem., **43** (1965), 1723.
- (9) L. Kulp and J. Perfetti: Mineralog. Mag., **29** (1952), 239.

- (10) F. Paulik, J. Paulik and L. Erdey: *Derivatograph*, Typ. 0D-102, Hungary, (1968), p. 37.
 - (11) O. Kubaschewski, E. L. L. Evans and C. B. Alcock: *Metallurgical Thermochemistry*, Pergamon Press, New York, (1967), p. 312.
 - (12) J. C. Southard and G. E. Moore: *J. Am. Chem. Soc.*, **64** (1942), 1769.
 - (13) K. K. Kelley: *U.S. Bur. Mines Bull.*, No. 476 (1949).
 - (14) H. J. Van Hook and M. L. Keith: *Am. Mineralogist*, **43** (1958), 69.
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