STUDY OF THE STABILITY OF MnCO$_3$ IN INERT ATMOSPHERES AND IN AIR

M. K. Seguin, *Département de Géologie, Université Laval, Québec 10, P.Q. Canada*
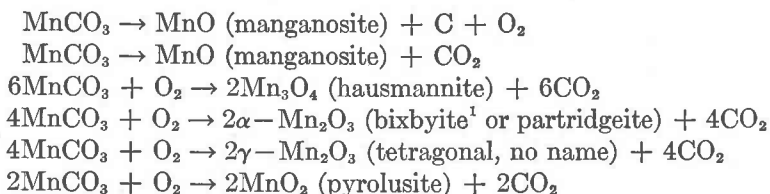
Abstract

The rate of dissociation and the degree of stability of MnCO$_3$ in air and in inert gases (nitrogen and argon) were studied over the temperature range 100 to 720°C. In the temperature range under consideration, the solid end-product is manganosite (Mn$_{1-x}$O), hausmannite (Mn$_3$O$_4$), partridgeite or bixbyite (α-Mn$_2$O$_3$), tetragonal γ-Mn$_2$O$_3$ or occasionally a combination of two or even three of these products depending on the temperature, the gaseous medium, and the grain size of the initial MnCO$_3$.

The rate of dissociation of MnCO$_3$ is practically independent of the initial amount of material and is mainly a function of the grain size, temperature, and composition of the gaseous medium in which the reaction takes place. Variations of rhodochrosite concentration are of minor importance. The order of the reaction is very close to one. The activation energies calculated for 71 medium-to high-temperature experiments and extrapolated down to 120°C vary between 18.1 and 27.2 kcal mole^{-1}. The instability or metastability of MnCO$_3$ in air (depending on the grain size) at 110°C is established. MnCO$_3$ appears to be stable at room temperature (25°C) in air. The metastability of MnCO$_3$ at 110°C is explained by a thin layer of α-Mn$_2$O$_3$ in the same way as the metastability of Al surrounded by a coating of Al$_2$O$_3$.

Introduction

Rhodochrosite (MnCO$_3$) is an important mineral in space and time. Its abundance in nature has been underestimated even at the economical point of view. It is believed that many manganese oxide deposits were at one time rhodochrosite which has been altered perhaps to Mn$_{1-x}$O and Mn$_3$O$_4$ (and manganite in hydrous systems) but certainly to α-Mn$_2$O$_3$ and γ-Mn$_2$O$_3$ and possibly later on to MnO$_2$ under the direct effect of the oxidizing atmosphere or the downward percolation of oxidizing waters. The Catamarca Province in Argentina is a typical example. Recent work on the relatively unaltered iron formations of the central part of the Labrador Trough and the metamorphosed iron formations of the southern part of the Trough has shown that Mn$_2$O$_3$ and MnO$_2$ comes mainly from the dissociation and oxidation of rhodochrosite (see Bricker, 1965, p. 1340–1350). Very few studies deal with the kinetics and equilibria of manganese minerals at conditions relatively close to those of their natural environments. More specifically, rhodochrosite is found in sedimentary rocks or in ocean bottom sediments at a relatively low temperature

($<100°C$) and at low to medium pressure conditions. Outside its stability field, $MnCO_3$ decomposes to one or more manganese oxides according to the following possible reactions:

$$MnCO_3 \rightarrow MnO \text{ (manganosite)} + C + O_2$$
$$MnCO_3 \rightarrow MnO \text{ (manganosite)} + CO_2$$
$$6MnCO_3 + O_2 \rightarrow 2Mn_3O_4 \text{ (hausmannite)} + 6CO_2$$
$$4MnCO_3 + O_2 \rightarrow 2\alpha-Mn_2O_3 \text{ (bixbyite[1] or partridgeite)} + 4CO_2$$
$$4MnCO_3 + O_2 \rightarrow 2\gamma-Mn_2O_3 \text{ (tetragonal, no name)} + 4CO_2$$
$$2MnCO_3 + O_2 \rightarrow 2MnO_2 \text{ (pyrolusite)} + 2CO_2$$

A detailed study of the rate of dissociation (kinetics of mass decomposition) and degree of thermal stability of $MnCO_3$ in air and inert gases (nitrogen and argon) was undertaken over the temperature range 100 to 720°C to determine the nature of the coating of the rhodochrosite. This mineral was found in the Catamarca Province in Argentina and in the southern part of the Labrador Trough (Wabush area), Newfoundland, Canada. This study was also conducted in order to gain some knowledge about the relative importance of grain size, temperature, degree of packing, gaseous medium, and concentration of the reactant ($MnCO_3$) and to explain certain characteristics that occur in the more general system Mn–O–C–S. Le Blanc and Wehner (1934), Moore (1943), Shomate (1943), Vlasov and Kozlov (1958), Mah (1960), Hahn and Muan (1960), Klingsberg and Roy (1960), Otto (1967), Schmahl and Stemmler (1965), Shenouda and Aziz (1967), as well as Huebner and Sato (1970), studied the equilibria of the different manganese oxide systems at intermediate to high temperatures. Huebner (1969) investigated the stability relations of rhodochrosite at high pressure.

The method of study is based on the rate of reaction of any order n, whose formula is:

$$S = -\frac{dC}{dt} = K_n C^n \tag{1}$$

where

S = rate of the reaction
C = concentration of the reactant(s) (Weight %)
t = time
K_n = rate constant of order n
n = order

[1] Preferable name

Experimental Method

Starting Material

The material used in all experiments consisted of natural $MnCO_3$ from the Catamarca Province, Argentina. A quantitative X-ray fluorescence and atomic absorption analysis revealed the following impurities:
FeO, 1.41 percent; MgO, 0.95 percent; CaO, 0.81 percent; Na_2O, 183 p.p.m.; CuO, 45 p.p.m.; and ZnO, 150 p.p.m. The rhodochrosite from this locality is zoned: some zones are colored white and others pinkish. In the pinkish zones, the percentage of FeO (2.31 percent) is higher than in the white zones (FeO: 1.22 percent), the percentage of MgO lower (0.83 percent *vs* 1.06 percent) and the percentage of CaO higher (0.84 percent *vs* 0.78 percent). The proportion of the other elements found in the impurities remains unchanged. Seven X-ray diffraction patterns of the starting material ($MnCO_3$) were obtained using a Guinier focussing camera with $Fe_{K\alpha_1}$ radiation (Mn filter, 30 KV, 10mA); the time of exposure varied between 15 and 44 hours. The averages of the d spacings values and the relative intensities are given in Table 1.[1]

Equipment

The decomposition of $MnCO_3$ was studied with two different experimental methods: a) thermogravimetric analysis (TGA) and b) differential thermal analysis (DTA). With the first method (TGA), two types of experiments were performed; one type consisted of measuring the variation of mass of the reactant ($MnCO_3$) as a function of temperature at a rate of 160°C min⁻¹ and obtaining a thermogram whereas the other type was a method of isothermal analysis. The thermobalance used was a Perkin-Elmer (Canada) model TGS-1. Ancillary equipment consisted of a Perkin-Elmer (Canada) temperature controller, a two pen recorder, and an inert gas circulator. Among other advantages, this system permits a more exact measure of the temperature, a great sensitivity, a rapid cooling rate, and almost instantaneous isothermal equilibrium. The relative accuracy in the measurements of the mass differences is of the order of 0.1 percent and the temperature is controlled with a precision of ±1°C. The experimental procedure is explained in detail by Moreau (1971). The differential thermal analyses were performed with a conventional Stanton (model Standata — 658) DTA instrument consisting of two cells: one containing a reference material (Al_2O_3) and the other the solid reactant (sample). Ancillary equipment included a temperature programmer and a Philips model type PM8100 dual pen flatback recorder. Platinum *vs* platinum + 13 percent rhodium thermocouples were used for these experiments. The variation in temperature (ΔT) is ± 2°C. The programmed temperature rate was 10°C min⁻¹ and the mass of the samples varied between 200 and 400 milligrams. A detailed description of the experimental DTA procedure is given in Nhut-Minh (1970).

[1] The results listed in this table may be ordered as NAPS Document Number 01716 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC-NAPS.

Control of P_{CO_2} and P_{O_2}

The experiments were conducted in free air or in an inert gas at the ambient temperature. Intentionally, no CO or CO_2 was circulated through the system. Buffered experiments using another method were also conducted but are not included in this paper.

Identification of the End Products

All crystalline products were identified by X-ray diffraction using either a Guinier focussing camera with $Fe_{K\alpha_1}$ radiation (30 kV, 10mA) or a Debye-Scherrer camera with $Cu_{K\alpha_1}$ or $Fe_{K\alpha_1}$ radiations. In cases of uncertainty, infra-red scanning was performed on the solid end-products. Occasionally, reflected and transmitted light microscopes with high power oil immersion objective lenses were used for identification purposes. In fifteen percent of the experiments, a chemical analysis for MnO and Mn_2O_3 was performed on the end-products.

Procedure

Except for the DTA experiments, the experimental procedure in use has its foundation in mass difference analysis. The calculations are made using the ratio of the material dissociated at time t over the total amount dissociated at infinite time $t = \infty$. In practice, the time for complete dissociation can be considered as finite (*e.g.*, time at 99.2 or 99.8 percent dissociation). Then the percentage of $MnCO_3$ dissociated was plotted against log time (see Figure 1).

The order n was then obtained as follows: Integrating equation (1), one obtains

$$K_n t = \frac{1}{(n-1)} \left[\frac{1}{C^{n-1}} - \frac{1}{C_o^{n-1}} \right] \text{ for } n \neq 1,$$

$$\text{or } K_n t = \frac{1}{(n-1)C_o^{n-1}} \left[\left(\frac{C_o}{C} \right)^{n-1} - 1 \right] \tag{2}$$

Changing the concentration to a percentage,

$$K_n t = \frac{1}{(n-1)C_o^{n-1}} \left[\left(\frac{100}{100-x} \right)^{n-1} - 1 \right] \tag{3}$$

where C_o = initial concentration of the reactant, and
        x = percentage of reactant dissociated.

From equation (2), at $C = C_o/2$,

$$\text{the half life } t_{\frac{1}{2}} = \left[\frac{2^{n-1} - 1}{(n-1)K_n} \right] \frac{1}{C_o^{n-1}} \tag{4}$$

Thus, the half-life is a function of the order of the reaction and is inversely proportional to the power $(n-1)$ of the initial concentration. This expression holds for any order n except $n = 1$, n being a whole or a fractional number, positive, negative, or zero.

An order n was asusmed for the reaction and the rate constant K_n calculated directly from the curve log t plotted against the percentage dissociated. Using

the individual values of K_n in some cases and the averaged K_n in others, the experimental curve was reproduced from theory. If the theoretical time obtained compared well with the experimental time obtained, the order was retained. The rate constant K_n can also be obtained graphically by dividing the slope of a $\log_{10}$ $(100 - x)$ against t curve.

It was established experimentally for the rhodochrosite reaction that the rate of dissociation is independent of the initial amount of reactant and that the order of the reaction is approximately one (the reaction order calculated from individual sets of experiments ranged from 0.92 to 1.08; the average value of n was close to one, and that order was adopted).
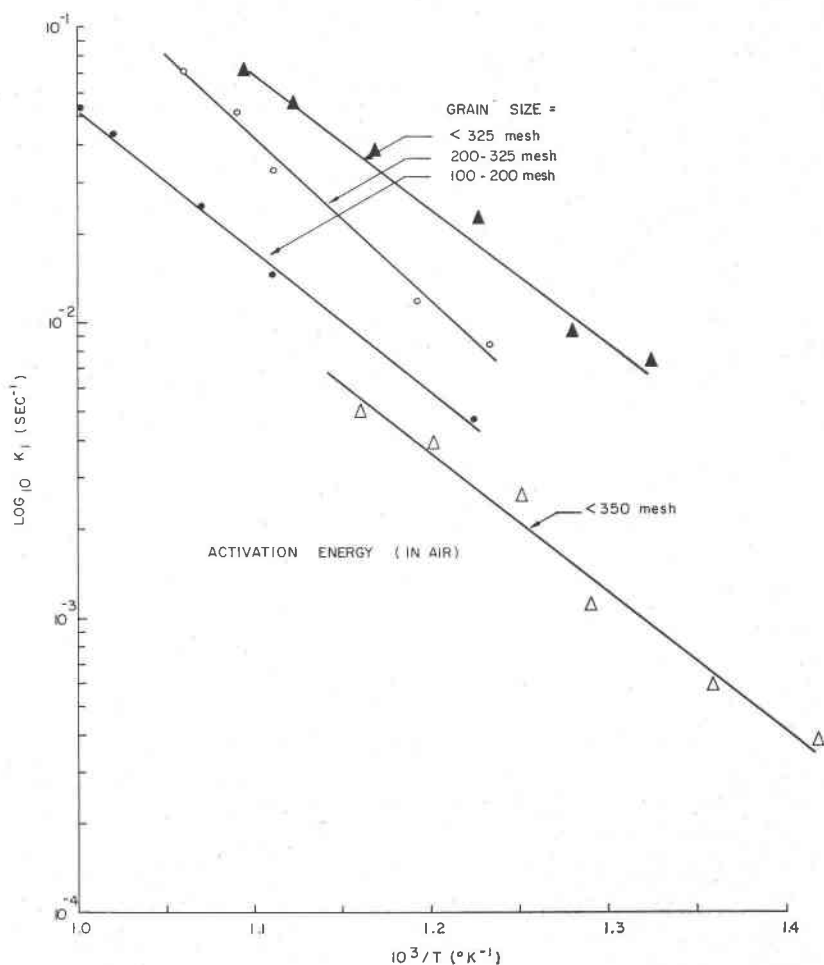

FIG. 1. Activation energy for the dissociation of $MnCO_3$ in air in the temperature range 420–730°C for different grain sizes.

Some 42 experiments were conducted with the thermobalance.[1] In a series of experiments, the grain size varies between 100 and 200 mesh, in another series between 200 and 325 mesh, and in a last series, it is smaller than 325 mesh. Some experiments were performed in a nitrogen atmosphere and others in air. The temperatures of the reactions taking place in an atmosphere of nitrogen range between 530 and 720°C whereas the temperature of the reactions taking place in air range between 480 to 720°C. Six experiments were duplicated under exactly the same conditions; they were performed to demonstrate the good repeatability of the results obtained. Additional experiments include a series of 7 thermograms obtained in a nitrogen atmosphere and covering the temperature range: 430 to 590°C as well as a series of 7 other thermograms obtained in air and covering the temperature range: 420 to 600°C. In both these series of experiments, the grain size of the reactant ($MnCO_3$) was smaller than 350 mesh. Finally, a complete set of thermograms was also obtained for the temperature range 420 to 720°C in an atmosphere of argon. The experimental results are very similar to the ones obtained in a nitrogen atmosphere and for this reason they are not presented here.

INTERPRETATION OF THE RESULTS

Equation (1) becomes

$$S = -\frac{dC}{dt} = K_1 C \tag{5}$$

$$\text{and the half-life } t_{1/2} = \frac{\ln 2}{K_1} \tag{6}$$

Knowing K_1 for any percentage of mass reacted, the corresponding time t may be calculated. That is, if the value of K_1 is correct, the experimental curve can be reproduced from theory; this was done. Once the rate constant K_1 is found, the activation energy of the reaction can be calculated by using Arrhenius' formula:

$$K_1 = K_o e^{-E/RT} \tag{7}$$

where

K_o = frequency factor or rate constant at infinite temperature
$$(1/T = 0).$$

E = activation energy
R = gas constant
T = temperature in degrees Kelvin

A plot of $\log_{10} K_1$ against $10^3/T$ will give a straight line the slope of which is $E/4.576$. Because the order, rate constants, and tempera-

[1] Figures 1 to 7 showing the results of these experiments may be ordered as NAPS Document Number 01716. See footnote on page 513.

tures are known, the activation energy is calculated from low temperature runs (430 and 460°C) of the reaction $MnCo_3 \rightarrow \alpha\text{-}Mn_2O_3$ ($\pm$ $\gamma\text{-}Mn_2O_3$) and extrapolated down to 125°C (approximate instability limit of $MnCO_3$ in air). For a grain size of approximately 325 mesh, the calculated activation energy is 19.9 kcal mole⁻¹ in air and 18.1 kcal mole⁻¹ in a nitrogen atmosphere. In the temperature range of 530 to 720°C and for approximately the same grain size, the calculated activation energy is 21.8 kcal mole⁻¹ in air and 21.2 kcal mole⁻¹ in a nitrogen atmosphere. For a grain size ranging between 200 and 325 mesh, the activation energy is calculated at 25.4 kcal mole⁻¹ in air and 26.9 kcal mole⁻¹ in a nitrogen atmosphere and finally for a grain size ranging between 100 and 200 mesh, the activation energy is calculated at 27.2 kcal mole⁻¹ in air and 26.8 kcal mole⁻¹ in a nitrogen atmosphere. Figure 1 shows a diagram of $\log_{10}K_1$ vs $10^3/T$ for the experiments performed in air and Figure 2 shows the same diagram for the experiments conducted in a nitrogen atmosphere. The activation energies are calculated directly from these diagrams.

The dissociation of $MnCO_3$ is a consecutive reaction. The intermediate products of the transition state are definitely manganosite (MnO) and hausmannite (Mn_3O_4). The final products are most commonly hausmannite (Mn_3O_4), $\gamma\text{-}Mn_2O_3$, and bixbyite ($\alpha\text{-}Mn_2O_3$); pyrolusite (MnO_2) was not observed.

Manganosite (MnO) is encountered as an end-product at all temperature ranges investigated, however its relative abundance is larger in the temperature range 570 to 680°C. Hausmannite (Mn_3O_4) is especially abundant in the temperature range 550 to 700°C. Tetragonal $\gamma\text{-}Mn_2O_3$ is encountered over the whole range of temperature, i.e., 500 to 720°C; it appears to be the most common phase amongst the solid end-products identified. The X-ray powder diffraction patterns of hausmannite and $\gamma\text{-}Mn_2O_3$ are almost indistinguishable, but the reddish to cinnamon brown color of the powdered material is indicative of hausmannite (Huebner, 1969, p. 460). The infrared technique is also quite useful to determine the relative abundance of hausmannite or tetragonal $\gamma\text{-}Mn_2O_3$. In the wavenumber range of 510 to 640, the manganese oxides depict a curve consisting of two adjacent valleys. In the case of almost pure hausmannite, the sequence is 630 (valley) — 580 (ridge) — 530 (valley) or, in others words, the wavelength sequence is 15.9, 17.3, and 19.7 μm. When manganosite is present, the valley at 530 is shifted to 523 and when partridgeite is present, it is shifted to 515. For almost pure manganosite the wavelength sequence is 15.85, 17.65, and 19.9 microns. For tetragonal $\gamma\text{-}Mn_2O_3$ (plus a
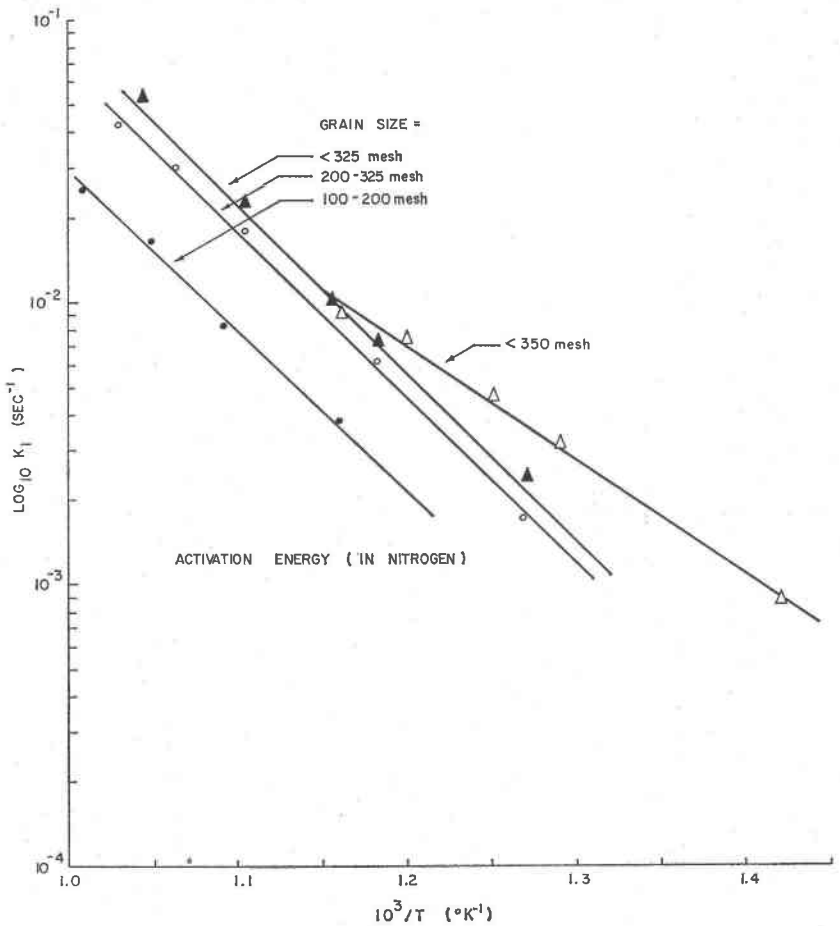
M. K. SEGUIN

Fig. 2. Activation energy for the dissociation of $MnCO_3$ in nitrogen in the temperature range 430–720°C for different grain sizes.

small amount of α-Mn_2O_3), the wavelength sequence becomes 16.35, 17.65 and 19.8 μ but when appreciable α-Mn_2O_3 is mixed up with γ-Mn_2O_3, the sequence is 16.3, 17.55, and 20.1 μm. α-Mn_2O_3 is more commonly encountered in the low temperature range.
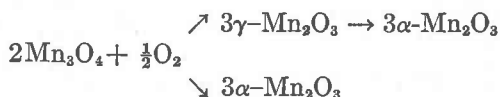
The existence of the intermediate (transition) compounds in the laboratory is ascertained without any doubt but their lifetime cannot be calculated easily in the present study. The following reaction appears to take place:

$$6MnCO_3 \rightarrow 6MnO + 6CO_2$$

However, MnO is metastable and oxidizes to Mn_3O_4 according to the formula

$$6MnO + O_2 \rightarrow 2Mn_3O_4.$$
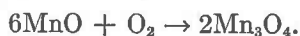
Because conditions are oxidizing at the earth's surface,

$$2Mn_3O_4 + \tfrac{1}{2}O_2 \begin{array}{l} \nearrow 3\gamma-Mn_2O_3 \rightarrow 3\alpha-Mn_2O_3 \\ \\ \searrow 3\alpha-Mn_2O_3 \end{array}$$

In the temperature range considered (especially in the low temperature region), the rate of oxidation at the earth's surface is much faster than the dissociation of $MnCO_3$. The time of nearly complete dissociation (99.2 percent) obtained by calculation for a temperature of 100°C and in air is of the order 1.2×10^5 years ($t_{1/2} = 1.4 \times 10^4$ years) for a grain size of the order of 350 mesh and at least twice as large for a size of approximately 250 mesh. The rate constant varies considerably with the grain size and at a temperature of 100°C, for instance, a large ideal crystal of $MnCO_3$ approximately 2 inches across is geologically stable. At room temperature (25°C) the time of nearly complete dissociation (99.2 percent) in the air is approximately 4.2×10^6 years ($t_{1/2} = 4.6 \times 10^5$ years) for a grain size of 350 mesh; this means that for all practical purpose, $MnCO_3$ is stable in air as well as an inert atmosphere at room temperature.

The degree of stability of rhodochrosite was verified experimentally by the following two methods

A) 995 milligrams of $MnCO_3$ (<350 mesh grain size) were put in an open tube (aluminum container) and left exposed to dry air at 100°C in an oven. After one month, the mass had decreased by 0.31 milligrams, indicating that approximately 0.03 percent of the initial $MnCO_3$ was changed to $\alpha-Mn_2O_3$. At room temperature, an initial mass of 753 milligrams had decreased by 0.33 milligrams after one year and a half, *i.e.*, 0.04 percent.

The degree of packing of $MnCO_3$ in the tubes as well as variations of concentration of rhodochrosite when mixing it with inert components such as MgO, CaO, Al_2O_3, SiO_2 does not change the order of the reaction.

B) Rhodochrosite heated in an oven in air at 300°C for some 4 or 5 hours develops a clearly visible coating of metallic reddish black oxide. Small grains of $MnCO_3$ observed in reflected light and oil immersion are coated with a thin white layer of $\alpha-Mn_2O_3$ (bixbyite) and a

small amount of γ-Mn_2O_3, indicating a preferential surface oxidation, this is also evident along the rhombohedral cleavage of $MnCO_3$. This thin coating of oxide(s) on $MnCO_3$ acts exactly the same way as α-Fe_2O_3 surrounding $FeCO_3$ in air (Seguin, 1966).

That the rate of dissociation of rhodochrosite is a function of temperature (see Fig. 3) in an atmosphere of nitrogen or in air is quite suggestive. In the low temperature range (250 to 425°C), the rate of dissociation of $MnCO_3$ is faster in air than it is in an atmosphere of nitrogen; actually, $MnCO_3$ is very stable in a nitrogen medium below 350°C and this is not the case in air. The dissociation of $MnCO_3$ in air is followed almost instantly by a complex process of oxidation. In the temperature range 425 to 500°C, the rate of dissociation is not very different in air and in an atmosphere of nitrogen, but above 500°C the different stages of oxidation are slower in air than in nitrogen. This means that the subsequent oxidation in air alters the rate of the reaction and influences the speed of dissociation. This unexpected result indicates that at higher temperature (roughly 500 to 600°C), $MnCO_3$ dissociates more slowly in air than in an inert medium. The only hypothesis that really can explain this kinetic process is that the outward diffusion of large polar molecules like CO_2 is slowed down by the surface layers of manganese oxides (closed-packed tetragonal Mn_3O_4, tetragonal γ-Mn_2O_3, and cubic α-Mn_2O_3) that formed during the oxidation process. For a percentage of dissociated $MnCO_3$ smaller than or equal to the percentage corresponding to the half-life, $MnCO_3$ persists longer in air than in nitrogen where oxidation is very limited.

DTA curves were obtained for rhodochrosite. A typical curve shows a double endothermic peak with the characteristic temperature at 530°C and the peak temperatures at 612 and 643°C, and a subsequent exothermic peak at 736°C. The endothermic effect is due to the decomposition of the carbonate of manganese and the exothermic one to the oxidation of manganosite (MnO) to hausmannite (Mn_3O_4). The accuracy of the temperature is $\pm$ 2°C and the one of the e.m.f., $\pm$ 0.2 μV; the programmed rate is 10°C min^{-1}.

Attempts were made to calculate the variation in enthalpy (ΔH_R) or heat of reaction in a semi-quantitative fashion. The quantity of heat absorbed or released during a reaction is proportional to the area under the DTA curves obtained. The instrument was calibrated with a standard of goethite, FeO(OH), T. M. Mapico.[1] The DTA curve

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[1] Supplier: Columbian Carbon Canada Co., Ltd., 3726 Jean Talon Ouest, Montréal 16, P.Q., Canada.
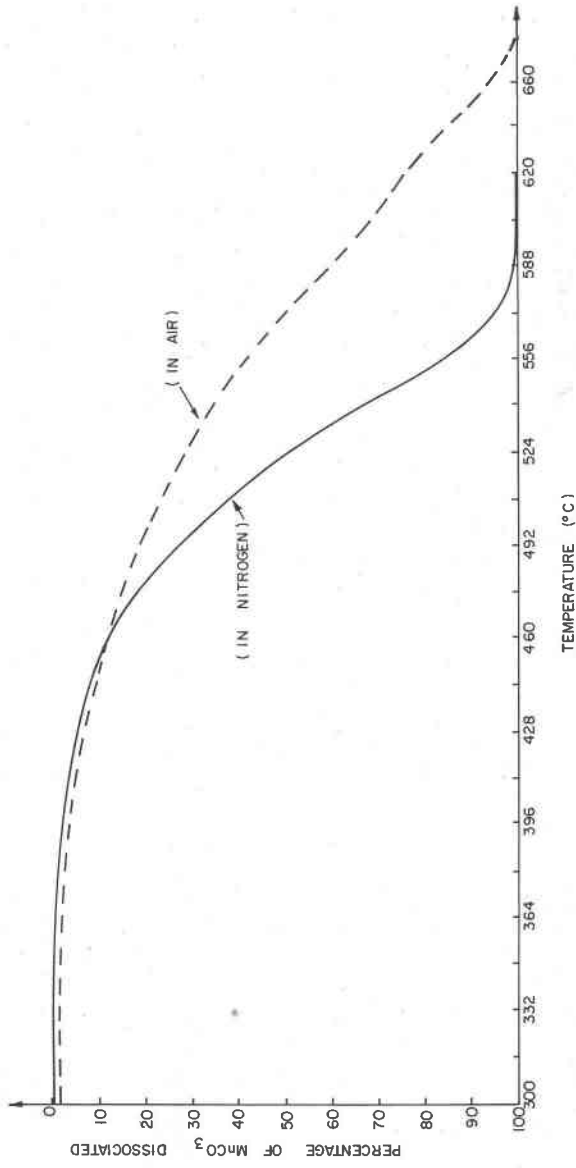
FIG. 3. Dissociation of rhodochrosite as a function of temperature in nitrogen and in air.

shows an endothermic peak at $330°C$ and the temperature range extends from 230 to $360°C$. The variation in enthalpy of this dehydration is 16.0 kcal mole^{-1} of H_2O and the equivalent area under the curve is 2.684 V°C. The equivalent area under the curve for the decomposition of $MnCO_3$ in the temperature range of 530 to $700°C$ is 3.926 V°C and so the variation in enthalpy is of the order of 23.4 kcal mole^{-1} of CO_2 for the decomposition of $MnCO_3$. In all these experiments, the grain size was fairly large.

CONCLUSION

In the temperature range 110 to $720°C$, the rate of dissociation of $MnCO_3$ is independent of the initial amount material. Consistently similar results obtained from experiments on systems with rhodochrosite concentration varied by admixture of inert components and with differing degrees of packing confirm this conclusion. In order of importance, the role of dissociation is a function of the temperature, the grain size, and the gaseous medium in which the reaction takes place. A first order equation is established for the reaction, and the activation energy is calculated for low and medium temperature reactions. The sequence of the chemical reactions taking place is demonstrated. Even though the intermediate products $Mn_{1-x}O$ and Mn_3O_4 are metastable, their existence is proven. At low temperature (200–$400°C$), the rate of oxidation is much faster than the rate of dissociation.

For all practical purpose, $MnCO_3$ persists indefinitely at room temperature and at $120°C$. At approximately $250°C$, $MnCO_3$ persists indefinitely in an inert atmosphere but would decompose rapidly in air were it not for a thin surface layer composed of a mixture of α-Mn_2O_3 and γ-Mn_2O_3 which inhibits the diffusion of Co_2 and CO out of the crystal lattice. Thus, the smaller the grain size and the total binding energy, the greater the surface energy per unit volume favoring outward diffusion of large polar molecules and extended oxidation by the surrounding medium. In an inert gaseous medium, $MnCO_3$ dissociates at $325°C$.   •

$MnCO_3$ is found in great abundance in nature. At the Earth's surface it occurs as coarse grains in veins. When present in small grains, for instance in sedimentary or slightly metamorphosed sedimentary manganese and iron carbonate deposits, the surface layers are usually altered. In metamorphic iron deposits, large crystals of $MnCO_3$ are often surrounded by a thin layer of α-Mn_2O_3. A great number of Fe_2O_3 and manganese oxides deposits (*e.g.*, Michipicoten, Labrador Trough) were at one time siderite and rhodochrosite ore bodies. Recent

work in relatively unaltered iron formation or metamorphosed iron ore bodies in the central and southern part of the Laborador Trough has shown that thin layers of α-Mn_2O_3 and MnO_2 surrounding crystals of $MnCO_3$ come partly from the dissociation and oxidation of rhodochrosite in the Wabush-Carol Lake (Labrador City) area in Newfoundland, Canada.

REFERENCES

BRICKER, O. (1965) Some stability relations in the system Mn-O₂-H₂O at 25°C and one atmosphere total pressure. *Amer. Mineral.* 50, 1296–1354.

GRAF, D. L. (1961) Crystallographic tables for the rhombohedral carbonates. *Amer. Mineral.* 46, 1283–1316.

HAHN, W. C., JR., AND A. MUAN (1960) Studies in the system Mn-O: The Mn₂O₃-Mn₃O₄-MnO equilibria. *Amer. J. Sci.* 258, 66–78.

HUEBNER, J. S. (1969) Stability relations of rhodochrosite in the system manganese-carbon-oxygen. *Amer. Mineral.* 54, 457–481.

———, AND M. SATO (1970) The oxygen fugacity—temperature relationships of manganese oxide and nickel oxide buffers. *Amer. Mineral.* 55, 934–952.

KLINGSBERG, C., AND R. ROY (1960) Solid-solid and solid-vapor reactions and a new phase in the system Mn-O. *J. Amer. Ceram. Soc.* 43, 620–626.

LEBLANC, M., AND G. WEHNER (1934) Beitrag zur Kenntnis der Manganoxyde. *Z. Phys. Chem.* 168A, 59–78.

MAH, A. D. (1960) Thermodynamic properties of manganese and its compounds. *U. S. Bur. Mines Rep. Invest.* 5600, 1–34.

MOORE, G. E. (1943) Heat content of manganese dioxide and carbonate at high temperature. *J. Amer. Chem. Soc.* 65, 1398–1399.

MOREAU, A. (1971) *Thermogravimetrie différentielle.* B.Sc.A. Thesis, Université Laval., 63 p.

NHUT-MINH, D. (1970) *Etude cinétique de la décomposition de masse du carbonate de manganèse.* B.Sc.A. Thesis, Université Laval, 54 p.

OTTO, E. M. (1964) Equilibrium pressures of oxygen over Mn₂O₃-Mn₃O₄ at various temperatures. *J. Electrochem. Soc.* 111, 88–92.

SCHMAHL, N. G., AND B. STEMMLER (1965) Equilibria of Mn₂O₃-Mn₃O₄-O₂ systems. *J. Electrochem. Soc.* 112, 365.

SEGUIN, M. (1966) Instability of FeCO₃ in air. *Amer. J. Sci.* 264, 562–569.

SHENOUDA, F., AND S. AZIZ (1967) Equilibria and hysterisis in the system Mn₂O₃-Mn₃O₄-O₂. *J. Appl. Chem. (London),* 17, 258–262.

SHOMATE, C. H. (1943) Heats of formation of manganomanganic oxide and manganese dioxide. *J. Amer. Chem. Soc.* 65, 785–790.

VLASOV, V. G., AND V. A. KOZLOV (1958) Kinetics of the dissociation of manganeses oxides. *Zh. Fiz. Khim.* 32, 2608–2613.