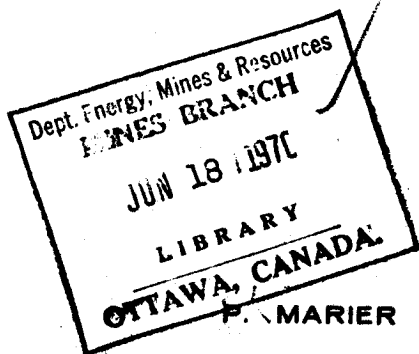




DEPARTMENT OF
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MINES BRANCH
OTTAWA

*Mines Branch Research Program
on Environmental Improvement*

*THE ROLE OF CALCIUM SULPHITE IN
DESULPHURIZING GASES CONTAINING
SULPHUR DIOXIDE*



F. MARIER AND T. R. INGRAHAM

EXTRACTION METALLURGY DIVISION

MARCH 1970

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THE ROLE OF CALCIUM SULPHITE IN DESULPHURIZING
GASES CONTAINING SULPHUR DIOXIDE

by

P. Marier* and T.R. Ingraham**

ABSTRACT

CaSO_3 is formed as an intermediate in the sulphation of CaO with gases containing SO_2 . CaSO_3 is a reactive material; it may be oxidized readily by O_2 , SO_2 , or SO_3 . In SO_2 atmospheres it reduces SO_2 to elemental sulphur. Calcium sulphite cannot be thermally decomposed to produce CaO and detectable pressures of SO_2 . It undergoes a peritectoid reaction preferentially, to a mixture of CaS and CaSO_4 . When the reaction temperature is above 800°C , CaSO_4 is the only oxidation product of CaSO_3 . CaSO_4 forms a protective coating on CaSO_3 . The coating retards the oxidation reaction.

*Research Scientist and **Head, Research Section, Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Rapport de recherches R 222

LE ROLE DU SULFITE DE CALCIUM DANS LA DÉSULFURATION
DES GAZ CONTENANT DE L'ANHYDRIDE SULFUREUX

par

P. Marier* et T.R. Ingraham**

RÉSUMÉ

Le CaSO_3 est un composé intermédiaire de la transformation en sulfate de CaO en présence de gaz contenant de l'anhydride sulfureux. Le CaSO_3 est une substance réactive; il peut être oxydé facilement par O_2 , SO_2 ou SO_3 . Dans les atmosphères qui contiennent du SO_2 , il réduit cet anhydride en soufre élémentaire. Le sulfite de calcium ne peut être décomposé sous l'action de la chaleur pour produire du CaO et des pressions discernables de SO_2 . Il subit une réaction péritectoïde préférentielle et on obtient un mélange de CaS et de CaSO_4 . Lorsque la température de réaction est supérieure à 800°C , le CaSO_4 est le seul produit d'oxydation du CaSO_3 . Le CaSO_4 forme une couche protectrice sur le CaSO_3 . Cette couche retarde la réaction d'oxydation.

*Chercheur scientifique et **Chef, Section de la recherche, Division de la métallurgie extractive, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

Sulphur dioxide is one of the primary atmospheric contaminants produced during the large-scale burning of fossil fuels and the roasting of sulphide minerals. Aside from the pollution aspects of the sulphur dioxide release, it represents an annual waste of millions of tons of sulphur.

The problem of sulphur recovery from stack gases is under study by many groups^(1,2,3). In general, the approaches may be classified as those seeking near-term, intermediate-term and long-term solutions to the problem. The long-term solutions will probably involve desulphurization of fuels⁽⁴⁾ and alternative metallurgical processes. The intermediate-term solutions are likely to involve readily reversible absorption of the sulphur⁽³⁾. The near-term solutions to the problem seem to centre around essentially irreversible processes that produce a throw-away product⁽¹⁾. Limestone injection into fossil-fueled power plant boilers is one of the most plausible of the essentially irreversible near-term processes. The Tennessee Valley Authority^(1,2) is now making full-scale tests of the process at Muscle Shoals, Ala. Ontario Hydro^(5,6) is also conducting limestone injection tests in its boilers at Toronto.

When powdered limestone is injected into the hot flue gases in a boiler, it calcines rapidly to produce CaO. As the gases cool, the CaO begins to combine with SO₂. Under appropriate conditions, the final reaction product is CaSO₄, a very stable sulphate that may be discarded. There has been widespread speculation⁽⁷⁾ regarding the mechanism by which CaSO₄ is formed. Elemental sulphur, calcium sulphide, and calcium sulphite have been mentioned as either intermediate or side-reaction products that may occur under various conditions⁽⁹⁾. This variety of products, and the fact that limestone injections are rarely more than 25% efficient in removing SO₂ from a gas stream⁽⁷⁾, prompted the initiation of this work to determine the reactions by which limestone may be converted to calcium sulphate. In a small-scale simulation of limestone injection, limestone utilizations of up to 85% have been achieved⁽⁸⁾.

EXPERIMENTAL

Materials

Reagent-grade CaCO₃ (99.6%), manufactured by Mallinckrodt, was used as the calcium source material for all experiments. The nitrogen, oxygen and sulphur dioxide gases were standard cylinder grades and were used without further purification. Calcium sulphite

was synthesized following a procedure suggested by Kelley and Moore⁽¹⁰⁾ for preparing a pure material. The procedure involved the dissolution of powdered CaCO_3 in a hot aqueous solution that was saturated with SO_2 . Air was excluded during the preparation. Differential thermal analysis of the product was used to reveal the presence of impurities and to determine the optimum conditions for converting it to anhydrous calcium sulphite. The DTA trace is shown in Figure 1, from which it is evident that the higher hydrate(s) of calcium sulphite may be converted to the hemi-hydrate by heating to a temperature in excess of 75°C . The peak at 130°C corresponds to the loss of water from the 5% of calcium sulphate impurity present in the sulphite. It is usual in this method of preparation to form a few percent of a sulphate impurity^(10,11). Calcium sulphite hemi-hydrate is stable up to a temperature of 275°C . It decomposes rapidly to the anhydrous sulphite at 375°C and shows a DTA peak at 400°C . These observations are in agreement with those of Matthews and McIntosh⁽¹¹⁾.

Apparatus

Thermogravimetric experiments were done in an Aminco THERMOGRAV balance. Powdered samples were suspended on a platinum tray. They were weighed continuously at known temperatures in selected atmospheres.

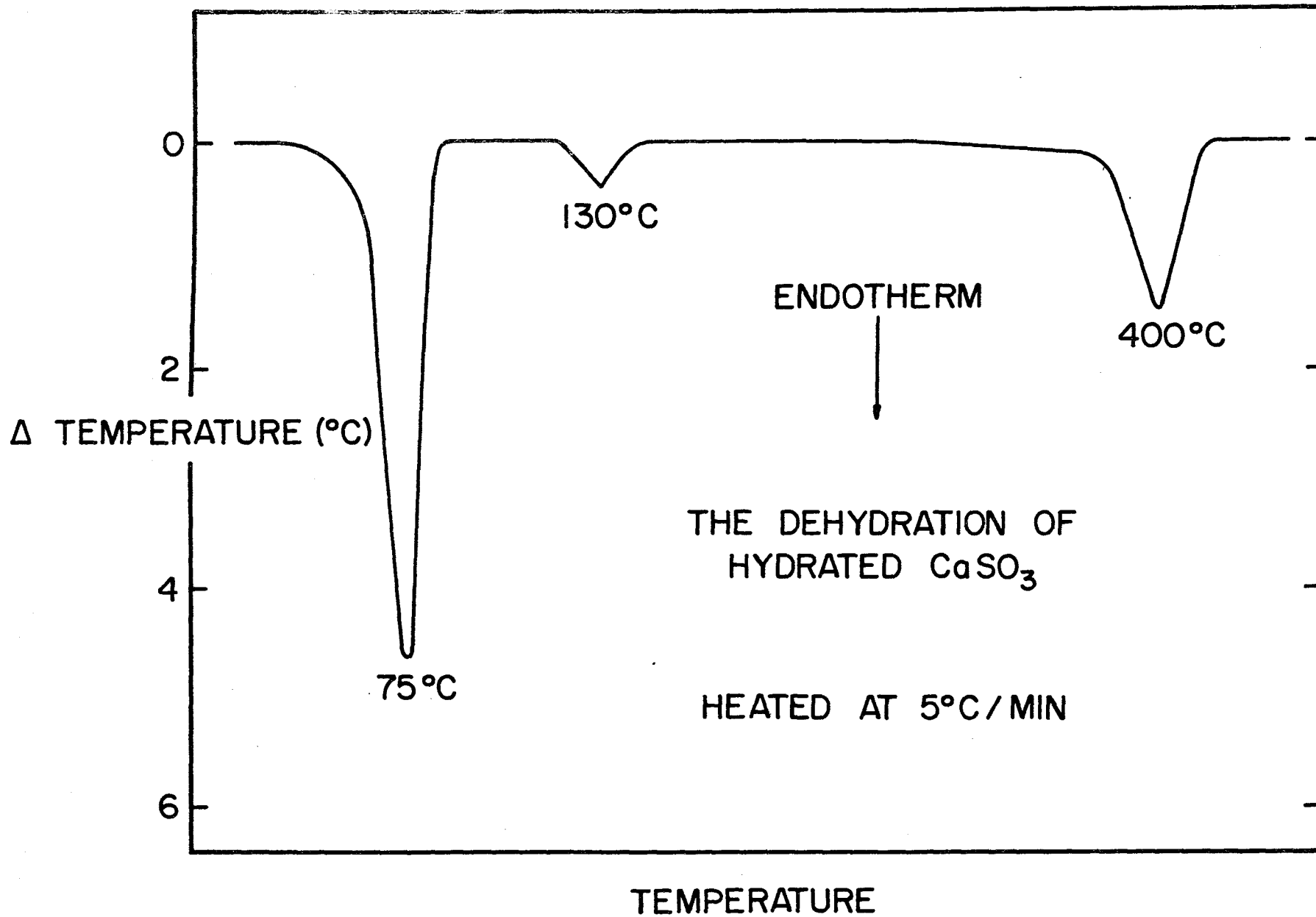


FIGURE 1. DTA Trace Showing the Dehydration of Calcium Sulphite.

Differential thermal analyses were made in a Robert L. Stone apparatus fitted with a boron nitride cell designed to permit the sweep gases to flow through the powdered sample. The arrangement also permitted the gaseous products to be collected.

RESULTS

The Reaction of SO₂ with CaO

CaO was prepared by thermally decomposing a sample of finely powdered CaCO₃ in the DTA cell in a stream of nitrogen at 800°C. The sample was then cooled in a stream of dry nitrogen, the atmosphere was changed to pure SO₂, and programmed heating of the cell was begun. The results are shown in Figure 2, from which it is apparent that the absorption of SO₂ begins at about 100°C when the sample is heated at a rate of 5°C/minute. The rate of absorption is a maximum under the experimental conditions at a temperature of about 330°C. When a similar experiment was done by a thermogravimetric method, the results showed that only about 30% of the theoretical amount of sulphur dioxide was absorbed before the reaction ceased. It is evident that the CaSO₃ coating on CaO is only slightly permeable at temperatures in the vicinity of 350°C.

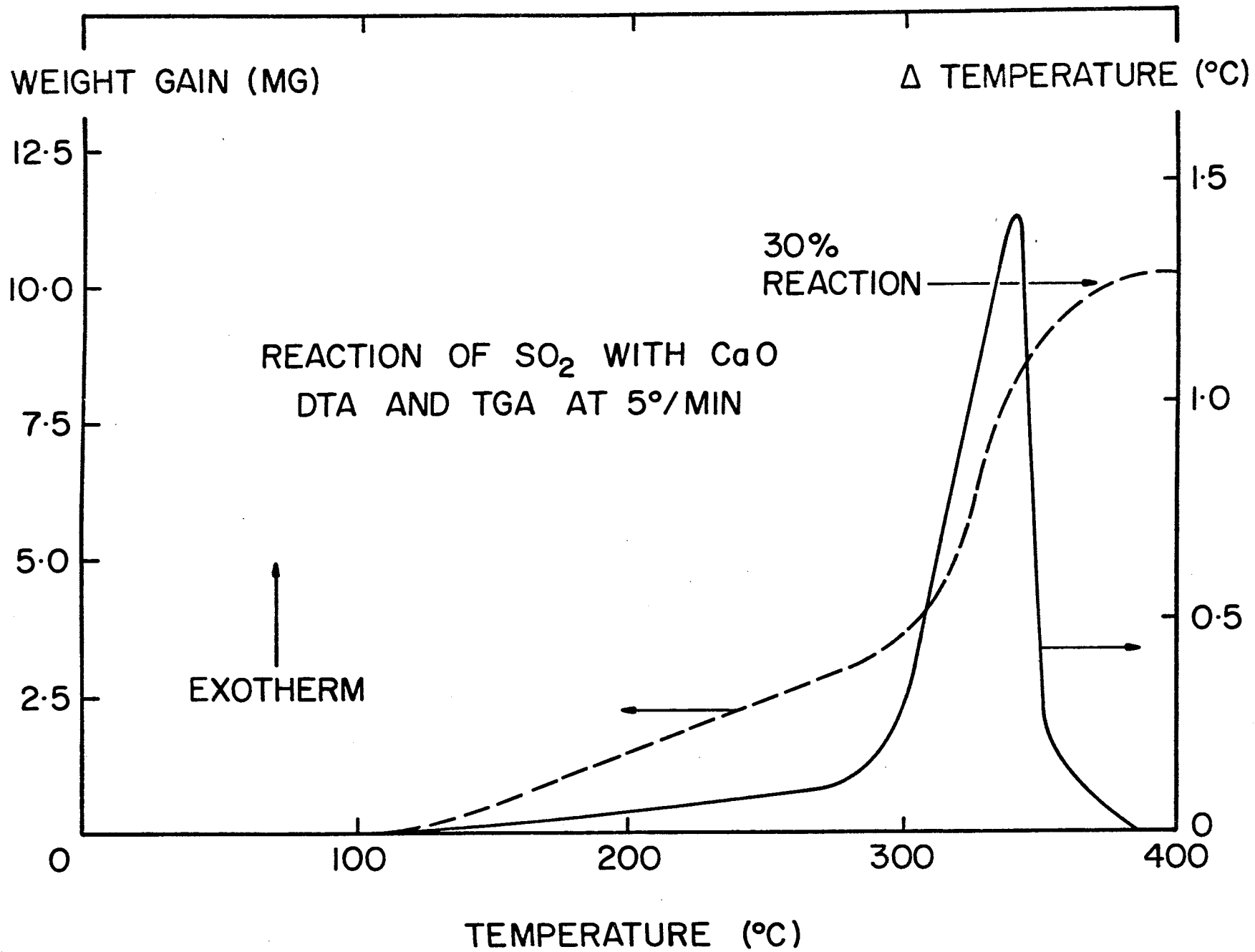


FIGURE 2. DTA and TGA Traces for the Reaction of Sulphur Dioxide with Calcium Oxide.

The Reactions of CaSO₃

The thermal stability of CaSO₃ was studied by heating samples of the finely powdered anhydrous material in a DTA cell that was heated at 5°C/minute. Gases of various compositions were passed through the samples. The results are shown in Figure 3, in which three curves are superimposed. Because of the difference in atmospheres, it was necessary to displace the temperature axis so that the similarity in shape of the curves could be demonstrated. The curves show that three processes may occur under the conditions of the study. They are represented by two exotherms and one endotherm.

a) The Exotherm for CaSO₃ Oxidation

To identify the processes that cause the exotherms, samples were removed from the DTA cell after the occurrence of the peaks. After the peak in the region 540-610°C, when the run had been done in an oxygen sweep, the only product was CaSO₄. When SO₂ was used as the sweep gas, the products were CaSO₄ and some elemental sulphur. There was no peak when CaSO₃ was heated through this temperature range in a nitrogen sweep.

When similar thermogravimetric experiments were done in the 540-610°C temperature range there was no weight change in nitrogen, as shown in Figure 4, but the samples in SO₂ and in O₂ were oxidized to 81% of the possible yield of CaSO₄.

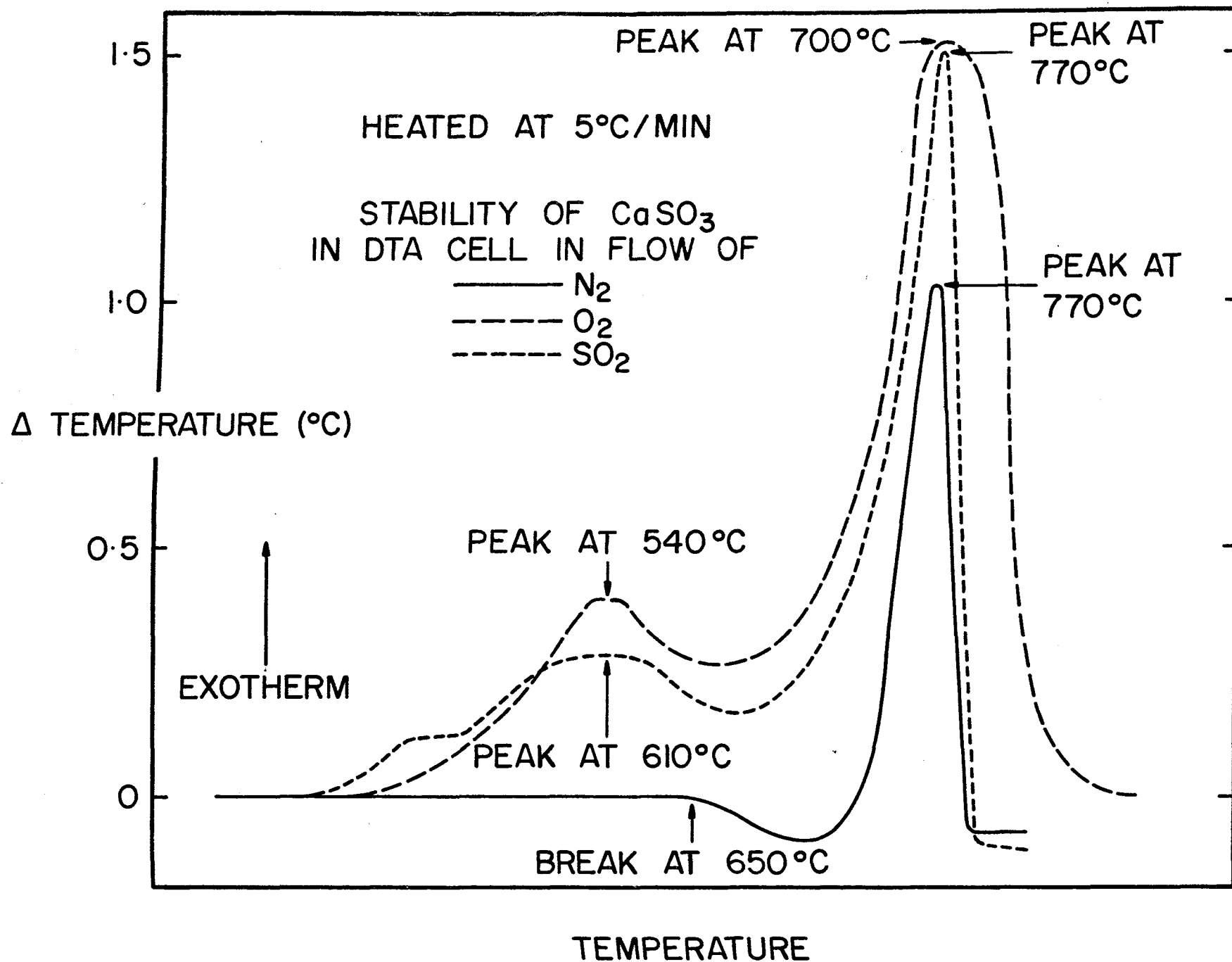


FIGURE 3. DTA Tracings for the Decomposition of Calcium Sulphite in Nitrogen, in Oxygen, and in Sulphur Dioxide.

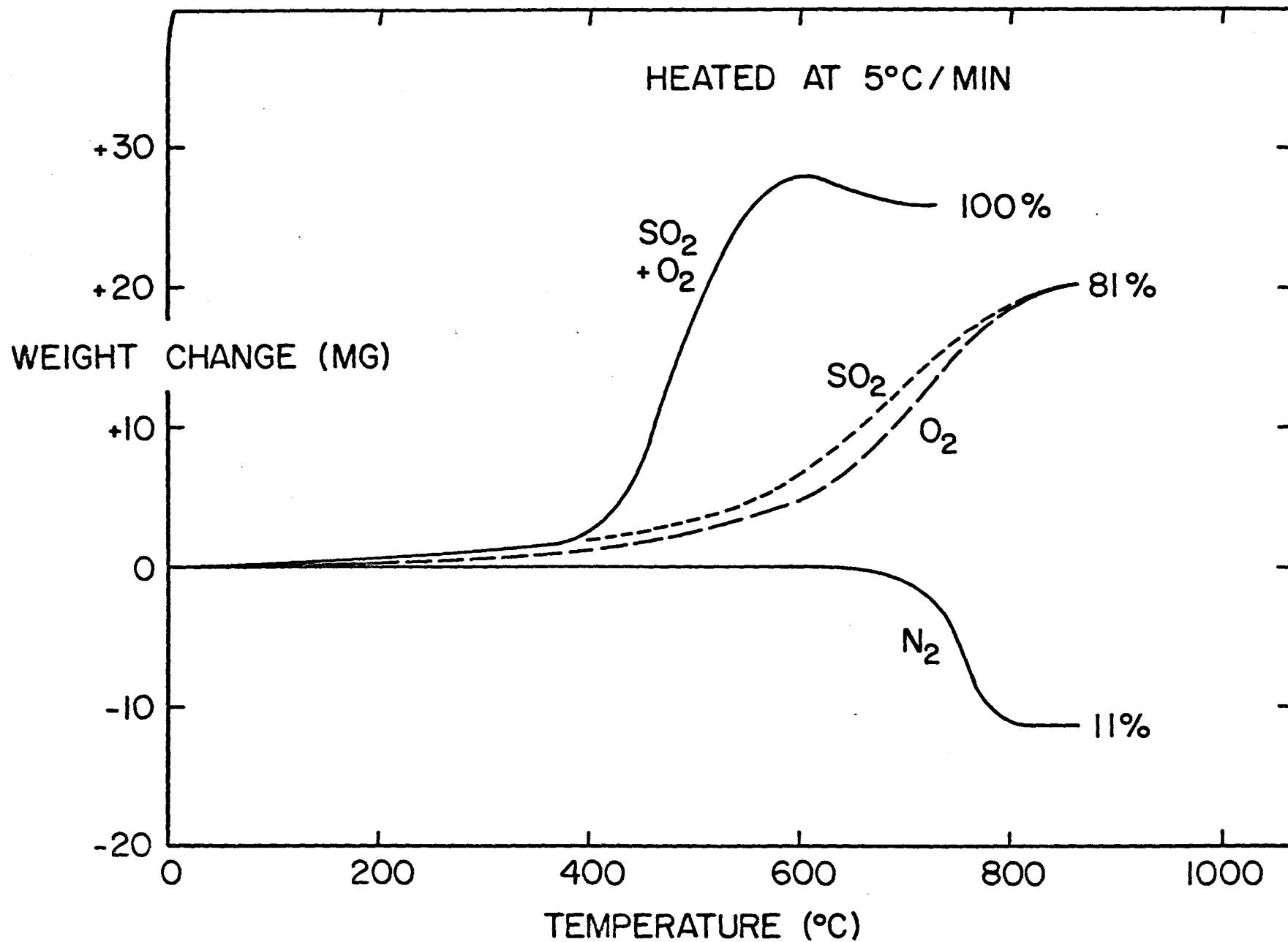


FIGURE 4. TGA Tracings for the Decomposition and Oxidation of Calcium Sulphite.

When SO_2 and O_2 were both present in the sweep gas, there was 100% conversion to CaSO_4 . The evidence is consistent with the oxidation of CaSO_3 according to the equation:



When only SO_2 is present, the source of the residual sulphur and also the source of oxygen for the oxidation is probably the reaction:



b) The Endotherm for CaSO_3 Decomposition to CaO

The DTA tracing in Figure 3 for the sample of CaSO_3 heated in nitrogen shows an endotherm beginning near 650°C . Figure 4 shows that there may be a weight loss accompanying the endotherm. The weight loss can vary from about 11% in a nitrogen sweep to about 90% when the experiment is done in vacuum (Figure 5). When the sample is heated slowly in vacuum ($3^\circ\text{C}/\text{min}$), only about 50% of the SO_2 is lost from the CaSO_3 . The behaviour is consistent with a partial thermal decomposition as represented by the equation:



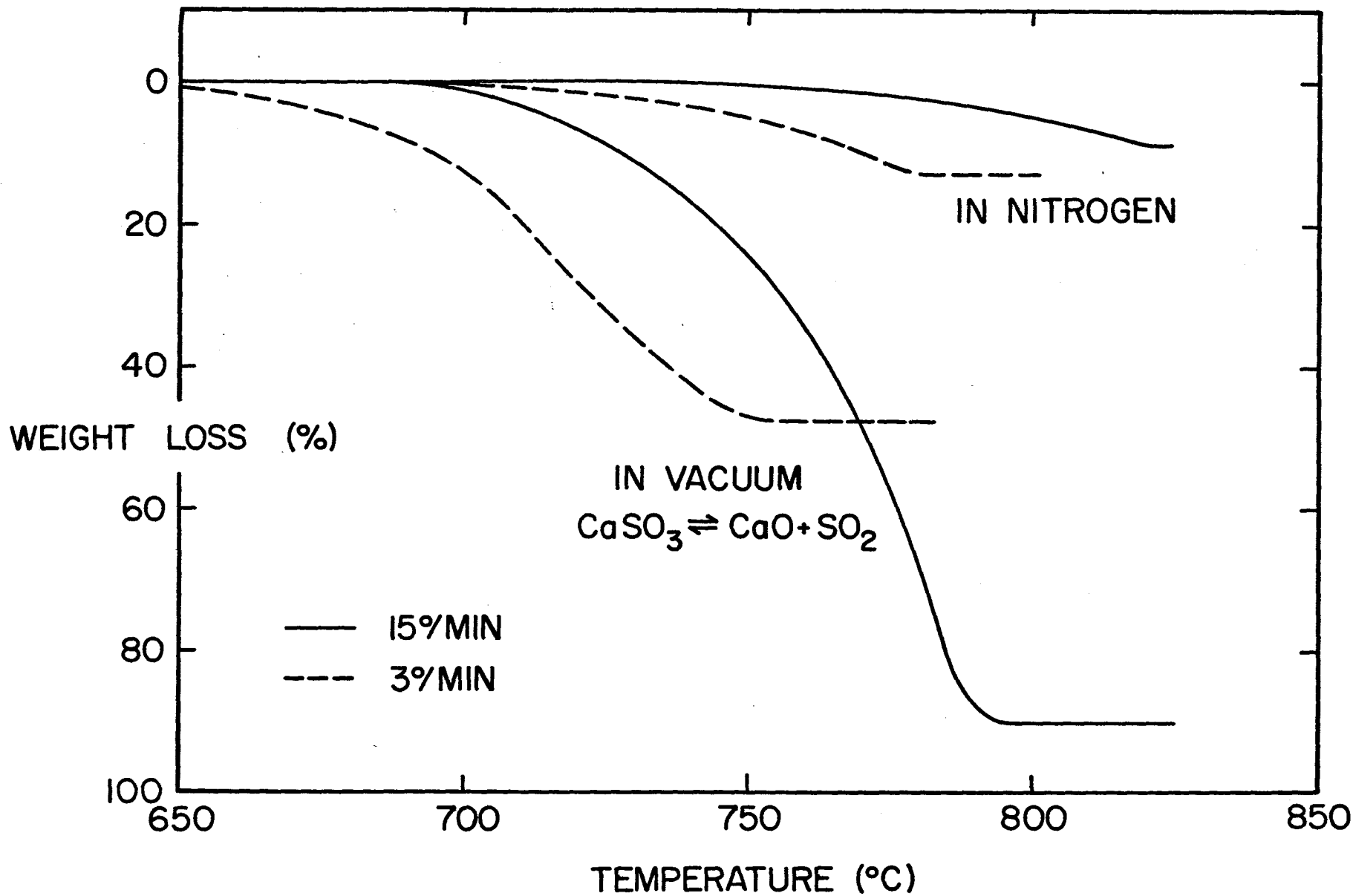


FIGURE 5. TGA Tracings for the Decomposition of Calcium Sulphite in Nitrogen and Under Vacuum.

c) The Exotherm for the Peritectoid Decomposition of CaSO₃

In additional experiments, an attempt was made to measure the equilibrium SO₂ pressure over CaSO₃⁽¹²⁾. When the temperature of the sample was high enough to initiate Reaction [3], the sample was converted to CaS and CaSO₄. Although both the DTA and TGA show that Equation 3 is possible, the SO₂ pressures that are developed are below the millimetre range in which we attempted to make the measurements. At temperatures where appreciable SO₂ pressures might have been developed, CaSO₃ undergoes the following binary peritectoid reaction:



This reaction is strongly exothermic and its peak temperature in a DTA experiment is in the 700 to 770°C range as shown in Figure 3.

When the oxidation of CaSO₃ is done in a mixture of SO₂ and O₂, that has been passed over a catalyst to develop the equilibrium amount of SO₃ in the mixture, the rate of weight increase, as shown in Figure 5, is much more rapid than that in either SO₂ or O₂ alone. The initial weight increase is greater than 100% of that required to convert sulphite to sulphate, because of the retention of some elemental sulphur (as is indicated by the sum of Equations 1 and 2).

The Effect of Water Vapour on the Rate of Oxidation of CaSO_3

To determine the effect of water vapour on the rate of calcium sulphite oxidation to sulphate, several experiments were done in which the weight of a CaSO_3 sample was followed, in different atmospheres, as the temperature was increased from 100 to 650°C. In the presence of SO_2 , O_2 (plus the equilibrium proportion of SO_3), and N_2 , the rate of oxidation in the absence of water vapour was initially more rapid than that in the presence of water vapour. On the contrary, after the initial period was over, the reaction in the presence of water vapour proceeded three times faster than in its absence.

Calcium carbonate is more stable than calcium sulphite. In a CO_2 atmosphere, at temperatures between 600 and 700°C, the SO_2 may be almost completely displaced from CaSO_3 during the formation of CaCO_3 .

The chemical reactions by which limestone may be converted to calcium sulphate are summarized in Figure 6, from which it will be evident that we consider that CaSO_3 is always an intermediate in the formation of CaSO_4 under the conditions likely to prevail in a steam boiler. The sulphate may arise from any of four secondary reactions with the sulphite: a direct oxidation by O_2 , or SO_2 , or SO_3 , or a peritectoid reaction in which 75% of the calcium in the sulphate is converted to sulphate and the remainder to sulphide. In additional reactions the sulphide may be oxidized to sulphate.

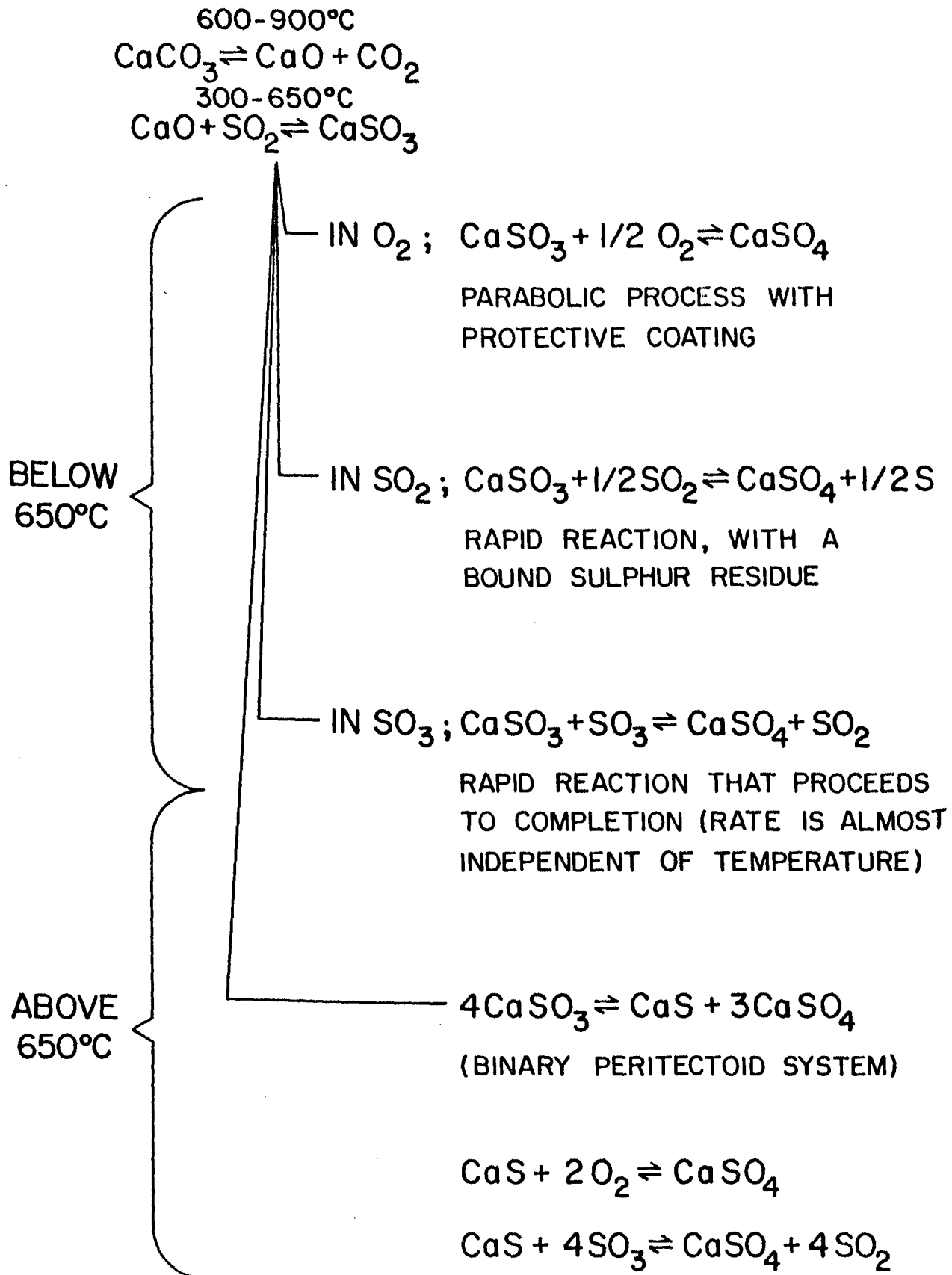


FIGURE 6. Summary of the Chemical Reactions by which Calcium Sulphate may be prepared from Limestone.

CONCLUSIONS

1. Calcium sulphite is an intermediate product in the formation of calcium sulphate from CaO and SO₂.
2. Calcium sulphite is initially formed from CaO and SO₂ in the temperature range 300-400°C.
3. Calcium sulphite is thermally unstable in an inert atmosphere at temperatures above 650°C. There are two competing processes in its decomposition. One liberates SO₂ and forms CaO, the other forms a mixture of CaS and CaSO₄.
4. Calcium sulphite may be readily oxidized to CaSO₄ by O₂, SO₂, or SO₃. The reaction forms a protective coating of CaSO₄ on the CaSO₃ particle and the coating may cause the reaction to cease if the particle size is large.
5. Calcium sulphite will reduce sulphur dioxide to elemental sulphur. Elemental sulphur is strongly retained in a reaction product containing calcium oxide, calcium sulphite and calcium sulphate.
6. When the products of oxidation of calcium sulphite were examined at temperatures above 800°C, calcium sulphate was the only product recovered.
7. Water vapour initially decreases the rate of oxidation of CaSO₃, but it increases the rate of oxidation to sulphate at higher temperatures.

ACKNOWLEDGEMENTS

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