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THE KINETICS OF THE THERMAL DECOMPOSITION OF $CoSO_4$ AND Co_3O_4

T. R. INGRAHAM AND P. MARIER
Mines Branch, Department of Energy, Mines and Resources, Ottawa (Canada)

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ABSTRACT

The thermal decomposition of compacts of powdered $CoSO_4$ occurs at a well defined interface. The rate-controlling step is the initial reaction to produce CoO and SO_3. Because of the highly oxidizing condition that prevails when SO_3 is released, the CoO is converted to Co_3O_4 by a secondary reaction. The Co_3O_4 persists as the final reaction product only when the partial pressure of O_2 in the sweep gas is greater than the equilibrium value for Co_3O_4 decomposition at the temperature of the experiment. The reaction rate is sensitive to the flow rate of the sweep gas when the reaction rate is rapid and the flow rate is slow. Within experimental error, the activation energies for the decomposition of $CoSO_4$ and Co_3O_4 are the same as their corresponding enthalpies.

A mathematical model was developed to analyze and predict the effects of changes in flow rate, in temperature, and in partial pressures of product gases, on the rate of $CoSO_4$ decomposition.

INTRODUCTION

At moderate temperatures, the oxides of manganese, cobalt, and copper react readily with SO_2 to form their sulfates. These reactions have been studied[1] in an antipollution context because they can be used to remove small concentrations of SO_2 from stack gases. The sulfates may be processed for recycling of the oxide, by leaching with water or by roasting. The latter procedure produces a rich gas that can be used for sulfuric acid production. The thermodynamics of the pertinent reactions have been elucidated[2-4], and the kinetics for the copper[5] and manganese[6] reactions have been studied. In this paper, studies of the pertinent reactions in the cobalt system will be reported.

Cobalt sulfate undergoes an $\alpha \rightarrow \beta$ transition[7] at about 617°C but this does not interfere with its decomposition, which is first detected by thermogravimetry[8] at about 730°C. The sulfate decomposes without the formation of intermediate oxysulfates[8]. The kinetics of cobalt sulfate decomposition were studied by Pechkovskii *et al.*[9]. They discussed the topochemical nature of the reaction and reported an activation energy of 76 kcal/mole for the reaction. This energy estimate is questionable because it is so much larger than the enthalpy of reaction[2] (53 kcal/mole), and because some of the activation energies reported in the same paper[9] for other decompositions are widely different from accepted literature values.

The reactions for the oxidation of CoO and Co_3O_4 and for the formation of $CoSO_4$ were reported by Alcock and Hocking[10], who found that during the sulfation reaction new $CoSO_4$ is formed at the $CoSO_4$–gas interface. This implies a free mobility of the cobalt ion in both the oxide and the sulfate.

EXPERIMENTAL

Materials and method

The cobalt source material used in all experiments was Baker and Adamson reagent-grade hydrated cobaltous sulfate, for which the following analysis was supplied by the manufacturer: insoluble 0.01%, Cl 0.001%, Fe 0.03%, Ni 0.10%, NO_3 0.005%, Cu 0.005%, Pb 0.005%, alkali and earth metals 0.25%.

Anhydrous cobalt sulfate was obtained by dehydration of this material at 400°C for 48 h in a muffle furnace. Tricobalt tetroxide was obtained by additional decomposition of the sulfate in the muffle furnace at 850°C for 50 h. Cobaltous oxide was prepared by decomposing Co_3O_4 in a stream of N_2 at 900°C over a 24-h period. Material compositions were confirmed by X-ray analysis.

An American Instrument Co. THERMOGRAV balance was used to determine the weight loss of the samples during their decomposition. In each instance the finely powdered sulfate or oxide sample was compressed at 100,000 lb/inch^2 to form a compact pellet which was 0.5 inch in diameter and 0.039 inch in height. Compressed powder compacts were used because it has been shown that the energy relationships established with them are identical with those obtained with larger blocks of solids[11]. The small height-to-diameter ratio was selected because it minimizes the influence of geometry change on the observed rate of reaction and permits the experimentalist to make a more rapid assessment of the effects of changes in variables without the necessity of detailed calculations.

Cylinder-grade N_2, SO_2, and O_2 were used in the experiments. The only precaution taken was to dry them thoroughly to prevent the formation of sulfuric acid in the system. Rotameter and electronic-heat-loss flowmeters were used to prepare the gas mixtures.

Chemical reactions

When cobaltous sulfate is thermally decomposed, the solid reaction product may be either CoO or Co_3O_4; the former is recovered at high temperatures and at low partial pressures of O_2, and the latter is recovered at low temperatures at higher partial pressures of O_2 (ref. 2). The reactions that may be involved are:

$$CoSO_4 \rightleftharpoons CoO + SO_3 \qquad (1)$$

$$SO_3 \rightleftharpoons SO_2 + \tfrac{1}{2}O_2 \tag{2}$$

$$3\,CoO + \tfrac{1}{2}O_2 \rightleftharpoons Co_3O_4 \tag{3}$$

$$3\,CoSO_4 \rightleftharpoons Co_3O_4 + 3\,SO_2 + O_2 \tag{4}$$

For the type of heterogeneous reactions shown in Eqn. (1) or (4), the probable rate-controlling step in the decomposition may be indicated by thermodynamic considerations. The method is based on the assumption that the onset of decomposition can be detected at the temperature at which the system develops an equilibrium decomposition pressure of about 1×10^{-3} atm. In simple systems, that is the temperature at which the free-energy change for the reaction is numerically equal to about fourteen times the value of the temperature in °K, *i.e.* $T = \Delta G^\circ/14$. For Reaction (1) this relationship indicates that decomposition should be detectable at about 725°C, while for Reaction (4) a temperature of at least 990°C would be required[2]. On this basis, it is reasonable to expect that Reaction (1) would take place first. It is also reasonable to expect that its activation energy would be approximately equal to the heat of reaction for Eqn. (1) at temperature near 900°C, *i.e.* about 50 kcal/mole.

RESULTS AND DISCUSSION

Geometrical changes

Heterogeneous decomposition reactions of the type to which the cobaltous sulfate system belongs are characterized by the fact that reaction occurs at a sharply defined interface between the solid reactant and its product. When the process is under chemical control, the interface recedes into the reactant at a constant velocity that is determined, in part, by the temperature of the interface. At a constant interface temperature, the rate of movement of the interface is constant. As the interface recedes into the pellet, the interfacial area decreases and there is a corresponding decrease in the measured reaction rate. If a meaningful correlation of the reaction rate is to be made, it is necessary to normalize the rate data for the change in geometry. Most normalization methods are based on the relationship between the fractional movement of the interface and the fraction of reaction[11-13]. In this paper we use an alternative method of normalizing the data by relating the fraction of reaction to a factor that converts the observed rate data to the area condition that prevailed at the beginning of an experiment. For example, the rate data obtained when the area is reduced to 50% of its original value would be multiplied by 2 to normalize them to the initial condition. The method of making the correction is as follows: the relationship between the fraction of reaction (α) and the fractional movement of the interface is established from the known geometry of a pellet[13], and then a factor is calculated in terms of the fractional movement of the interface. The observed reaction rate is multiplied by the factor to obtain the equivalent rate for the initial conditions. In the case of a pellet which is 0.5 inch in diameter and 0.039 inch in height, the factor, M, is related to the fraction of reaction (α) by the following five-term polynomial relationship:

$$M = 0.999758 + 0.241840\alpha + 0.081428\alpha^2 + 0.011549\alpha^3 + 0.0246589\alpha^4 \qquad (5)$$

A graph of M *vs.* α is shown in Fig. 1. To check the validity of this method of relating the factor for the observed reaction rate to the fraction of reaction, studies were made of the rate of sublimation of paradichlorobenzene pellets and the rate of unzipping of poloxymethylene. Because neither of these materials leaves a residue, it is possible to make a direct calculation of the factor by which the interfacial area decreases as the reaction progresses. The results are shown also in Fig. 1. The data for both compounds are, when averaged, in good agreement with the theoretical interface migration relationship up to $\alpha \approx 0.7$ (70% decomposition). There is some divergence in excess of that amount of reaction. The divergence is caused by a rounding at the edges of the pellets. On the basis of the good agreement up to 70%, Eqn. (5) was applied with confidence for the normalization of reaction-rate data from the pellets used in this work.

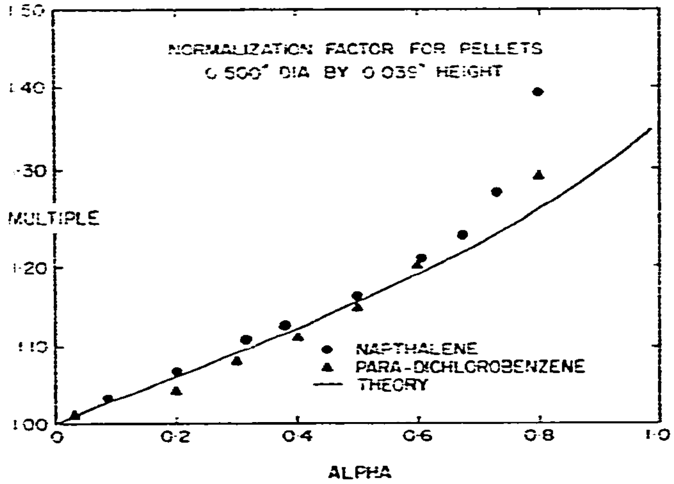

Fig. 1. Comparison of a calculated normalization factor with those obtained experimentally from sublimation and depolymerization experiments.

Decomposition of $CoSO_4$ in N_2

Pelletized samples of cobaltous sulfate were preheated to their reaction temperature in a 2:1 mixture of SO_2 and O_2 that was passed over a platinum catalyst at the reaction temperature. At zero time, the holding gases were purged from the system and the sample was decomposed in a preheated stream of dry N_2 at a series of temperatures between 735 and 825°C. The final reaction product at temperatures below 800°C was Co_3O_4, and for the 805, 815, and 825°C runs, it was CoO. The reaction interface between the sulfate and oxide was well defined and Co_3O_4 always seemed to be the intermediate reaction product. The observed reaction rates were normalized with the relationship in Eqn. (5) and are shown in Fig. 2. The loss in weight per unit area is a linear function of time through at least the first 70–80% of the reaction. The rate of reaction (slope of the lines) increases regularly with increasing temperature. An Arrhenius relationship for the reaction rate is shown in Fig. 5. The activation energy is 50 ±3 kcal/mole.

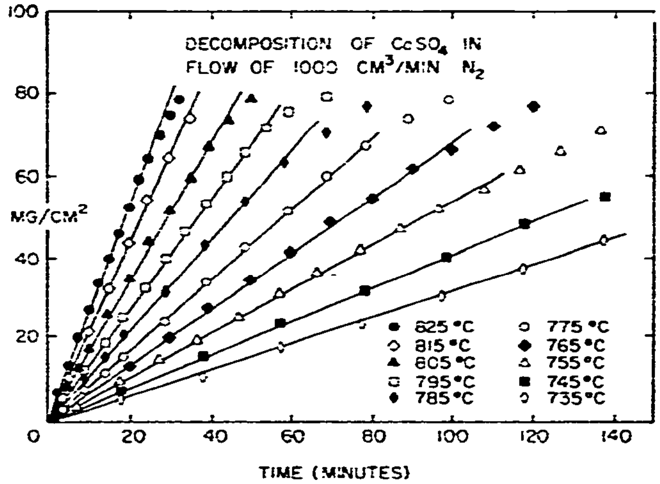

Fig. 2. Normalized rates of decomposition for $CoSO_4$ in a N_2 flow.

Decomposition of $CoSO_4$ in O_2

A similar series of experiments was done with an O_2 sweep instead of N_2. The presence of the O_2 retarded the rate of decomposition and made it necessary to examine the rate of decomposition at higher temperatures. The results are shown in Fig. 3. A duplicate run at 815°C is included to permit assessment of reproducibility.

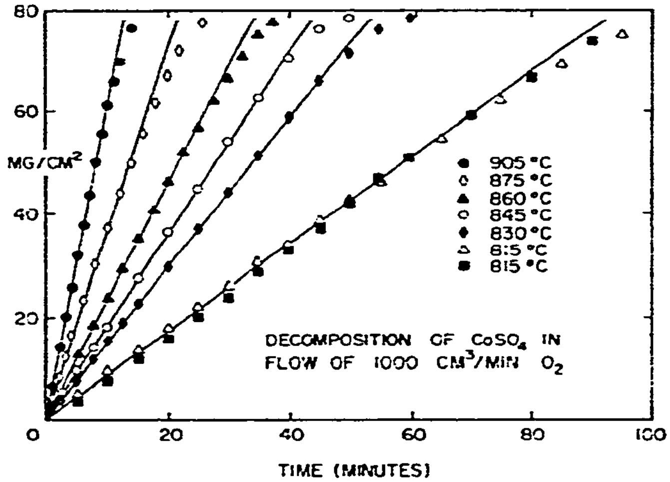

Fig. 3. Normalized rates of decomposition for $CoSO_4$ in an O_2 flow.

It was generally good. The same pattern of behaviour was observed for the decomposition in both N_2 and O_2. The solid product of decomposition was Co_3O_4 only. When the Arrhenius relationship shown in Fig. 5 was drawn, it was evident that the activation energy for the rate-controlling reaction is the same as that found in the N_2 system. This probably means that the rate-controlling reaction is the same in both reaction systems. The difference in frequency factor is related to the retarding influence of O_2 on the reaction rate.

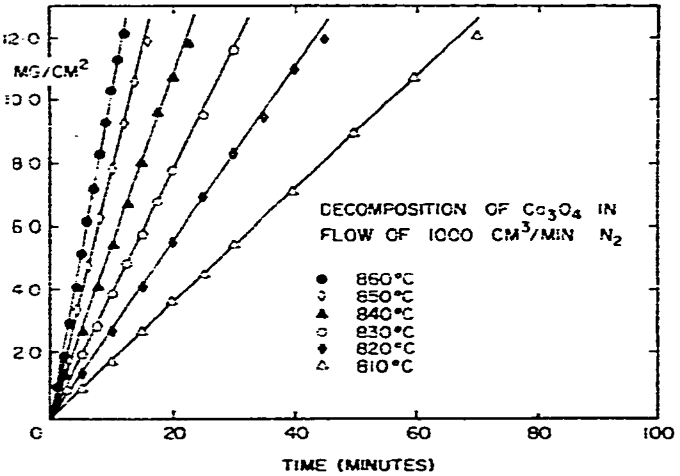

Fig. 4. Normalized rates of decomposition for Co_3O_4 in a N_2 flow.

Decomposition of Co_3O_4 in N_2

Pelletized samples of Co_3O_4 were heated to the required reaction temperature in an O_2 stream. At zero time the O_2 was purged from the system and replaced by a flow of dry N_2. Over the range of temperature from 810 to 860°C, the Co_3O_4 was rapidly converted to CoO. The reaction was also characterized by a well defined interface between the Co_3O_4 and CoO. The results were normalized using Eqn. (5) and are shown in Fig. 4. The weight loss per unit area is a linear function of time and is

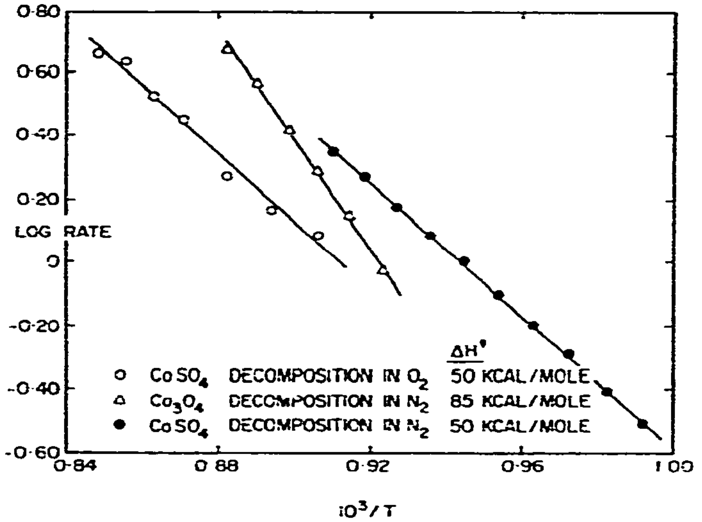

Fig. 5. Arrhenius relationships for $CoSO_4$ decomposition in N_2 and O_2 flows and for Co_3O_4 decomposition in a^4N_2 flow.

valid for the initial 80–90% of reaction. The corresponding Arrhenius relationship is shown in Fig. 5. The activation energy is 85 ±3 kcal/mole.

Effects of p_{SO_3}, p_{SO_2}, p_{O_2}, *and carrier-gas flow rate on the decomposition of* $CoSO_4$

In the next group of experiments, pellets of cobaltous sulfate were decomposed in the presence of various partial pressures of SO_3, SO_2, and O_2 and at total flow rates of 350 and 1000 cm^3/min through the reaction vessel. The cross-sectional area of the vessel is 20 cm^2 and therefore the linear flow past the sample was 50 cm/min at the most rapid rate.

The partial pressures of SO_3, SO_2, and O_2 were generated from 2:1 mixtures of SO_2 and O_2 equilibrated over an asbestos-supported platinum catalyst at reaction temperature. The partial pressures were calculated from the equilibrium data of Evans and Wagman[14]. The effects of the gas mixtures on the reaction rate were correlated by setting up a series of linear equations and solving them by determinants with a computer program. At any constant flow the reaction rate may be expressed as

$$\text{Rate} = A\,e^{-E/RT}\,p^{a}_{SO_3}\cdot p^{b}_{SO_2}\cdot p^{c}_{O_2} \tag{6}$$

When this is transformed to the logarithmic form,

$$\log \text{Rate} = \log A - \frac{E}{2.303\,RT} + a\log p_{SO_3} + b\log p_{SO_2} + c\log p_{O_2} \tag{7}$$

This equation is of the linear form:

$$Y_1 = A_0 + A_1X_1 + A_2X_2 + A_3X_3 \tag{8}$$

and the coefficients A_0, A_1, A_2, and A_3 can be solved from a series of values of Y_1, X_1, X_2, and X_3. The resulting equation is a partial mathematical model for the system. When the constant A_0 is segregated into its component parts, the components, log A and $E/4.576T$, may be evaluated separately and an additional equation generated for the effect of flow. In this manner a complete model for the rate of reaction as a function of temperature, flow, and partial pressure of SO_3, SO_2, and O_2 may be constructed.

We have constructed such a model and tested it against our experimental data at selected points. The results are shown in Table I. The conditions are shown in the first four columns. In columns 5 and 6 the observed and predicted reaction rates are compared. In general, the agreement is fair to good. It is at least sufficient to permit meaningful comparisons of the effects of the individual variables on the reaction rate. Some of these comparisons are shown in the following figures. The model was used to predict the effect of changes in flow rate at a variety of reaction temperatures. The results shown in Fig. 6 indicate that, at 800 and 850°C, the reaction rate is unaffected by flows of N_2 in the range from 10 to 50 cm/min past the sample. However, at 900°C, the model predicts that flows of less than about 20 cm/min are insufficient to sweep away the reaction product gases as rapidly as they are formed, and thus the reaction is retarded by the presence of the product gases. At 950°C, where the reaction rate

TABLE I

SPOT CHECKS OF MODEL

T (°C)	*Conditions*			*Rate* (*mg/cm*^{2} *per min*)	
	Flow (*cm*^{3}/*min*)	SO_2 (p_2)	O_2 (p_1)	*Observed*	*Predicted*
885	350	0	0	7.3	7.9
885	350	0.106	0.053	2.8	3.6
885	350	0.180	0.090	0.4	0.6
905	350	0	0	10.3	9.7
905	350	0.160	0.080	3.3	3.4
905	350	0.200	0.100	1.3	1.1

is much more rapid, the model predicts that the reaction is likely to be stifled by the presence of product gases unless the linear flow rate is in excess of about 32 cm/min. Even at a flow rate of 50 cm/min, the maximum rate of reaction was not attained.

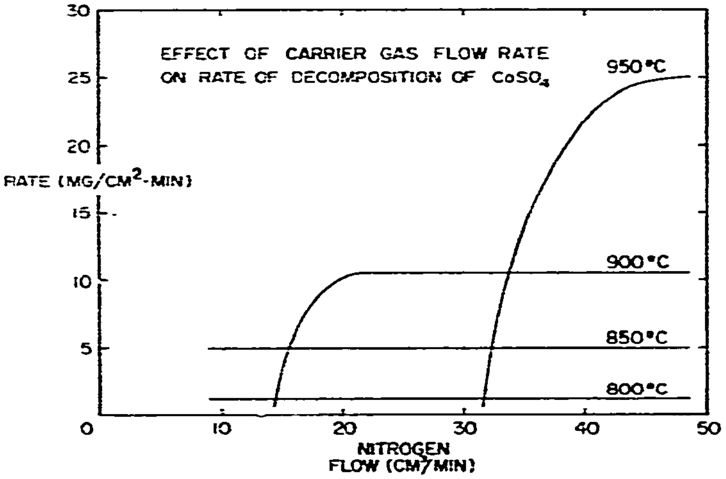

Fig. 6. The effect of carrier-gas flow rate on the rate of decomposition of $CoSO_4$.

In the next group of predictions, the model was used to examine the effect of O_2 partial pressures on the rate of reaction. A constant partial pressure of SO_3 equivalent to 1% was used to approximate actual conditions more closely. The program automatically included the equilibrium amount of SO_2 that would exist with 1% O_2 at various levels of O_2 partial pressure. The results are shown in Fig. 7. At all partial pressures of O_2 in excess of about 10%, the change in rate is linearly related to the change in partial pressure of O_2. At lower temperatures the deviation from linearity is more pronounced. The principal feature of the prediction is that there is only a small change in reaction rate over a wide range of O_2 pressures. For example, at 925°C the model predicts only a 12% reduction in the rate of reaction when the partial pressure of O_2 is increased to 40%.

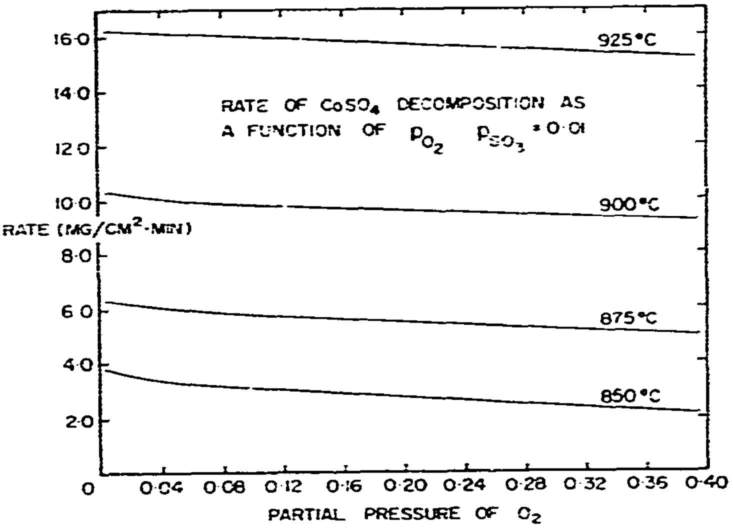

Fig. 7. Rate of $CoSO_4$ decomposition as a function of p_{O_2}. The p_{SO_3} was held at 1% for the prediction.

In the next group of predictions, the model was used to examine the change in reaction rate that results from changes in the partial pressure of SO_2. The partial pressure of O_2 was maintained at 1% and the equilibrium amount of SO_3 was present. Except at the lowest temperature (850°C), the relationships were essentially linear up to 40% SO_2 in the gas stream. The results are shown in Fig. 8.

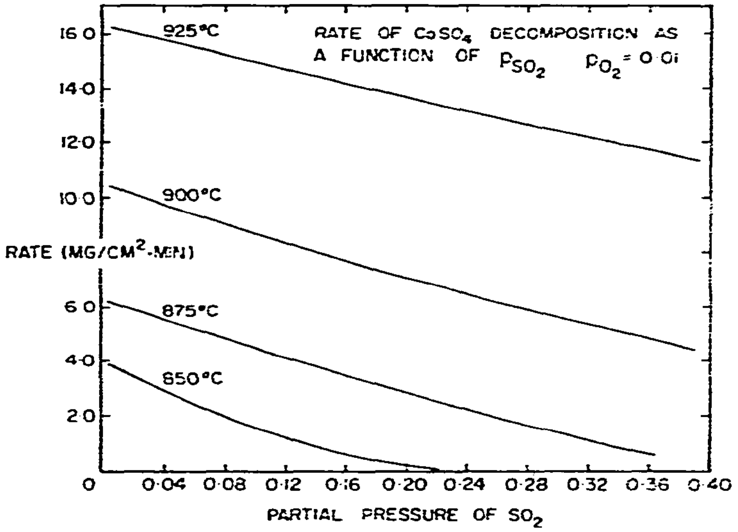

Fig. 8. Rate of $CoSO_4$ decomposition as a function of p_{SO_2}. The p_{O_2} was held at 1% for the prediction.

In the next group of predictions, the model was used to examine the effect of SO_3 partial pressure on the rate of reaction. The model automatically includes the equilibrium amounts of SO_2 and O_2 at each temperature and SO_3 level. The results of the prediction are shown in Fig. 9. The shape of the curves indicate that for small changes in the SO_3 partial pressure, the rate reduction is approximately linear. For larger changes, the relationship becomes non-linear and indicates that, in the presence of amounts in excess of about 2% SO_3, increasingly large amounts of SO_3 are required to produce the same amount of rate reduction. This might be expected if the SO_3 were strongly adsorbed on the solid reaction product.

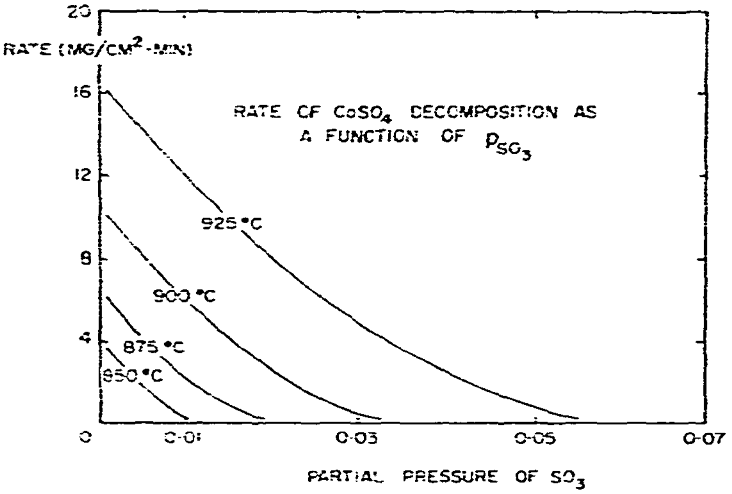

Fig. 9. Rate of $CoSO_4$ decomposition as a function of p_{SO_3}. Equilibrium amounts of SO_2 and O_2 were present.

The comparative effects of partial pressures of SO_3, SO_2, and O_2 are illustrated in Fig. 10, which is constructed from data predicted at 925 °C. The comparatively small effects of O_2 and SO_2 partial pressures are contrasted with the effect of SO_3. The predictions indicate that the primary rate control in the decomposition of $CoSO_4$ is vested in the partial pressure of SO_3 in the sweep gas.

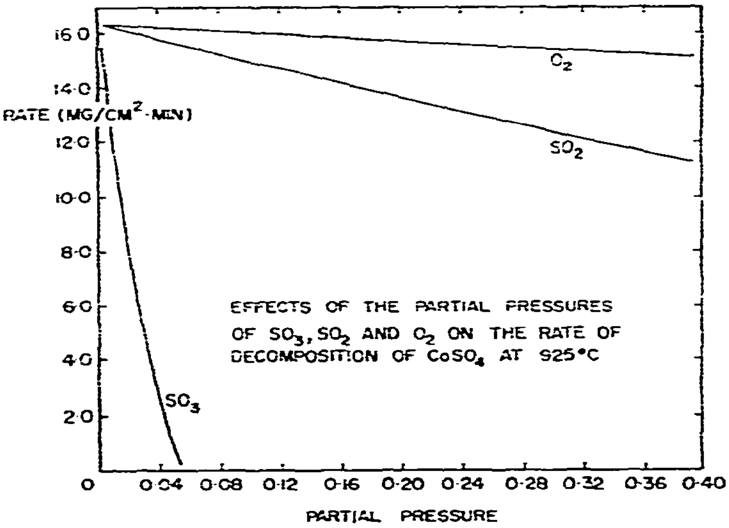

Fig. 10. Comparison of the effects of changes in p_{SO_3}, p_{SO_2}, and p_{O_2} on the rate of $CoSO_4$ decomposition at 925 °C.

CONCLUSIONS

The results support the conclusion that when $CoSO_4$ is thermally decomposed the rate-controlling reaction is the formation of CoO with the accompanying release of SO_3. In subsequent steps, that are not rate-controlling, the CoO may or may not be converted to Co_3O_4, in accordance with the partial pressure of O_2 prevailing in the reaction interface. During conditions of rapid release of SO_3 from the interface, the equilibrium partial pressure of O_2 is sufficiently high to immediately oxidize all of the CoO to Co_3O_4. In subsequent stages it may revert to CoO if the partial pressure of O_2 in the carrier gas is sufficiently low.

Changes in the flow rate of carrier gas affect the rate of decomposition through their influence on the concentration of product gases around the sample.

The effect of partial pressure of SO_3, SO_2, and O_2 is complex, because of the equilibrium existing between SO_3, SO_2, and O_2. The primary rate control is vested in the partial pressure of SO_3: SO_2 and O_2 exert a smaller influence.

The close agreement between the enthalpy of reaction and the observed activation energies (53 and 50 kcal/mole for the $CoSO_4$–CoO system and 85 and 84 for the Co_3O_4–CoO system) indicates that there is no significant activation energy required for the decomposition processes. The attainment of the required enthalpy of reaction is a sufficient energy acquisition to initiate the reaction. In effect, the temperature coefficient of the reaction rate is the temperature coefficient of the enthalpy.

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