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## KINETIC STUDY OF REACTIVITY OF MARBLE WITH SULPHUR DIOXIDE BY REVERSED-FLOW GAS CHROMATOGRAPHY

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### SUMMARY

Reversed-flow gas chromatography was used to study the kinetics of the action of sulphur dioxide ( $\text{SO}_2$ ) on calcium carbonate ( $\text{CaCO}_3$ ) and to draw some conclusions about the mechanism of the phenomenon and its rate-determining step.  $\text{SO}_2$  was fed to the solid by gaseous diffusion at constant temperature, using a short diffusion column, either empty or filled with  $\text{CaCO}_3$ . The rate of diminution of the sample peak height with time gave the diffusion coefficient of  $\text{SO}_2$  in the carrier gas when the diffusion column contained no solid material. In the presence of  $\text{CaCO}_3$ , the diffusion flux along the column was disturbed and the rate of diminution of the sample peak height was usually greater than before. Suitable mathematical relationships were derived, by means of which the experimental data were analysed and the rate constant of the action of  $\text{SO}_2$  on  $\text{CaCO}_3$  was calculated. This rate constant pertains to the mass transfer of  $\text{SO}_2$  from the gas phase to the solid surface, which is the rate-determining step. It increases with increasing specific surface area of  $\text{CaCO}_3$  and when the carrier gas is loaded with water vapour, but decreases with increasing temperature.

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### INTRODUCTION

The object of this work was to study the action of sulphur dioxide ( $\text{SO}_2$ ) on calcium carbonate ( $\text{CaCO}_3$ ) kinetically and, from the kinetic behaviour, to draw conclusions about the mechanism of the phenomenon and its rate-determining step. Such a study must be conducted (i) under mild conditions of temperature, pressure, humidity and  $\text{SO}_2$  concentration, close to those which prevail in the atmosphere, and (ii) under conditions of feeding the gas to the solid material close to those occurring in the atmosphere. Both of these requirements are connected with certain experimental and theoretical problems, which must be solved. The main problems are as follows: (a) the atmospheric temperatures do not ensure rates of action that are sufficiently high to be measured accurately; (b) the range of temperatures in the atmosphere at the same location is not wide enough to permit the calculation of activation energies for the process; (c) the concentration of  $\text{SO}_2$  in the atmosphere is very low, so that a very sensitive method is needed to measure its diminution with time as the action on  $\text{CaCO}_3$  proceeds; and (d) the whole phenomenon is a hetero-

geneous action of a gas on a solid and, although there are gas streams in the atmosphere, the gas is being fed on to the solid mainly by gaseous diffusion. Therefore, the experimental arrangement must be such that it creates an  $\text{SO}_2$  feed to the solid which resembles that of gaseous diffusion. Leaving the solid in contact with  $\text{SO}_2$  in a closed vessel, or passing a stream of air containing  $\text{SO}_2$  over the solid embedded inside a tube, are far from the natural conditions.

Problems (a) and (b), namely those of temperature, were overcome by working at temperatures as near to that of the atmosphere as measurements permit, for example  $50^\circ\text{C}$ , and in a range of temperatures slightly wider than that of the atmosphere, for example a range of  $100^\circ\text{C}$ .

Problem (c), regarding  $\text{SO}_2$  determination, was solved by using gas chromatography (GC) with flame photometric detection (FPD). The detector has a limit of detection for  $\text{SO}_2$  of  $2 \cdot 10^{-11}$  g/s and this, divided by the flow-rate ( $0.283 \text{ cm}^3/\text{s}$ ), gives the lowest detectable  $\text{SO}_2$  concentration as  $7 \cdot 10^{-11}$  g/cm<sup>3</sup> or 54 ppb. This is low enough, considering that the level of  $\text{SO}_2$  concentrations in the atmosphere lies in the range 100–200 ppb. However, FPD has a disadvantage over other methods of detection, being non-linear. Therefore, the response factor, which depends on the nature of the sulphur compound and the conditions, must be easily determined and a simple method for this had to be developed.

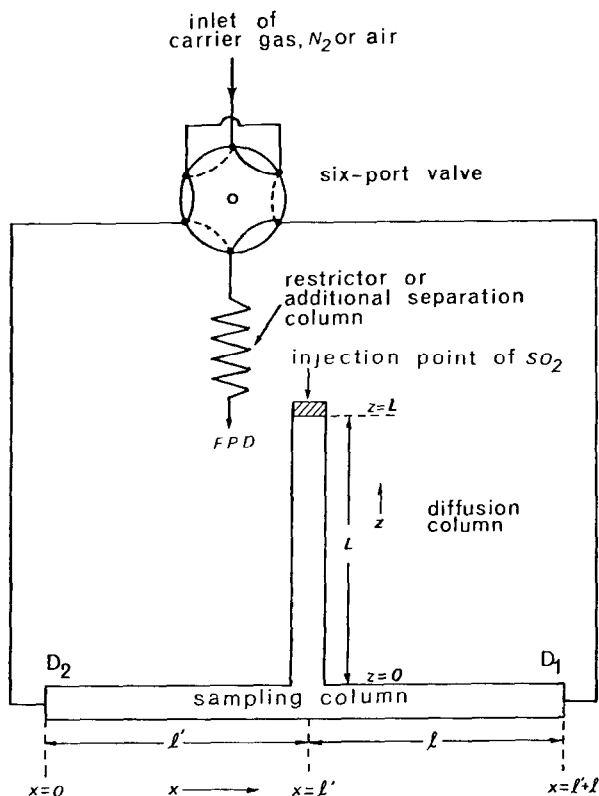


Fig. 1. Schematic representation of the reversed-flow cell used to study the action of  $\text{SO}_2$  on  $\text{CaCO}_3$ .

The main problem, however, was (d), *i.e.*, feeding the  $\text{CaCO}_3$  with  $\text{SO}_2$  by gaseous diffusion and measuring the rate coefficient of its action on the solid. This was solved experimentally and theoretically by using and further developing a method termed "reversed-flow gas chromatography". This method, which has been reviewed<sup>1</sup>, has been used successfully to study the kinetics of surface-catalysed reactions<sup>2-11</sup>, rates of drying of catalysts<sup>12</sup>, diffusion coefficients in binary and ternary gas mixtures<sup>13-15</sup>, adsorption equilibrium constants<sup>16</sup>, molecular diameters and critical volumes of gases<sup>17</sup>, Lennard-Jones parameters<sup>18</sup>, rate coefficients for the evaporation of liquids<sup>19</sup>, activity coefficients<sup>20</sup> and mass-transfer coefficients for adsorption on solids<sup>21</sup> and for evaporation of liquids<sup>22</sup>.

## THEORETICAL

The principle on which the method is based can be understood by reference to Fig. 1. A diffusion column, of length  $L$ , is connected perpendicularly to the midpoint of a so-called sampling column, of length  $l' + l$ , and the whole cell is thermostated inside the oven of the chromatograph. The two ends,  $D_2$  and  $D_1$ , of the sampling column are connected to the carrier-gas inlet and the flame-photometric detector through a four- or six-port valve, as shown. By switching this valve from one position to the other, the direction of flow of the carrier gas (nitrogen or air) through the column of length  $l' + l$  is reversed, producing "sample peaks" in the recorder line, as shown in Fig. 2.

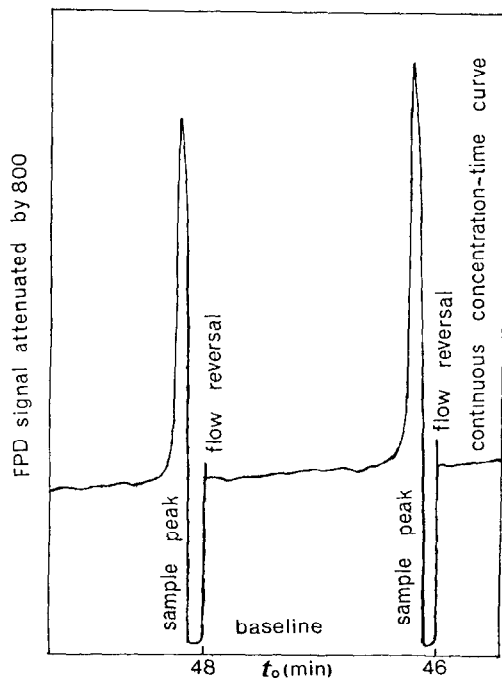


Fig. 2. Sample peaks obtained for the diffusion of  $\text{SO}_2$  ( $10 \text{ cm}^3$ ) into  $\text{N}_2$  ( $\dot{V}_{\text{N}_2} = 0.5 \text{ cm}^3/\text{s}$ ) at  $373.2 \text{ K}$  and  $1.04 \text{ atm}$ .

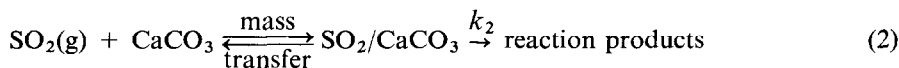
The height,  $h$ , of the peaks, measured from the baseline, is given by the equation<sup>1,14</sup>

$$h = [2c(l', t_0)]^m \quad (1)$$

where  $c(l', t_0)$  is the gaseous concentration of  $\text{SO}_2$  at the junction of the cell, and at time  $t_0$  from the injection of  $\text{SO}_2$ , diluted with nitrogen or air, into the column of length  $L$ . The volume of the mixture injected is about twice the gaseous volume of the column of length  $L$ . The parameter  $m$  is equal to 1 for a linear detector such as a flame ionization detector, but different from unity for a flame photometric detector, and it has to be determined.

If the column of length  $L$  is empty and sufficiently long (about 1 m), the rate of change of the peak height with time depends only on the diffusion coefficient of  $\text{SO}_2$  into the carrier gas (nitrogen or air), so that from this rate the precise value of the diffusion coefficient can be calculated<sup>13,14</sup>. Suppose now that the diffusion column is filled with  $\text{CaCO}_3$  (powder, chips or larger pieces of any form); what would happen? The diffusion current of  $\text{SO}_2$  into the carrier gas stream still exists, carrying  $\text{SO}_2$  on to the surface of the solid. If there is no action (physical or chemical) of the diffusing gas on the solid, the rate of the diminution of the peak height with time would be the same as before, leading to the diffusion coefficient of  $\text{SO}_2$  again. However, if  $\text{SO}_2$  reacts with the solid  $\text{CaCO}_3$ , the rate of diminution of the peak height is different from that before. Hence the diffusion phenomenon is disturbed by the action of  $\text{SO}_2$  on  $\text{CaCO}_3$ , and this disturbance can be used to measure the rate of the process. However, in order to extract values for the various coefficients of the action we need: (a) a short column ( $L \approx 30$  cm) and not one 1 m long, as used to measure the diffusion coefficients, so that a sufficient  $\text{SO}_2$  concentration reaches the junction at  $x = l'$ ; (b) the exact value of  $m$  for the detector; (c) a suitable mathematical relationship to analyse the experimental data and calculate from them the numerical value of the rate constant of the action of  $\text{SO}_2$  on  $\text{CaCO}_3$ . The shorter column makes the mathematical analysis more difficult, because it does not permit certain approximations that have been used with long columns. This is outlined below.

Consider again the diffusion column of length  $L$ , filled with pieces of  $\text{CaCO}_3$ . Inside this column, the following physical and chemical phenomena are possible: (a) longitudinal diffusion of  $\text{SO}_2$  in the gas phase along the coordinate  $z$ , (b) mass transfer phenomena of  $\text{SO}_2$  in the gas–solid boundary and (c) chemical reaction with  $\text{CaCO}_3$  of the  $\text{SO}_2$  transferred to the solid. The latter two phenomena can be represented by



where the mass transfer rate is governed by the mass-transfer coefficients in the gas and in the solid. Based on this scheme, the concentration  $c(l', t_0)$  in eqn. 1 and hence the height  $h$  of the sample peaks will be found as an analytical function of the time  $t_0$ .

The mass-balance equation of a solute A (SO<sub>2</sub>) in the column L is

$$\frac{\partial c_G}{\partial t_0} = D \cdot \frac{\partial^2 c_G}{\partial z^2} - K_S S \rho \cdot \frac{m_S}{a_z} (c_S^* - c_S) \quad (3)$$

where  $c_G$  = concentration of A in the gas phase in the column of length  $L$  (mol/cm<sup>3</sup>);  $c_S$  = concentration of A in the solid (mol/g);  $c_S^*$  = concentration of A in the solid in equilibrium with the gas phase (mol/g);  $D$  = diffusion coefficient of A into the carrier gas (cm<sup>2</sup>/s);  $K_S$  = overall mass transfer coefficient of A between gas and solid (cm/s);  $S$  = surface area per unit mass of solid (cm<sup>2</sup>/g);  $\rho$  = density of the solid (g/cm<sup>3</sup>);  $m_S$  = mass of solid per unit length of column  $L$  (g/cm);  $a_z$  = cross-sectional area of void space in the column (cm<sup>2</sup>).

The rate of change of  $c_S$  under non-steady-state conditions is

$$\frac{\partial c_S}{\partial t_0} = K_S S \rho (c_S^* - c_S) - k_2 c_S \quad (4)$$

where  $k_2$  is the rate constant (in s<sup>-1</sup>) for the reaction of SO<sub>2</sub> with CaCO<sub>3</sub>.

The system of partial differential equations (eqns. 3 and 4) can be solved by using Laplace transformations under given initial and boundary conditions. The initial condition depends on the mode of introducing solute A into the column of length  $L$  through the point at  $z = L$ . We chose the introduction of SO<sub>2</sub> by slow injection of a large enough volume of it (diluted with carrier gas) to fill initially the entire length of the diffusion column with an approximately uniform concentration  $c_0$  of SO<sub>2</sub>. Hence the initial condition is

$$c_G(z, 0) = c_0 \quad \text{and} \quad c_S(z, 0) = 0 \quad (5)$$

The boundary conditions are

$$(\partial c_G / \partial z)_{z=L} = 0 \quad (6)$$

at  $z = L$ , as there is no flux across this boundary, and

$$c_G(0, t_0) = c(l', t_0) \quad (7)$$

$$Da_z(\partial c_G / \partial z)_{z=0} = va_x c(l', t_0)$$

at the boundary  $z = 0$ . In these equations  $c(l', t_0)$  is the gaseous concentration in the sampling column at  $x = l'$  (cf., Fig. 1),  $v$  is the linear velocity of the carrier gas in the column of length  $l' + l$  and  $a_x$  is the cross-sectional area of this column.

In eqns. 3 and 4,  $c_S^*$  can be replaced by  $Kc_G$ , according to the linear isotherm  $c_S^* = Kc_G$ , where  $K$  is the partition coefficient (cm<sup>3</sup>/g) for the distribution of solute between the gaseous and solid phases. After this substitution, Laplace transformation with respect to time  $t_0$  (transform parameter  $p_0$ ) of eqns. 3 and 4, with the initial

condition 5, gives two ordinary differential equations, which are combined to yield

$$\frac{d^2 C_G}{dz^2} - q^2 C_G = -\frac{c_0}{D} \quad (8)$$

where  $C_G$  is the  $t_0$ -transformed function of  $c_G$  and  $q$  is given by the equation

$$q^2 = \frac{1}{D} \left[ p_0 + \frac{k_1 (p_0 + k_2)}{p_0 + k_{-1} + k_2} \right] \quad (9)$$

with  $k_1$  and  $k_{-1}$  denoting the groups of constants:

$$k_1 = K_S K S \rho m_S / a_z \quad (10)$$

$$k_{-1} = K_S S \rho \quad (11)$$

If the mass transfer mechanism of  $\text{SO}_2$  in the gas and in the solid phase consists of simple adsorption-desorption phenomena,  $k_1$  and  $k_{-1}$  (in  $\text{s}^{-1}$ ) are the rate constants for adsorption and desorption, respectively.

The linear second-order eqn. 8 can be integrated by using  $z$  Laplace transformation, subject to the boundary conditions 6 and 7. The result is

$$C(l', p_0) = \frac{c_0}{Dq^2} \cdot \frac{\sinh qL}{\sinh qL + (va_x/Da_z q) \cosh qL} \quad (12)$$

giving the  $t_0$ -transformed function of  $c(l', t_0)$ .

Inverse Laplace transformation of this equation to find  $c(l', t_0)$  is difficult. It can be achieved using certain approximations, the first of which is to omit  $\sinh qL$  from the denominator. This is based on the fact that  $\sinh qL \leq \cosh qL$  and, for high enough flow-rates,  $va_x/Da_z q \gg 1$ . Eqn. 12 then reduces to

$$C(l', p_0) = (c_0 a_z / \dot{V} q) \tanh qL \quad (13)$$

where  $\dot{V} = va_x$  is the volumetric flow-rate of the carrier gas in the sampling column of length  $l' + l$ . Before going to other approximations, let us find the inverse of eqn. 13 for  $k_1 = 0$ , i.e., when only longitudinal diffusion of  $\text{SO}_2$  in the gas phase takes place without any mass transfer of it to the solid phase. Under this condition, eqn. 9 becomes  $q^2 = p_0/D$ , and eqn. 13 gives

$$c(l', t_0) = N \sum_{n=0}^{\infty} \exp \left[ - \left( n + \frac{1}{2} \right)^2 \pi^2 D t_0 / L^2 \right] \quad (14)$$

where

$$N = 2c_0 a_z D / \dot{V} L \quad (15)$$

In the series 14 only the first term with  $n = 0$  is important under our experimental

conditions, since the second term with  $n = 1$  has an exponent nine times greater than that of the first term and becomes negligible after a short time period. The same applies to the other terms with  $n = 2, 3, \dots$ . Thus, eqn. 14 with the first term only retained reads

$$c(l, t_0) = N \exp(-\pi^2 D t_0 / 4L^2) \quad (16)$$

and this, on substitution in eqn. 1 and taking logarithms, gives

$$\ln h = m \ln(2N) - m\pi^2 D t_0 / 4L^2 \quad (17)$$

Therefore, by plotting  $\ln h$  vs.  $t_0$  the value of  $m\pi^2 D / 4L^2$  is found from the slope. Then, using the theoretically calculated<sup>23</sup> value of  $D$ , we can find  $m$ , as  $L$  is accurately known. Hence eqn. 17 provides a simple and accurate method for determining the response factor of a non-linear detector such as a flame photometric detector. The only requirement is that  $k_1 = 0$ , but this is easily substantiated by working with a diffusion column containing no solid material, and simply injecting into it a small volume of the diluted solute, e.g.,  $\text{SO}_2$ .

With the diffusion column filled with  $\text{CaCO}_3$ , which reacts physically or chemically with  $\text{SO}_2$ ,  $k_1$ ,  $k_{-1}$  and  $k_2$  must be taken generally as having non-zero values, and consequently eqn. 16 does not hold true. To correct this equation for the case that  $q$  is given by eqn. 9 and not simply by  $p_0/D$ , we take the Laplace transform of eqn. 16 with respect to  $t_0$ :

$$C(l, p_0) = \frac{N/D}{p_0/D + \pi^2/4L^2} \quad (18)$$

and replace  $p_0/D$  in the denominator by the right-hand side of eqn. 9. This approximation is based on the assumption that  $k_1(p_0 + k_2)/(p_0 + k_{-1} + k_2)$  is a perturbation added to  $p_0$ . Reverting now eqn. 18 so corrected, one finds, after rearrangement,

$$c(l, t_0) = \frac{N}{2} \left[ \left( 1 + \frac{Z}{Y} \right) \exp\left(-\frac{X+Y}{2} t_0\right) + \left( 1 - \frac{Z}{Y} \right) \exp\left(-\frac{X-Y}{2} t_0\right) \right] \quad (19)$$

where

$$X = \frac{\pi^2 D}{4L^2} + k_1 + k_{-1} + k_2 \quad (20)$$

$$Y = \left[ \left( \frac{\pi^2 D}{4L^2} + k_1 + k_{-1} + k_2 \right)^2 - \frac{\pi^2 D}{L^2} (k_{-1} + k_2) - 4k_1 k_2 \right]^{\frac{1}{2}} \quad (21)$$

$$Z = \frac{\pi^2 D}{4L^2} + k_1 - k_{-1} - k_2 \quad (22)$$

and  $N$  is given by eqn. 15.

If eqn. 19 is substituted for  $c(l', t_0)$  in eqn. 1, the height  $h$  of the sample peaks, due to the flow reversals, is given as an analytical function of the time  $t_0$ .

Two limiting cases of eqn. 19 are interesting. They arise from the relative magnitudes of the terms in eqn. 20. First, when  $k_1$  is small compared with the diffusion or the other terms, *i.e.*, when the mass transfer from the gas phase to the solid is slow, eqn. 19 reduces to eqn. 16 for simple diffusion, as expected. Second, when  $k_{-1}$  is small compared with the other terms, meaning that mass transfer from the surface to the bulk of the solid phase (when  $c_s^* > c_s$ ) or *vice versa* (when  $c_s^* < c_s$ ) is slow, eqn. 19 becomes

$$c(l', t_0) = N \exp \left[ - \left( \frac{\pi^2 D}{4L^2} + k_1 \right) t_0 \right] \quad (23)$$

*i.e.*, it reduces to a simple exponential function of the same form as eqn. 16, but with a different exponent. These two limiting cases work irrespective of the rate of the chemical reaction in the solid, as expressed by  $k_2$ .

In order to see whether the experimental data conform to either eqn. 16 or eqn. 23, it is only necessary to use eqn. 1 with  $c(l', t_0)$  substituted by the right-hand side of these equations, and taking logarithms. For eqn. 16 this leads to eqn. 17, whereas for eqn. 23 the following expression is obtained:

$$\ln h = m \ln (2N) - m \left( \frac{\pi^2 D}{4L^2} + k_1 \right) t_0 \quad (24)$$

The common criterion is that after the first few points, owing to the second and the higher terms in series 14, a straight line is obtained on plotting  $\ln h$  vs.  $t_0$ . The absolute value of the slope of this line is either  $m\pi^2 D/4L^2$  corresponding to the limiting case  $k_1 \approx 0$ , or  $m(\pi^2 D/4L^2 + k_1)$ , *i.e.*, greater than before, corresponding to the second limiting case  $k_{-1} \approx 0$ . From the latter slope  $k_1$  is determined.

If the plot of  $\ln h$  vs.  $t_0$  is not linear, it corresponds to the general form of eqn. 19, which predicts a curve described by the sum of two exponential functions. These functions have different exponential coefficients,  $(X + Y)/2$  and  $(X - Y)/2$ , and if the difference between them is large enough,  $X$  and  $Y$  can be calculated from the slopes of the plot. Then, using also the known value of  $\pi^2 D/4L^2$  in eqns. 20–22, combinations of the constants  $k_1$ ,  $k_{-1}$  and  $k_2$  can be found.

## EXPERIMENTAL

A Pye Unicam (Cambridge, U.K.) PU 4500 gas chromatograph was used, equipped with a flame photometric detector. Inside the oven of the chromatograph the cell depicted in Fig. 1 was accommodated, having the dimensions  $l' = l = 29$  cm and  $L = 32.5$  cm, all made from a glass tubing of 4 mm I.D.

The diffusion column of length  $L$  was filled with marble chips prepared from a product from Dionyssos-Pentelicon Commercial & Industrial Marble (Athens, Greece). The commercial product was crushed and sieved to obtain two ranges of particle size, 22–44 and 120–150 mesh. The chemical analysis of the marble is given



TABLE I

CHEMICAL ANALYSIS OF THE MARBLE USED TO STUDY THE KINETICS OF THE ACTION OF SO<sub>2</sub> ON CaCO<sub>3</sub>

<i>Component</i>	<i>Concentration</i> (%, w/w)	<i>Component</i>	<i>Concentration</i> (%, w/w)
CaCO <sub>3</sub>	96.27	Fe <sub>2</sub> O <sub>3</sub>	0.12
SiO <sub>2</sub>	1.23	Mn (as Mn <sub>2</sub> O <sub>3</sub> )	0.002
MgO	1.80	H <sub>2</sub> O (combined)	0.15
Al <sub>2</sub> O <sub>3</sub>	0.08	Moisture (max.)	0.05
P <sub>2</sub> O <sub>5</sub>	0.005	Other losses	0.31
SO <sub>3</sub>	0.02		

in Table I. The specific surface area of the two samples was measured with a Perkin-Elmer (Norwalk, CT, U.S.A.) 212D Sorptometer.

Pure nitrogen (99.99%) or synthetic air was used as carrier gas, purchased from Linde (Athens, Greece). They were dried by using a 4X molecular sieve tube. In one series of experiments the carrier gas (air) was loaded with water vapour by passing it through a saturator containing distilled water, and thermostated at 49°C. Only in the kinetic experiment at the lowest temperature studied there was a risk of condensation of water upon and between the particles. All other temperatures were higher than the saturator temperature and therefore the carrier gas was loaded with water vapour at a partial pressure much below the saturation value.

Before kinetic experiments were carried out, each marble sample (5.897 g of 22–44 mesh, and 5.551 g of 120–150 mesh) was conditioned *in situ* by heating it at 200°C for 48 h, under continuous carrier-gas flow at a flow-rate of 0.283 cm<sup>3</sup>/s. The same flow-rate was also used in all kinetic experiments.

After conditioning, the oven was brought to the appropriate working temperature and kept there overnight before the actual experiments were carried out. The detector temperature was always 175°C, and the flow-rate of the detector gases (hydrogen and air) was 1 cm<sup>3</sup>/s. The pressure inside the cell was 1.04–1.05 atm.

In all experiments, a uniform initial SO<sub>2</sub> concentration in a column of length  $L$  was used, by injecting into it 10 cm<sup>3</sup> of a gas mixture, consisting of SO<sub>2</sub> and carrier gas (1:60 to 1:6, v/v).

At each temperature, kinetic experiments were also conducted with an empty diffusion column of length  $L$ , to find the FPD response factor  $m$ , as described in the Theoretical section. It is noteworthy that this factor may change with the conditions of the experiment and must be determined frequently.

## RESULTS AND DISCUSSION

An example of plotting the experimental data as  $\ln h$  vs.  $t_0$  is given in Fig. 3. It is seen that both kinds of plot with empty and filled diffusion column are linear to a good approximation, differing only in their slopes, in accordance with eqns. 17 and 24. This was observed with both marble samples, at all temperatures, and with either dry or wet carrier gas.

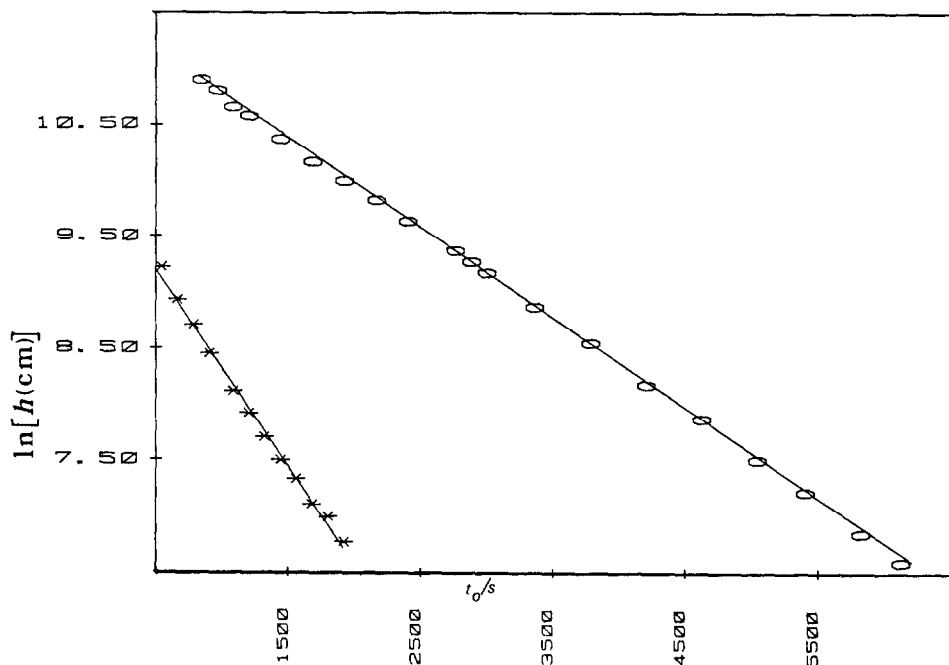


Fig. 3. Plot of sample peak height vs.  $t_0$  on a semi-logarithmic scale. The points  $\circ$  correspond to an empty diffusion column ( $L = 32.5$  cm) and the points  $*$  correspond to the diffusion column filled with 5.15 g of 22-44-mesh marble chips.

The response factor,  $m$ , determined at all working temperatures by means of eqn. 17, is given in Table II. The values found agree with those given in the literature<sup>24</sup> and, because they do not change much with the column temperature, their mean value can be used in the analysis of the experimental results obtained when the diffusion column of length  $L$  is filled with a solid. However, in this work the value determined at the appropriate temperature was used in each instance.

TABLE II

RESPONSE FACTOR,  $m$ , OF THE FLAME PHOTOMETRIC DETECTOR FOR  $\text{SO}_2$  AT VARIOUS COLUMN TEMPERATURES ( $T$ ) AND A DETECTOR TEMPERATURE OF 448.2 K

$T$ (K)	$m$
296.2	1.96
322.2	2.00
333.2	1.90
353.2	1.94
373.2	1.89
393.2	1.89
413.2	1.86
423.2	1.95
Mean	1.92

TABLE III

VALUES OF THE KINETIC PARAMETER  $\pi^2 D/4L^2 + k_1$  IN EQN. 23 AND THE RATE CONSTANT  $k_1$  IN EQN. 10 FOR MARBLE PARTICLES OF 22-44 MESH AND SURFACE AREA 0.68 m<sup>2</sup>/g

$T$ (K)	$10^4 (\pi^2 D/4L^2 + k_1) (s^{-1})$		$10^4 k_1 (s^{-1})$ (wet air)
	Dry air	Wet air	
322.2	3.44	12.50	9.19
353.2	3.80	7.29	3.43
373.2	3.26	4.18	—
393.2	3.18	4.23	—
423.2	4.32	7.00	1.74

From the results obtained with the column filled with CaCO<sub>3</sub>, it seems that the slopes of the plots of  $\ln h$  vs.  $t_0$  decrease initially as the number of SO<sub>2</sub> injections increases. This is reasonable because, as the total amount of SO<sub>2</sub> that passes over CaCO<sub>3</sub> increases, various active centres of the surface are saturated and the rate of mass transfer to the solid decreases. After a certain number of SO<sub>2</sub> injections, the interaction with CaCO<sub>3</sub> is stabilized and the slope of the plots remains unchanged. Dividing each slope by the appropriate  $m$  value in Table II, one finds the value of  $\pi^2 D/4L^2 + k_1$  (cf., eqn. 24). Tables III and IV give such values for the two marble species, obtained with dry and wet air as carrier gas. Each of these values represents the mean of at least three kinetic experiments, conducted under identical conditions. The  $k_1$  values in eqn. 10, given in Tables III and IV, were found by using the calculated values of  $\pi^2 D/4L^2$  in Table V.

From the experimental finding that all plots of  $\ln h$  vs.  $t_0$  are linear, we can conclude that the rate of the action of SO<sub>2</sub> on CaCO<sub>3</sub>, under the conditions used, conforms to the limiting cases described by eqns. 16 and 23. Comparing the values of the diffusion parameter  $\pi^2 D/4L^2$  in Table V with the values of the kinetic parameter  $\pi^2 D/4L^2 + k_1$  in Table III, it is seen that there is no significant difference between the two parameters at the same temperature when dry air is used as the carrier gas. This means that the rate constant  $k_1$  is very small, owing to the small values of one

TABLE IV

VALUES OF THE KINETIC PARAMETER  $\pi^2 D/4L^2 + k_1$  IN EQN. 23 AND THE RATE CONSTANT  $k_1$  IN EQN. 10 FOR MARBLE PARTICLES OF 120-150 MESH AND SURFACE AREA 1.15 m<sup>2</sup>/g

$T$ (K)	$10^4 (\pi^2 D/4L^2 + k_1) (s^{-1})$		$10^4 k_1 (s^{-1})$	
	Dry air	Wet air	Dry air	Wet air
322.2	7.61	13.78	4.30	10.47
353.2	8.02	10.23	4.16	6.37
373.2	9.96	15.77	5.70	11.51
393.2	3.13	4.53	—	—
423.2	5.59	8.85	—	3.59

TABLE V

VALUES OF THE DIFFUSION PARAMETER  $\pi^2 D/4L^2$  IN EQNS. 16 AND 23

$T$ (K)	$D_{calc.}$ ( $cm^2/s$ )	$p$ (atm)	$10^4 \pi^2 D/4L^2$ ( $s^{-1}$ )
322.2	0.147	1.038	3.31
353.2	0.172	1.040	3.86
373.2	0.190	1.043	4.26
393.2	0.209	1.046	4.67
423.2	0.236	1.049	5.26

or more of the factors on the right-hand side of eqn. 10. However, when the carrier gas (air) is saturated with water vapour, there is a significant difference between the kinetic and the diffusion parameters, but only at temperatures below 100°C. At these temperatures there is a non-zero rate of action of SO<sub>2</sub> on CaCO<sub>3</sub> and eqn. 23 is obeyed, meaning that mass transfer from the surface to the bulk of the solid phase or *vice versa* is very slow ( $k_{-1} \approx 0$ ). Obviously, the difference observed with wet air is due to water condensing or being adsorbed on the solid surface. At temperatures near 100°C, most of this water is removed from the surface of the solid, and the effect of its presence diminishes. Therefore, an increase in temperature cannot bring about an increase in the rate of transfer of SO<sub>2</sub> on to the solid surface.

With eqn. 10 as a guide, one can increase  $k_1$  at the same temperature by increasing the specific surface area,  $S$ , using a smaller particle size. This may also increase  $m_s$  and decrease  $a_z$ , both increasing the value of  $k_1$ . The results in Table IV confirm this prediction, at least qualitatively, at four of the five temperatures tested. At the higher temperatures there is another factor diminishing the rate of SO<sub>2</sub> action, namely the partition coefficient  $K$ , which is expected to decrease with increasing temperature, thus causing a decrease in  $k_1$ .

In conclusion, at relatively high temperatures and with dry air, the rate of action of SO<sub>2</sub> on CaCO<sub>3</sub> having a low specific surface area is negligible. At lower temperatures, increasing the water content of the air and the specific surface area of the solid increase the rate of action, its rate-determining step being the mass transfer from the gas phase to the surface of the solid. The rate of mass transfer from the surface to the bulk of the solid phase (or *vice versa*), including uptake of SO<sub>2</sub> by pores within the marble particles, and the rate of the chemical reaction between SO<sub>2</sub> and CaCO<sub>3</sub> are very slow.

Other experiments, with the diffusion column partly filled with solid, are well under way to elucidate further details of the mechanism of action.

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