CONTRIBUTION TO THE STUDY
OF THE REACTION BETWEEN SOLID SODIUM CARBONATE
# AND GASEOUS SULPHUR DIOXIDE

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The heterogeneous reaction between solid sodium carbonate and gaseous sulphur dioxide of partial pressures from 1·2 to 7·5 kPa has been investigated in a fixed-bed reactor at temperatures of 54 and 81°C in the presence of water vapour of partial pressures from 0·30 to 1·25 kPa. An independence of the reaction course of the sulphur dioxide content in the gas phase and a linear dependence of the reaction rate on the partial pressure of water vapour were found under the above conditions. The rate equation derived previously has been simplified and the set of differential equations describing the reaction in a fixed bed has been solved. The relations obtained have been applied to an evaluation of the effective rate constant. The true rate constant has been estimated to be independent of temperature.

The previous study of the reaction between solid sodium carbonate and gaseous sulphur dioxide has shown that anhydrous sodium carbonate exists in two forms differing one from another by orders of magnitude from the kinetic point of view[1,2]. It has been found in a study carried out in the temperature range of 120−160°C under conditions, when the partial pressure of sulphur dioxide was lower than 0·4 kPa and the partial pressure of water vapour was in the range from 0·6 to 2·0 kPa, that the active form of sodium carbonate reacts with sulphur dioxide with an exceptionally high rate. At contact times of the gas phase with the solid in hunderths of seconds, a removal of sulphur dioxide from the gas by more than 99% has been attained. At the same time, the degree of conversion of the solid carbonate to sulphite exceeded 95% after some tens of minutes. The inactive form reacted under the same conditions very slowly and incompletely with a degree of conversion to sulphite of about 5%. With respect to a potential application of the studied reaction for removing sulphur dioxide from waste gases[3], the previous study has been carried out at temperatures and compositions of the gas phase approaching real conditions[4]. At the same time, the main parameter investigated has been the degree of purification of the gas phase. The object of the present paper is an extension of the temperature range in the direction to lower values, and that of the sulphur dioxide concentrations to values higher by an order of magnitude. With respect to the previous finding[1], enabling to attain high degrees of the solid conversion, the feasibility of preparing sodium sulphite in a heterogeneous reaction by a dry process has been investigated.
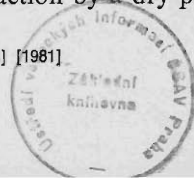
THEORETICAL

Fundamental relations

The rate of the heterogeneous reaction of

$$Na_2CO_3(s) + SO_2(g) = Na_2SO_3(s) + CO_2(g) \qquad (A)$$
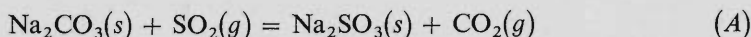
has been defined as

$$r = \partial x / \partial \tau . \qquad (1)$$

For a differential section of the bed[5] containing dn_s moles of the solid, it follows from the material balance assuming piston flow

$$-F \, \partial y / \partial n_s = \partial x / \partial \tau . \qquad (2)$$

Equation (2) has been simplified by neglecting the accumulation of sulphur dioxide in the free space of the bed. The relations (1) and (2) represent a set of equations, which may be written in the form

$$\partial x / \partial \tau = r , \qquad (3a)$$

$$-F \, \partial y / \partial n_s = r . \qquad (3b)$$

The kinetics of reaction (A) may be described by the rate equation[6]

$$r = \frac{k_t p_{H_2O} p_{SO_2}}{(1 + K_{SO_2} p_{SO_2})(1 + K_{H_2O} p_{H_2O})} x^{1/2}(1 - x)^{3/2} , \qquad (4)$$

where the reaction rate is a function of partial pressures of sulphur dioxide, p_{SO_2}, and of water vapour, p_{HO_2}, of equilibrium adsorption constants of sulphur dioxide K_{SO_2} and of water vapour K_{H_2O}, and of the degree of conversion, x. The form of the rate equation has been derived in agreement with the classic Langmuir's idea of adsorption. Assuming that $K_{H_2O} p_{H_2O} \ll 1$ and $K_{SO_2} p_{SO_2} \gg 1$, which has been found experimentally in the present paper, it is possible to simplify equation (4) into the form

$$r = k_{ef,t} p_{H_2O} x^{1/2}(1 - x)^{3/2} , \qquad (5)$$

where

$$k_{ef,t} = k_t / K_{SO_2} . \qquad (6)$$

In this case, the set (3) is of the form

$$\partial x / \partial \tau = k_t p_{H_2O} x^{1/2} (1 - x)^{3/2} , \tag{7a}$$

$$-F \, \partial y / \partial n_s = k_t p_{H_2O} x^{1/2} (1 - x)^{3/2} . \tag{7b}$$

The solution has been carried out for usual boundary conditions, namely that the initial state of the fixed bed is everywhere the same $(x_0 = 0)$, and the composition of the feed is constant

$$x(n_s; 0) = 0 , \tag{8a}$$

$$y(0; \tau) = y_0 . \tag{8b}$$

The solution of the set of equations (7) with boundary conditions (8) represents a complete, quantitative description of the reactor under given conditions.

Solution

Equation $(7a)$ has been integrated after separation of variables, and the following relation has been obtained

$$k_{ef,t} p_{H_2O} \tau = 2 \left(\frac{x}{1 - x} \right)^{1/2} + \varphi(n_s) . \tag{9}$$

The integration constant φ is generally a function of n_s. On substituting the boundary condition $(8a)$ into equation (9), the following relation is obtained

$$\varphi(n_s) = 0 . \tag{10}$$

The independence of the degree of conversion x of the position of the studied differential section in the bed leads to the conclusion, that in the range of validity of the rate equation (5), the reactor has differential features despite of the decrease of the reacting gas concentration during its passage through the bed. On substituting the value (10) into relation (9) and on rearrangeing, a dependence of the degree of conversion x on the time is obtained

$$x = \left[\left(\frac{2}{k_{ef,t} p_{H_2O} \tau} \right)^2 + 1 \right]^{-1} . \tag{11}$$

The limiting value of this relation $x(n_s, \infty) = 1$ is in agreement with the notion of the course of reaction (A).

Since the degree of conversion is independent of the position in the bed, it has been possible to integrate directly even equation $(7b)$, with the following relation being obtained

$$y_r = -\frac{k_{ef,t}p_{H_2O}}{F} x^{1/2}(1-x)^{3/2} n_s + \psi(\tau) . \tag{12}$$

The integration constant ψ is generally a function of τ. On substituting the boundary conditions $(8b)$ into equation (12), the following relation is obtained

$$\psi(\tau) = y_0 . \tag{13}$$

On substituting this value into relation (12), a dependence of the mole fraction of the sulphur dioxide y on the position in the bed and on the degree of conversion of the solid is obtained

$$y_r = y_0 - \frac{k_{ef,t}p_{H_2O}n_s}{F} x^{1/2}(1-x)^{3/2} . \tag{14}$$

Equations (11) and (14) represent a complete description of reaction (A) in a fixed bed.

EXPERIMENTAL

The measurements have been carried out on a flow apparatus in a reactor with a fixed layer of the solid amounting to 10^1 mg by the order of magnitude. The isobaric–isothermal conditions have been ensured by means of a small pressure drop along the bed, of an efficient thermostatic control of the reactor, and by means of sufficient gas rate. Twenty measurements have been evaluated at temperatures of 54 and 81°C with nitrogen as a carrier gas at partial pressures of sulphur dioxide from 1·2 to 7·5 kPa and of water vapour from 0·3 to 1·3 kPa. The content of sulphur dioxide in the gas phase has been determined after absorption in a hydrogen peroxide solution, as sulphuric acid by an electric conductivity method, as described previously.

Reagents. The precipitated $NaHCO_3$ was the parent substance for the preparation of the sodium carbonate. It has been prepared by a procedure described previously[1]. A uniform particle size of 0·25—0·33 mm has been used in all the experiments. The sample contained 99·4 or 99·7% by weight of $NaHCO_3$ and 0·6 or 0·3% by weight of Na_2CO_3. The anhydrous sodium carbonate used in the measurements has been prepared by thermal decomposition of $NaHCO_3$ *in situ* in a stream of nitrogen. Sulphur dioxide and nitrogen for lamps have been taken from pressure tanks. The remaining reagents were of the A.G. purity.

The apparatus contained three gas lines — that of the dry nitrogen, of the sulphur dioxide, and that of the humid nitrogen, which enabled to adjust the composition of the gas phase for the kinetic measurements, and which yielded the dry nitrogen for the decomposition of $NaHCO_3$. The gaseous mixture of SO_2 and N_2 for the sulphur dioxide line has been prepared by mixing these components into a low-pressure container. Before entering the reactor,

the gas mixture was divided into two branches. By the first of them, the gas was led to the reactor and ball absorbers, by the second one, it was led to a circulation absorber. The ball absorbers were switched over in selected time intervals of 1·5 min or 5 min, and the amount of sulphur dioxide passed through the bed was determined by subsequent analysis. The analysis of the circulation absorber served for the calculation of the sulphur dioxide concentration in the feed.

RESULTS AND DISCUSSION

The degree of the solid conversion has been determined by analysis of the gas phase from difference between the amount of sulphur dioxide entering the bed and the amount passed through. The analysis of the gas phase was carried out in selected time intervals. In evaluating the experimental data, the degree of the solid conversion, the mole fraction of the sulphur dioxide in the gas phase, and the reaction rate have been replaced by a mean degree of conversion, a mean mole fraction of SO_2, and by a mean reaction rate. The latter values are accessible for individual time intervals by experiment.

The effect of the sulphur dioxide content in the gas phase on the reaction rate is illustrated in Fig. 1 to 3. It has been found, that for partial pressures of sulphur dioxide higher than 1·3 kPa the reaction rate is independent of the SO_2 concentration in the gas phase.
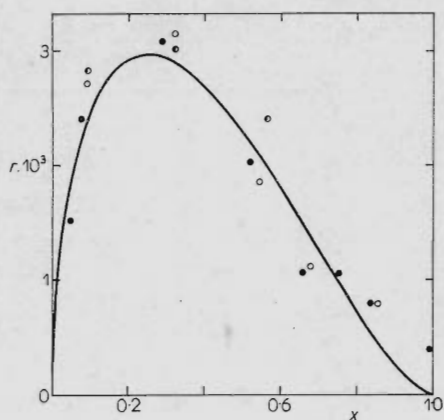

FIG. 1

Dependence of reaction rate r (s^{-1}) on the degree of conversion x. $p_{H_2O} = 1·16$ kPa; $t = 54°C$; ○ $p_{SO_2} = 1·23$ kPa; ● $p_{SO_2} = 1·30$ kPa; ◑ $p_{SO_2} = 3·54$ kPa; the curve has been plotted according to relation (5)
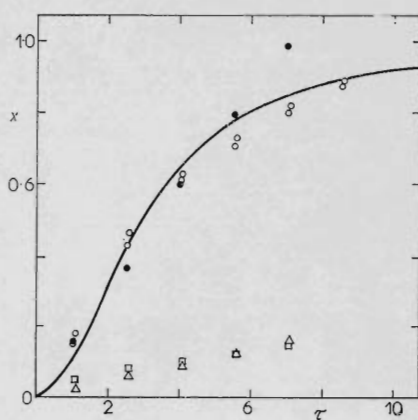

FIG. 2

Dependence of the degree of conversion x on reaction time (min). $p_{SO_2} \sim 1·2—3·5$ kPa; $t = 54°C$; ○ ● ◑ $p_{H_2O} = 1·16$ kPa; △ □ $p_{H_2O} = 0$; the curve has been plotted according to relation (11)

In the range of partial pressures of sulphur dioxide from 1 to 7 kPa, the presence of water vapour exerts a significant effect on the reaction course acting as a gaseous catalyst (Fig. 2), and being in agreement with the finding obtained in previous experiments with concentrations of the sulphur dioxide lower by an order of magnitude and at temperatures which were approximately 100°C higher[4]. In the range of partial pressures of water vapour up to 1·2 kPa, the reaction rate is approximately directly proportional to the content of water vapour, as is evident from Fig. 3. The same type of dependence has been found with experiments carried out at a temperature of 81°C as well. From Fig. 1 and 3, the character of the dependence of the reaction rate on the degree of the solid conversion is evident as $r \sim x^{1/2}(1 - x)^{3/2}$ with a maximum of the reaction rate at $x = 0.25$. The dependence is the same as found in the study of this reaction in a differential reactor at temperatures 100°C higher and at concentrations of the sulphur dioxide lower by an order of magnitude[3].

TABLE I

Dependence of effective k_{ef} and true rate constant k (s^{-1} kPa^{-1}) on temperature

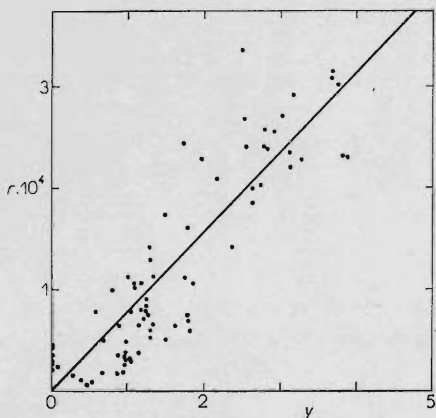| Relation	$k_{ef,54}$	$k_{ef,81}$	$\dfrac{k_{ef,54}}{k_{ef,81}}$	$\dfrac{k_{54}}{k_{81}}$ (estimated)
(5)	$7.88 \cdot 10^{-3}$	$15.19 \cdot 10^{-3}$	0·519	1·02
(11)	$9.75 \cdot 10^{-3}$	$16.92 \cdot 10^{-3}$	0·576	1·14
(14)	$8.38 \cdot 10^{-3}$	$20.42 \cdot 10^{-3}$	0·410	0·809

FIG. 3

Dependence of the reaction rate r (s^{-1}), according to kinetic equation (5). $t = 54°C$; $p_{SO_2} \sim 1.2-7.5$ kPa; $p_{H_2O} \sim 0-1.25$ kPa, the direct proportionality has been fitted by means of the method of least squares. $r \sim p_{H_2O} x^{1/2}(1 - x)^{3/2}$

On the basis of these notions, it was possible to simplify the rate equation (4) into the form (5), representing the starting relation for a mathematical description of the reactor.

The differential equations (5) and integral relations (11) and (14) have been used for an evaluation of the effective rate constant at temperatures of 54 and 81°C. The ratio of true rate constants has been estimated. The ratio of the equilibrium adsorption constants, which was necessary for this purpose, has been calculated according to the van't Hoff equation, in which the heat of adsorption of sulphur dioxide on sodium carbonate has been approximated by the heat of condensation. The results are summarized in Table I.

It has been shown, that the data obtained at degree of conversion higher than 0·9 cannot be interpreted by the relations mentioned above; under these conditions, a consecutive reaction of the sulphite with sulphur dioxide evidently begins to take place under formation of disulphite. In addition, the integral relations could not be used for the evaluation of data obtained in experiments with a dry gas phase, since even under these conditions, a partial reaction of the solid takes place during a longer time interval (Fig. 3), what is at variance with the assumptions under which the relation were derived.

An approximate calculation has shown a practical independence of the true rate constant in equation (5) of temperature. This fact could be explained in terms of the classical theory of reaction rates by a very low energy of activation of reaction (A).

The results of our study of the heterogeneous reaction between active sodium carbonate and gaseous sulphur dioxide may be summarized into the following conclusions. The reaction rate is independent of the content of sulphur dioxide in the gas phase in the investigated range of partial pressures. The presence of water vapour is necessary for the reaction course, and in the range up to 1·3 kPa, the reaction rate is directly proportional to the partial pressure of the water vapour. The character of dependence of the reaction rate on the degree of the solid conversion is the same as found in a previous study with concentrations of sulphur dioxide lower by one order of magnitude, and at temperatures 100°C higher. On increasing the reaction temperature by 30°C the effective rate constant increases approximately to a twofold. The true rate constant does not practically change with temperature.

LIST OF SYMBOLS

F	total feed rate
k_t	true rate constant at temperature t
$k_{ef,t}$	effective rate constant at temperature t
K_{SO_2}	adsorption constant of sulphur dioxide
K_{H_2O}	adsorption constant of water vapour
n_s	amount of reacting solid in bed
p_{SO_2}	partial pressure of sulphur dioxide

p_{H_2O} partial pressure of water vapour
r reaction rate
x degree of conversion of sodium carbonate
x_0 initial degree of solid conversion
y mole fraction of sulphur dioxide
y_0 mole fraction of sulphur dioxide at reactor inlet
y_r mole fraction of sulphur dioxide at reactor outlet
τ time
φ, ψ integration constants in equations (9) and (12)

Translated by the author (E. E.).

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