KINETICS OF THE OXIDATION OF THE SOLID SODIUM SULPHITE BY OXYGEN

J.MAREČEK, † J.BAREŠ and E.ERDÖS

The Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2

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A method has been elaborated for a continuous measurement of the rate of oxidation of solids by gaseous oxygen in a differential fixed-bed reactor. The kinetics of the oxidation of the solid sodium sulphite has been measured in the temperature range from 260 to 315°C, using humid air as an oxidant. The solid was prepared by reaction of gaseous sulphur dioxide with an active sodium carbonate. The reaction course can be expressed by a kinetic equation $x = 1 - \exp z$. $[-(k\tau)^n]$, where x and τ denote the degree of oxidation of the solid and time, resp.; the temperature dependence of the constant k is given by the relation

$$k = (2.71 \pm 0.06) \cdot 10^4 \exp \left[(-11154 \pm 463)/T \right]$$

In a previous study¹ of the kinetics of the reaction between the sulphur dioxide and the solid sodium carbonate, an unfavourable effect of the presence of oxygen in the gas phase on the reaction course at temperatures exceeding 160° C has been observed. An opinion has been put forward that the retarding process causing both a lowering of the reaction rate and an incomplete solid conversion stems from a simultaneous formation of the sodium sulphate interfering in the growth of the phase boundary between the sodium carbonate and the sodium sulphite.

In the present paper, a study of the kinetics of oxidation of the solid sodium sulphite, prepared from an active sodium carbonate in a reaction with the gaseous sulphur dioxide, is set forth. An experimental method based on the application of the oxygen analyzer with a very short response time² has been used. This technique permits a continuous measurement of the dependence of the reaction rate on time, and by digitalisation and further numerical integration, the corresponding composition of the solid can be computed.

THEORETICAL

Let us consider the reaction

$$\operatorname{Na_2SO_3}(s) + 1/2 \operatorname{O_2}(g) \rightarrow \operatorname{Na_2SO_4}(s), \qquad (A)$$

which takes place in a flow system in which a fixed bed is formed by n_s moles of the sodium sulphite, and through which a gas passes with the total feed rate F_0 . The mole fraction of oxygen in the gas feed is y_0 .

Let us define the reaction rate r in terms of the conversion degree of the solid by means of the following equation

$$r \equiv dx/d\tau = -d(n_{\text{Na}_2\text{SO}_3}/n_s)/d\tau .$$
⁽¹⁾

From the stoichiometry of the reaction (A), a relation follows for the oxygen balance in both phases:

$$2 dn_{0} = n_{s} dx. (2)$$

Simultaneously, the following relation is valid for the gas phase:

$$\mathrm{d}n_{\mathrm{O}_2}/\mathrm{d}\tau = \mathrm{d}(Fy)\,.\tag{3}$$

Therefrom, the amount of oxygen, which has been reacted in the time τ , is obtained

$$(1/2)n_{s}x_{\tau} = \int_{0}^{\tau}F_{0}y_{0} d\tau - \int_{0}^{\tau}Fy d\tau .$$
(4)

The time-dependent quantity of flow rate behind the bed, F, may be evaluated from the balance of inert gas components

$$F_0(1 - y_0) = F(1 - y)$$
(5)

and therefrom, on rearrangement and substitution into the equation (4), a relation is obtained for the time dependence of the degree of conversion x under steady state condition $(dF_0/d\tau = 0)$ and for a constant feed composition:

$$x = \frac{2F_0}{n_s} \int_0^\tau \frac{y_0 - y}{(1 - y_0) + (y_0 - y)} \, \mathrm{d}\tau \,. \tag{6}$$

According to the equation (1), the following relation is valid for the reaction rate

$$r = (2F_0/n_s) \cdot (y_0 - y)/[(1 - y_0) + (y_0 - y)].$$
⁽⁷⁾

Consequently, in the case of measurements in a differential flow reactor, the reaction rate is a simple function of the continuously recorded quantity $(y_0 - y)$. In a differential reactor the value of the $(y_0 - y)$ is much smaller than the $(1 - y_0)$ term,

and, practically, the reaction rate is directly proportional to the difference of $(y_0 - y)$; the record of the quantity y in time gives then an instantaneous idea of the nature of the dependence of the reaction rate on time.

EXPERIMENTAL

Chemicals

The sodium sulphite has been prepared *in situ* in the reactor. The accurately weighed sodium hydrogencarbonate of known sodium content has been decomposed in a stream of purified air at a temperature of 150 to 200°C. The active sodium carbonate¹ formed has reacted with the sulphur dioxide (approx. 1% of SO₂ in the nitrogen) at 120 to 140°C. The sulphite sample prepared in this way has not contained any detectable amount of the sulphate and the content of carbonate amounted to 1.5-2 mol%. The exact content of the carbonate has always been determined at the end of the oxidation and it has served for the calculation of the quantity n_s .

The samples of various particle sizes have been prepared. The greater part of measurements has been carried out with the sample of the particle size up to 0.1 mm; the other samples have been of sizes 0.2-0.33 mm, 0.33-0.5 mm, and greater than 0.5 mm. Particles greater than 0.2 mm have been prepared from either monocrystals or fragments of sodium hydrogencarbonate monocrystals.

The sodium hydrogencarbonate has been prepared in the way described previously³. Larger monocrystals have been prepared by a slow crystallization in a stream of the carbon dioxide.

The gases have been taken from the pressure tanks. The air has been purified by means of the ascarite and saturated with water vapour in a saturation vessel kept at a constant temperature. The nitrogen has been freed from oxygen in a reaction with hydrogen on a copper-alumina catalyst; the content of oxygen in the purified gas has been of the order of p.p.m. units.

Analytical Methods

The solids, most frequently the samples after oxidation, have been analyzed as to the content of the sulphite, carbonate and sodium. The determination of the sulphite has been carried out by means of the iodometric titration and the determination of the carbonate has been carried out by the alkalimetric titration⁴. The sodium has been determined by alkalimetric titration. In an aliquot part of the neutral solution of the sodium sulphate, formed by the oxidation of the sulphite and by the titration of the carbonate by the sulphuric acid⁴, an ion exchange to the hydroxide has been carried out in a column of a strongly basic anion exchanger (Ionenaustauscher III, Merck). The total useful capacity of the column amounted to $8\cdot3 \cdot 10^{-3}$ mol of sodium ions; the column has been regenerated with a IM-NaOH solution and washed out with the decarbonized water. The error of all the determinations did not exceed $0\cdot1\%$.

To determine the oxygen in gases, a laboratory version of the electrochemical oxygen analyzer² with a linear dependence of the response on the partial pressure of oxygen has been used. The electric signal corresponding to the feed composition (the quantity y_0) has been recorded with a sensitivity of 50 mm to 1% of oxygen in the gas. This sensitivity made it possible to record differential changes in the gas composition during the reaction course ($y_0/y < 1.05$), and, consequently, to determine the reaction rate with an accuracy better than five relative percents. In long-run experiments, the limiting factor of the accuracy consisted in the stability of the analyzer and of the recorder (EZ 2).

Apparatus

The flow apparatus (Fig. 1) has rendered the preparation of the sample, the heating of the reactor up to the temperature of measurement in the purified nitrogen, and the calibration of the analyzer by the gas of feed composition up to the instant of measurement possible. The flow rate of the gas has been stabilized by means of membrane manostats and roughly adjusted in accordance with the capillary flow meters. The accurate volume of the gas which has passed through the reactor has been measured by means of two changed-over eudiometers⁵. The value of the feed rate, F_0 , has been determined from the time of filling the eudiometer, measured by means of a stop watch, from the amount of the gas passed through the reactor, and from the amount of oxygen retained by the bed. The amount of the reacted oxygen has been determined both from the analysis of the solid and from the changes of the gas composition. In the latter case, an iteration procedure has been used in computations, where the amount of the gas passed through the bed in the time of eudiometer filling has been used as the value of the feed rate as the first approximation. The selected accuracy of the calculation for determination of the F_0 amounted to 0.5. 10^{-6} mol/s.

The stability of the flow rate on changing-over the eudiometers has been better than 0.5% and the accuracy of the flow rate measurement was of the order of 0.1%.

The reactor (Fig. 2) has been designed for the amount of the solid up to 1 g and for the gas space velocities in the range of $10^2 - 10^4$ h⁻¹. These values resulted from the necessity of analysing the solid reaction product and of securing differential changes of the gas composition at feed rates of the order of 10^{-5} mol of the gas per second. The preparation of the active sodium carbonate¹ has been carried out at space velocities of the order of 10^4 h⁻¹. With respect to the wide range of flow rates, the reactor has been designed with emphasis on a small pressure drop which amounted approximately one Torr under the conditions of measurements. All the reactor has been made of glass.

Into a layer of the solid **a** of the maximum height of 8 mm resting on a sintered glass **b**, the feed has been conducted from above from a preheated space, where the contact time of the gas has been prolonged by means of the helix **e**. The temperature of the bed has been measured in the space **d** by means of a sensor (thermometer, thermocouple). The zone of constant temperature $(\pm 0.2^{\circ})$ in the steady state was of the height of 25 mm above the sintered glass **b**. The reactor has been heated by means of the resistance heating **g** (160 Ω) the surface temperature of which has been measured by means of the sensor **c**. The following sensors have been used: either a contact thermometer which has been switching one third of the input necessary for a steady state, or a platinum resistance thermometer which served as a sensing element for the thyristor controller **PTT-3500** (Institute of Physics, ČSAV) with a continuous control of the supply voltage in the range from 0 to 120 V. The long-rung precision of the temperature control amounted to $\pm 0.5^{\circ}$

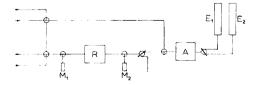


FIG. 1 Block Diagram of Measuring Section of Apparatus A Analyzer, E₁, E₂ eudiometers, M₁, M₂ manometers. in the first case, and it was better than 0.1° in the second case. The reactor has been sealed by a flat ground joint f and situated in an isolated evacuated glass jacket. The heat losses of the system in the steady state amounted approx. to 10 W at a temperature of 300°C. The volume of the reactor was 63 ml at the room temperature.

The flow characteristics of the reactor were determined by the measurement of the residence time distribution in the reactor by means of the method of a short oxygen pulse injected into a nitrogen stream and of the continuous measurement of the outlet oxygen concentration in the gas. In this way, the frequency function of the residence times $E(\Theta)$ has been determined, where Θ is the dimensionless time defined as a multiple of the mean residence time⁶. The maximum of the function $E(\Theta)$ corresponded exactly to the value $\Theta = 1$. The flow approached very nearly a piston flow without dead spaces and bypassings. In the time corresponding to $\Theta = 1.5$, only 3% of the reactor content are older than the residence time. This characteristic is of importance from the point of view of the wash out of nitrogen from the reactor volume at the beginning of the reaction. In washing out the relatively large reactor volume (analogy to a nondifferential pulse), the outlet concentration curve has been unsymmetrical (inertia of the system) with a maximum at $\theta = 1$. At the value of $\theta = 2$ no nitrogen has been recorded, and this value (corresponding to $\tau_0 = 1 - 2.5$ min, where τ_0 is the time from the admission of the air into the system) has been arbitrarily taken as the time of the reaction start. The inaccuracy of the time determination amounts to 5-10 seconds in measurements lasting tens of minutes, as it has been found from the graphical extrapolation of the x vs τ dependences. The measurements have been usually terminated at a low reaction rate $(r = 10^{-5} \text{ s}^{-1})$ and, therefore, the determination of the time datum is very accurate as compared with the accuracy of the analytical determination of the corresponding degree of conversion of the solid.

The atmospheric pressure has been measured by means of the Paulin barometer (Stockholm) with an accuracy of 0.1 Torr, and the pressure above atmospheric before and behind the reactor (approx. 7 Torr) due to the pressure resistance of the analyzer, of the damping capillary and of the eudiometers has been measured by means of mercury manometers. In the experimental arrangement described above, it is possible to measure the oxidation rates of the order of 10^{-8} to 10^{-7} mol of oxygen per second.

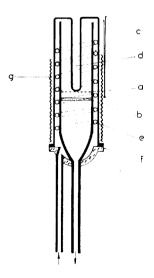


FIG. 2

Reactor

a Bed of solid, b sintered glass, c sensor of temperature control, d space for measurement of temperature, e coil in preheating space, f flat ground joint, g heating coil.

Procedure of Measurement and Treatment of Experimental Data

The reactor containing thousandths of moles of the sodium sulphite has been heated up to the reaction temperature in a stream of purified nitrogen. Prior to the measurement, the signal of the analyzer has been recorded for the pure nitrogen and, for the humid air ($p_{H_2O} = 17.535$ Torr), and in this way the record has been calibrated. Subsequent to the change-over to gas containing oxygen, the curve of the dependence of y on τ has been recorded continuously. The time, the pressure drop across the reactor bed, the atmospheric pressure, the temperature of the bed and that of the saturator have been recorded at regular intervals and at changing-over the eudiometers. At the end of the measurement the reactor section has been changed-over to the purified nitrogen and the reactor has been admitted into the analyzer at the same pressure conditions in the analytical section, and in this way the record has been recalibrated. The composition of the solid phase has been established subsequently by means of chemical analysis.

The values of $(y_0 - y)$ have been read off from the record of the $y vs \tau$ dependence at time intervals of 0.2 to 5 minutes corresponding to changes of the degree of conversion from 0.5 to 5%. This set (20-40 pairs) served as input data for a subsequent computer treatment of results. Additionally, the input data involved the values of the feed, gas composition, total pressure in the bed, amount of the sodium sulphite in the bed, degree of conversion at the end of the experiment, and the time of the start of measurement ($\Theta = 2$).

Several computer programs for treatment of experimental data have been prepared. By means of the first program (I) the following values have been computed for each selected time τ_j : the reaction rate according to the equation (7), the partial pressure of oxygen in the bed, the relative changes of the mole fraction of oxygen in the bed, and the degree of conversion.

The computation of the degree of conversion, x_j , in the time sequence τ_j $(j = 0; \tau = 0, x = 0)$ has proceeded from the analytically found value of x_j $(j = \max.)$ at the end of the measurement, and the other values have been computed according to the relation

$$x_{j-1} = x_j - \frac{2F_0}{n_s} \int_{\tau_{j-1}}^{\tau_j} \frac{y_0 - y}{(1 - y_0) + (y_0 - y)} d\tau.$$
 (8)

The integral in the relation (8) has been evaluated numerically by means of the trapezoid rule; an agreement of the order of 10^{-6} with the results according to the Simpson's rule has been attained in the values of x if the computer worked with an accuracy of 11 decimals. If a desk calculator was used, the errors due to rounding-off were accumulated in an intolerable way. The results of these computations have yielded an information of the differentialness of the reaction course and of the agreement of the mass balance of both phases the measure of which is represented by the computed value of x in the time $\tau = 0$. An average value of ± 0.026 with a standard deviation of 0.012 has been found. From an error analysis it was concluded that the main source of inaccuracies in the integration according to the relation (8) consists in an accumulation of errors in long time intervals at relatively low reaction rate, where the accuracy of determining the value of $(y_0 - y)$ from the graphical record decreased. For instance, a computation with another set of values $(y_0 - y)$ differing by the width of the recorded line y or of the base line y_0 (amplitude of fluctuations or stability of the recorder) has yielded different values of x in the time $\tau = 0$, differing sometimes even in the sign.

For that reason, another program (II) was prepared which — in addition — carried out an adjustment to physical boundary conditions ($\tau = 0$, x = 0; $\tau = \tau_{jmax}$, $x = x_{anal}$) by means of an iteration procedure with an accuracy of 5. 10^{-6} in x at $\tau = 0$. The computation has been based

1 Curve computed by means of program II

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on the proportional distribution of the error (which is considered as the value of x at $\tau = 0$ in the first calculation) and it has confronted the magnitude of the produced changes in the $(y_0 - y)$ values with the accuracy of the record. This procedure affected very little the dependence of the reaction rate on time, however, the effect on the assignment of the values of reaction rates to the values of x was significant (Fig. 3).

Measurements which have not satisfied the criteria of the differential reaction course and of the adjustment feasibility have not been considered in the subsequent treatment. The reason has been usually a lowered stability of the analytical system in the course of measurement, an unsuitable experimental regime (the ratio of F_0/n_s), or failures.

In addition to the pure sodium sulphite, the measurements with partially preoxidized substances have been carried out. First the sample has been oxidized to an estimated degree of oxidation, subsequently it has been brought to the reaction temperature in a stream of nitrogen, and the kinetics of oxidation has been measured in the usual way. In this way it has been possible to measure the reaction rate in the range of higher conversions more precisely than in the case, where the total reaction course has been measured and the values of reaction rates have changed in orders. Results of these measurements have been treated by the program of the type I, however, the value of the feed rate F_0 has been computed from the changes of the gas composition in the course of the measurement.

RESULTS AND DISCUSSION

r 10

3

FIG. 3

of Conversion x

The measurements in the atmosphere of humid air $(y_0 = 0.2052 - 0.2053 \text{ according})$ to the value of the total pressure, $p_{\rm H_2O} = 17.535$) have been carried out in the temperature range from 220 to 335°C. Results of satisfactory accuracy and meeting



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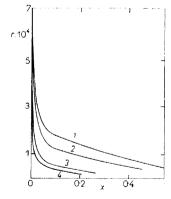


FIG. 4

Dependence of Reaction Rate on Degree of Conversion x

Temperature: 1 313.7, 2 305.4, 3 207.4, 4 260·4.

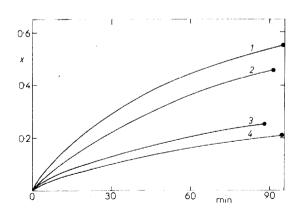


the condition of an isothermal course have been obtained in the range of $260-315^{\circ}$ C. Thirty experiments have been carried out, most of them at a temperature of 305° C.

The role of the temperature gradient inside the particles and between the particles and the gas has been tested by means of the criteria proposed by Mear⁷ and it has been found as entirely negligible. The rate of heat generation in the bed containing approximately 10^{-3} mol of the Na₂SO₃ at rates of the order of 10^{-4} s⁻¹ is about 0·1 W, *i.e.* about 1% of the heat losses of the reactor: (Heats of the reaction (A) have been computed from thermodynamical data^{8,9}: $\Delta H^0_{298,16} = -70.3$ kcal, $\Delta H^0_{600} = -71.8$ kcal). At temperatures higher than 315°C, where the initial reaction rate amounted to about 10^{-3} s⁻¹, the reaction did not take place isothermally. The increase of the bed temperature has been recorded most sensitively by a continuous record of the *y* vs τ dependence or of the derived *r* vs τ dependence. Oscillations of the reaction rate typical for an unstable reaction course have been occurring, or, at higher temperatures, an uncontrolled increase of the reaction rate limited by the feed rate of oxygen have been taking place.

The effect of the particle size of the sodium sulphite on the rate of oxidation has not been observed. The crystal habitus remained unchanged in the course of preparation of the active sodium carbonate, of formation of the sulphite, and of its oxidation.

In the Figs 4 and 5, four experimental dependences r on x and x on τ are presented in the temperature range of $260-314^{\circ}$ C. The reaction rate is a monotonously decreasing function of the degree of conversion x in contrast to the formation of the sodium sulphite^{1,3}.





Dependence of Degree of Conversion x on Time

• Values found analytically. Temperature: 1 313.7, 2 305.4, 3 270.4, 4 260.4 °C.

If it is assumed that the reaction rate (at a constant partial pressure of oxygen) may be expressed in the form

$$r = k(T) \cdot f(x) , \qquad (9)$$

the following equation is valid in combination with the Arrhenius relation

$$\left(\partial \ln r / \partial T\right)_{\mathbf{x}, \mathbf{p}_{\mathbf{O}_{\mathbf{v}}}} = E / \mathbf{R} T^2 . \tag{10}$$

It is possible to determine the activation energy of the reaction from the slope of the dependence of $\ln r vs 1/T$.

From the measured dependences of the reaction rate on the degree of conversion, the values of reaction rates at x = 0.1, 0.2, 0.3 have been obtained by interpolation. The data obtained have been treated by means of the method of least squares, and the results are given in the Table I. The values of A and B are defined by the equation

$$-\log r = A \cdot 1/T + B$$
. (11)

The values of activation energies computed from the values of the slope A are given in the Table I too. The dependence is illustrated in the Fig. 6. The average value of the activation energy is 24.17 ± 0.92 kcal/mol.

TABLE I

Temperature Dependence of Reaction Rate at Constant Values of Degree of Conversion Constants A and B of the equation (11).

x	$A \cdot 10^{-3}$	В	Correlation coefficient of equation (11)	E kcal/mol
0.1	5.015	5.001	0.983	22.95
0.5	5.580	- 5.841	0.941	25-54
0.3	5.247	- 5.005	0.994	24.01

Kinetic Equation

Attempts have been made to express the course of the reaction (A) found experimentally by means of some types of kinetic equations which are used for a description of heterogeneous reactions; a review of equations and methods of treatment see Johnson and Gallagher¹⁰. With respect to the fact that no dependence of the reaction rate on the particle size has been found in the range of almost two orders, the models

including the diffusion into the interior of particles as a rate limiting process have been excluded.

The best and uniform description of the reaction course has been obtained with the use of a two-parameter equation of the Avrami-Erofeev type

$$x = 1 - \exp\left[-(k\tau)^{n}\right]. \tag{12}$$

The linearized form of this equation

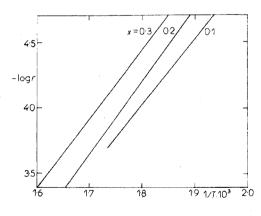
$$\xi = n \ln k + n \ln \tau , \qquad (13)$$

where ξ is a function of the conversion x defined by the relation

$$\xi = \ln\left[-\ln\left(1-x\right)\right],\tag{14}$$

has been used for the evaluation of the quantities of k and n.

A program has been prepared which evaluated the quantities of k and n in the equation (13) by the method of least squares. The dependences of ξ on ln τ correspond-



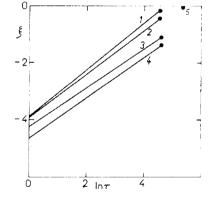


FIG. 6 ,

Temperature Dependence of Reaction Rate at Constant Degree of Conversion x

x = 0.1, E = 22.95; x = 0.2, E = 25.54;x = 0.3, E = 24.01.



Linearized Time Dependence of Degree of Conversion according to Equation (13)

Time τ is given in minutes. • Values found analytically. 1 $t = 313 \cdot 7$, n = 0.815, $k = 1.422 \cdot 10^{-4}$; 2 $t = 305 \cdot 4$, n = 0.762, $k = 9.63 \cdot 10^{-5}$; 3 $t = 270 \cdot 4$, n = 0.669, $k = 2.94 \cdot 10^{-5}$; 4 $t = 260 \cdot 4$, n = 0.709, $k = 2.373 \cdot 10^{-5}$; 5 $t = 305 \cdot 3$. Values of correlation coefficients of straight lines: 1 0.9997, 2 0.9997, 3 0.9995, 4 0.9999.

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ing to the dependences from the Fig. 4 and 5. are illustrated in the Fig. 7. All the relevant data have been treated by means of this program, and it has been found that the correlation coefficient of the equation (13) has been in 96% of cases greater than 0.99 and in 71% of cases greater than 0.999. The time dependence of the degree of conversion x (Fig. 5), has been reproduced by the computation according to the equation (12) with an accuracy better than 1%.

In addition to that, the data have been treated by a method using the experimental values of reaction rates. By differentiation of the equation (12), a relation is obtained for the dependence of r on x

$$r = k n(1 - x) \left[-\ln (1 - x) \right]^{(n-1)/n}, \qquad (15)$$

the complexity of which does not make it possible to determine the value of k and n in a simple way. From the equation (12), however, it is possible to derive simply a relation

$$r/(1-x) = nk^{n}\tau^{(n-1)}, \qquad (16)$$

which has been used in a linearized logarithmic form for the evaluation of the quantities of n and k. The results obtained by this method have been essentially in agreement with the previous ones, however, they have shown a greater dispersion. The reason consists partly in the mathematical form of the equation (16) partly in the high sensitivity of results to the accuracy of assignment of the values of the reaction rates to the values x.

By means of both methods of data treatment described above, the following results have been obtained. The values of the exponent n as evaluated from ten measurements at a temperature of 305° amounted to $n = 0.756 \pm 0.013$; the extreme limits of the values of n were 0.67 and 0.87 (Fig. 7). In the temperature range of $260-314^{\circ}$ C, the value of n may be considered as independent of temperature.

The temperature dependence of k obeys the Arrhenius relation

$$\log k = -4.8488 \cdot 10^3 / T + 4.4326 \cdot . \tag{17}$$

An effective activation energy of E = 22.2 corresponds to the equation (17) and this value is in agreement with the values obtained from the temperature dependences of reaction rates. From an analysis of data, a relation follows for the value of k

$$k = (2.71 \pm 0.06) \cdot 10^4 \exp\left[(-11154 \pm 463)/T\right].$$
 (18)

It has been found by extrapolation of the established temperature dependence and by a computation according to the equations (12) and (15) that the sample of the sodium sulphite, prepared in the described way, could be oxidized by the humid air more than 90% at temperatures of $380-410^{\circ}$ C within some tens of minutes. At temperatures lower than 200°C, practically no oxidation of the sulphite takes place.

CONCLUSIONS

The experimental technique proposed in this paper makes possible to measure the oxidation rates of solids by gaseous oxygen in the range of rates from 10^{-8} up to 10^{-7} mol of oxygen per second.

The reaction course of oxidation of the solid sodium sulphite, prepared from the active sodium carbonate, may be expressed by the kinetic equation (12) in the temperature range of $220-315^{\circ}$ C in the oxidation by humid air, and the temperature dependence of the constant k appearing in this equation may be expressed by the relation (18).

At temperatures higher than 320°C, the rate of oxidation is very high and it is not possible to ensure an isothermal reaction course in the fixed bed.

LIST OF SYMBOLS

- A quantity defined by equation (11)
- B quantity defined by equation (11)
- *E* energy of activation (kcal mol⁻¹)
- F flow rate of gas after passing bed (mol s⁻¹)
- F_0 feed rate (mol s⁻¹)
- k constant defined by equation (12)
- n exponent defined by equation (12)
- $n_{\rm s}$ number of moles of sodium sulphite in bed
- n_i number of moles of the component *i*
- p_i partial pressure of the component *i* (Torr)
- P average total pressure in bed (Torr)
- r reaction rate defined by equation (1) (s^{-1})
- **R** gas constant
- t temperature ($^{\circ}C$)
- T absolute temperature \cdot (K)
- x degree of conversion of sodium sulphite defined by equation (I)
- x_{τ} value of x in time τ
- y_0 mole fraction of oxygen in feed
- y mole fraction of oxygen in gas after passing bed
- ξ quantity defined by equation (14)
- τ time (s)
- Θ reduced time defined as multiple of mean residence time

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