KINETICS OF THE REACTION OF SOLID ANHYDROUS POTASSIUM CARBONATE WITH GASEOUS SULFUR DIOXIDE

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Results are presented of an experimental kinetic study of the heterogeneous reaction between gaseous sulfur dioxide and solid anhydrous potassium carbonate. The measurements were carried out in an all glass kinetic flow apparatus with nitrogen as the carrier gas and a fixed bed of the solid working in the differential regime at atmospheric pressure and a temperature of 423 K (150 °C). The reaction course was studied in dependence on the partial pressures of sulfur dioxide (p_{SO_2}) and water vapour (p_{H_2O}) in concentration ranges p_{SO_2} = 13 – 430 Pa and p_{H_2O} = 0 – 2 100 Pa. In the reaction, water vapour acts as a gaseous catalyst. Based on the experimental data, the corresponding kinetic equation was found together with the numerical values of the relevant rate and equilibrium adsorption constants.

The studied heterogeneous gas–solid reaction can be written in the following generalized form (Eq. (*A*)), where Me denotes any alkaline metal, potassium of course included.

$$Me_2CO_3(s) + SO_2(g) \longrightarrow Me_2SO_3(s) + CO_2(g) \qquad (A)$$

The reaction proceeds without change in the number of molecules and also the heat of reaction is not very significant[1]. An important factor, however, which affects the course of reaction (*A*) very profoundly is the way of preparation of the solid anhydrous carbonate. This was confirmed by a number of previous contributions especially in the case of sodium carbonate[1–6]. It was shown that in dependence on their way of preparation there exist two forms of sodium carbonate which differ considerably in their reactivity not only towards sulfur dioxide, but also towards other gases with acid character, e.g. hydrogen chloride[2,7]. These two forms, which were termed as active and inactive soda, show a difference in terms of rate constants for sulfur dioxide up to two and even three orders of magnitude. For instance, commercially available anhydrous sodium carbonate is towards sulfur dioxide almost inactive.

Previously[1], it was also shown that the mentioned differences in the reactivity of sodium carbonate towards sulfur dioxide may be found also in the case of carbonates of the other alkaline metals where besides sodium the greatest difference in the reactivity of both forms is shown by potassium carbonate.

A detailed description of the chemico-kinetic behaviour of reaction (*A*) was so far presented only for the active sodium carbonate prepared by thermal decomposition of sodium hydrogen carbonate, according to Eq. (*B*) (refs[6,8–13]).

$$2\ MeHCO_3 \longrightarrow Me_2CO_3(s) + CO_2(g) + H_2O(g) \qquad (B)$$

It was found that besides the preparation procedure, a further primary factor enabling a fast reaction (*A*) is the presence of water vapour in the reacting gaseous mixture. Although water does not appear in the total reaction (*A*), during the conversion of carbonate to sulfite water molecules act as a gaseous catalyst. The dependence of the rate of the reaction of solid carbonate with sulfur dioxide on the water vapour concentration shows an asymptotic behaviour. Thus, at a certain constant partial pressure of sulfur dioxide, the reaction rate does not increase from a certain point significantly on further increasing the water vapour concentration[6]. The so called saturation region is reached when for the adsorbed amount of sulfur dioxide molecules a sufficient number of water molecules are available. Furthermore the rate determining step of the whole process is the chemical reaction at the surface of the solid and the adsorption and desorption of gaseous components participating in the reaction are so rapid that they can be considered as equilibrium processes. Kinetic data obtained with a reactor working in the differential regime at 423 K (150 °C) and nitrogen as a carrier gas enabled to formulate the rate equation (*1*), where r (s^{-1}) denotes the reaction rate, x is the degree of conversion and t is the reaction time; $k_0 = 2.78 \,.\, 10^{-2}$ (s^{-1}) denotes the rate constant and $K_{SO_2} = 9.23 \,.\, 10^{-4}\ Pa^{-1}$ and $K_{H_2O} = 0.62 \,.\, 10^{-4}\ Pa^{-1}$ are equilibrium adsorption constants of sulfur dioxide and water vapour. p_{SO_2} and p_{H_2O} denote the corresponding partial pressure

$$r \equiv dx/dt = k_0 \frac{K_{SO_2}\, p_{SO_2}}{(1 + K_{SO_2}\, p_{SO_2})} \frac{K_{H_2O}\, p_{H_2O}}{(1 + K_{H_2O}\, p_{H_2O})}\, x^{1/2}\,(1-x)^{3/2} \quad . \qquad (1)$$

Later[12], kinetic measurements were performed with considerably more reactive samples of the active soda (decomposition in situ in a stream of dry nitrogen), using a reactor working in the integral regime. This experimental results have been described by a formally identical rate equation (*2*) but already adjusted for practical purposes and conditions (p_{H_2O} > 600 Pa), where $k_0' = 1.58 \,.\, 10^{-4}\ s^{-1}\ Pa^{-1}$ is valid for 423 K (150 °C) and nitrogen as the carrier gas[6,12].

$$r \equiv \mathrm{d}x/\mathrm{d}t = k_0' \, p_{\mathrm{SO}_2} \, x^{1/2} \, (1 - x)^{3/2} \qquad (2)$$

The hitherto obtained knowledge on the course of the reaction between solid anhydrous potassium carbonate prepared according to reaction (*B*) with gaseous sulfur dioxide indicates that under comparable conditions its reaction rate compared to that of the analogous sodium carbonate system is about one order of magnitude lower[1]. This fact enabled us to use a reactor working in the differential regime. The rate of the reaction of the same system where the solid anhydrous potassium carbonate is prepared by thermal dehydration of the hydrate $K_2CO_3 . 1.5\ H_2O$ (inactive potash) is under comparable conditions by two orders of magnitude lower than with the carbonate prepared by decomposition of the hydrogen carbonate ($KHCO_3$). For the unit stoichiometric loading of the bed, the achieved conversion degrees differ for the two solids (active and inactive potash) up to a factor of five (0.77 and 0.16, ref.[1]). The goal of the present work was to formulate the complete rate equation which describes the heterogeneous reaction between gaseous sulfur dioxide and solid anhydrous potassium carbonate prepared according to Eq. (*B*) by thermal decomposition. The variables followed were the partial pressures of sulfur dioxide and water vapour (p_{SO_2}, $p_{\mathrm{H}_2\mathrm{O}}$) and also the degree of conversion x of the solid carbonate.

EXPERIMENTAL

The experimental arrangement and the measurement procedure, did not differ considerably from those described previously[9,12]. The essential part was an all-glass flow apparatus working in the differential regime.

The preparation procedure of solid potassium hydrogen carbonate was described previously[1], involving precipitation of the salt from a solution of potassium carbonate by gaseous carbon dioxide. The particle size used for the measurements was in the range 0.25 – 0.33 mm; the total amount of solid hydrogen carbonate used in a single experiment was in the range of several miligrams. Its thermal decomposition took place in situ at 458 K (185 °C) in a stream of dry nitrogen. The actual kinetic measurements were performed after the temperature decreased to 423 K (150 °C), whereby nitrogen was again used as the carrier gas. The gas phase composition with respect to sulfur dioxide between the inlet and the outlet differed only by several per cent. Only just after the start of the kinetic run it sometimes amounted to about 10 per cent. The sulfur dioxide concentration in the gas phase was determined conductometrically (as sulfuric acid) after its absorbtion in a diluted hydrogen peroxide solution[14,15].

Because the preliminary kinetic experiments indicated that the reactivity of the system $K_2CO_3(s)$–$SO_2(g)$–$H_2O(g)$ is extremely sensitive towards the presence of water vapour in the partial pressure range of 0 – 400 Pa, it was necessary to use a special all-glass mixing apparatus for the continual gaseous mixture preparation which was constructed in a modified form according to refs[16,17]. Considerable attention had to be given to the precise calibration of the glass capillaries used in the apparatus which enabled the adjustment of mixing ratios of two gaseous streams in the range of 1 : 1 to 1 : 250. The mixing process proceeded continually by admixing a stream of nitrogen saturated by water vapour at 291 K (18 °C) with p_{H_2O} = 2 066 Pa into a stream of dry nitrogen containing a precalculated and preadjusted concentration of sulfur dioxide. This stream was prepared by a saturation method described previously[18], the water vapour being removed by a phosphorus pentoxide column. The equilibrium water vapour pressure in the system $P_2O_5(s)–H_2O(g)$ reaches[16] almost the value of $1.3 \cdot 10^{-3}$ Pa (dry gas). The maximum flow rates used amounted up to 500 ml/min at normal conditions.

The unreacted potassium carbonate, i.e. the residual alkalinity, was determined immediately after the end of the kinetic run by an usual titration (acidimetric) method using Phenol Red as an indicator, whereby the sulfite was previously oxidized to sulfate by hydrogen peroxide.

Altogether 66 single kinetic experiments were performed, the range of partial pressures being 13.3 – 427 Pa for sulfur dioxide and 0 – 2 070 Pa for water vapour.

RESULTS

The primary experimental data provided information on the gaseous mixture composition at the inlet and outlet of the reactor, on the volume, temperature and pressure of the total volume of gases which had passed through the bed of the solid, and further also on the composition of the solid after the kinetic run. From these data the dependence of the degree of conversion *x* of the solid on time *t* was calculated. For a series of experiments it is shown in Fig. 1.

The primary data treated in this way served further for the calculation of the reaction rate *r* as a function of the degree of conversion illustrated in Fig. 2.

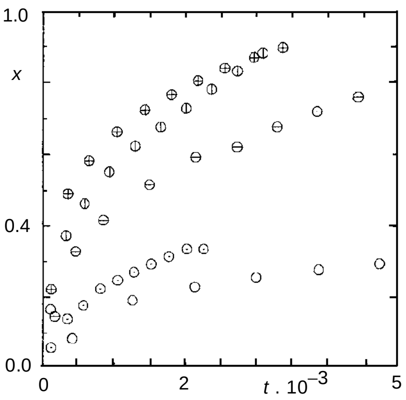

FIG. 1

Dependence of the degree of conversion *x* of the active potassium carbonate on time *t* at different partial pressures of sulfur dioxide (p_{SO_2}) and two partial pressures of water vapour (p_{H_2O}). p_{H_2O} = 0 Pa, p_{SO_2} = 430 Pa (❍); p_{H_2O} = 400 Pa and p_{SO_2} = 16 Pa (❍); 57 Pa (❍); 200 Pa (❍); 400 Pa (⊕)

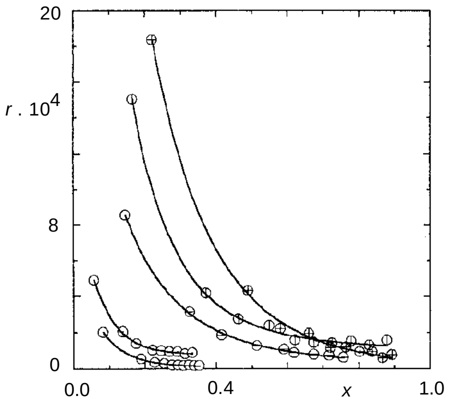

FIG. 2

Dependence of the reaction rate *r* (s^{-1}) on the degree of conversion *x* of the active potassium carbonate at different partial pressures of sulfur dioxide (p_{SO_2}) and two pressures of water vapour (p_{H_2O}). Designation of points see Fig. 1

A further important step was the verification of the possibility to transform the family of rate curves as in Fig. 2 affinely with respects to the degree of conversion x. The principle of affine transformation applied to gas–solid reactions is based on the assumption of a time independent sequence of morphological structures of the reacting and forming solid substances, including the independence on the partial pressures of the active gaseous components. In the case this assumption is valid it is possible to separate in the rate equation the relevant variables into a term dependent only on the degree of conversion x and a term dependent exclusively on the partial pressures of the gas components (in our case p_{SO_2} and p_{H_2O}). However, often as in this work, the opposite procedure is applied, i.e. in the case it is found that the rate curves obtained for various pressure levels of the active gaseous components are affinely transformable with respect to the degree of conversion x, the above mentioned separation in the rate equation is justified without a detailed investigation of the morphological structure of the solid. This approach enables to treat mathematically the influence of the degree of conversion x and of the partial pressures p_{SO_2} and p_{H_2O} on the reaction rate separately. (A detailed procedure of the application of the affine transformation principles to gas–solid reactions can be found in ref.[19].)

The results of the affine transformation are shown in Fig. 3 which illustrates the dependence of the transformed reaction rates from Fig. 2 on the degree of conversion x for the constant water vapour pressure p_{H_2O} = 400 Pa and different partial pressures of sulfur dioxide p_{SO_2}. The rate curves from Fig. 2 were affinely transformed with respect to the conversion x to a common level of the partial pressure of sulfur dioxide p_{SO_2} = 401 Pa. It is evident that after multiplying the individual rate values by a corresponding average factor Φf the individual curves yield a single wholly satisfying smooth curve. Thus, the rate equation can be mathematically expressed by Eq. (*3*), where $f(p_{SO_2}, p_{H_2O})$

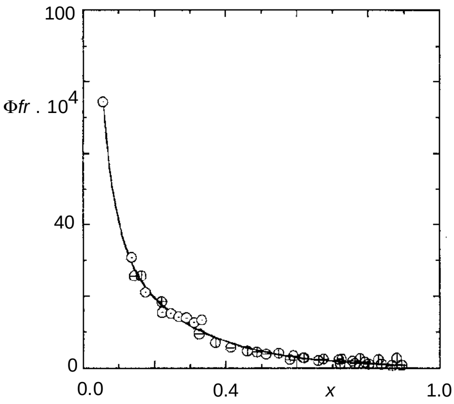

FIG. 3
Dependence of the affinely transformed experimental values of the reaction rate r Φf (s^{-1}) on the degree of conversion x of the active potassium carbonate. The transformation was performed by a multiplying average factor Φf with respect to p_{SO_2} = 400 Pa at p_{H_2O} = 400 Pa. ❍ p_{SO_2} = 16 Pa, Φf = 15.1; ❍ p_{SO_2} = 57 Pa, Φf = 3.0; ❍ p_{SO_2} = 200 Pa, Φf = 1.7; ⊕ p_{SO_2} = 400 Pa, Φf = 1

denotes the term dependent at constant temperature only on the partial pressures p_{SO_2} and p_{H_2O} and $f'(x)$ depending only on the degree of conversion x

$$r = f\,(p_{SO_2}, p_{H_2O})\, f'(x) \quad . \tag{3}$$

A further important finding resulting from Figs 2 and 3 is, that the studied reaction belongs to the type of gas–solid reactions distinguished by a maximum initial reaction rate[19]. This fact is in principal difference from the analogous active soda system where the initial reaction rate is zero and a maximum reaction rate is observed[6] at a degree of conversion of about 25 per cent.

In deriving the actual form of the kinetic equation it is thus necessary to evaluate first the term $f'(x)$, whereby for a given experiment $f(p_{SO_2}, p_{H_2O})$ is constant. The geometrical form of the rate dependences in Figs 2 and 3 intuitively indicates that they correspond to a hyperbolic function. Therefore, the rate values were correlated in the first approximation by the reciprocal value of the degree of conversion x and in the second approximation by the function $(1 - x)/x$. Thereby, it was found that the second function describes the experimental data in a completely satisfying way, resulting in the desired linear function shown in Fig. 4 for the same series of experiments as in Figs 1 – 3, which was obtained by the method of least squares. The slope of the linear function represents the effective rate constant k' whereby in relation to Eq. (*3*) $f(p_{SO_2}, p_{H_2O}) = k'$ and $f'(x) = (1 - x)/x$. Thus, Eq. (*3*) can be rewritten in a more concrete form (*4*) which after analytical integration yields Eq. (*5*), whereby the dependence of x on t cannot be expressed in an algebraic explicit form.

$$r = k'(1 - x)/x \tag{4}$$

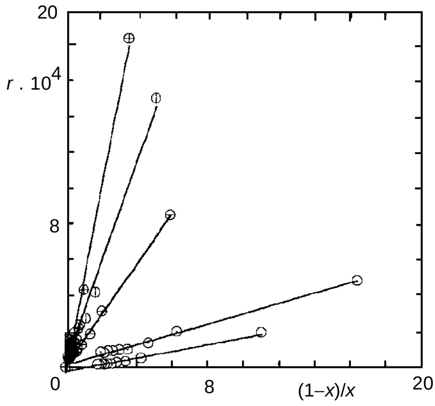

FIG. 4
Dependence of the reaction rate r (s^{-1}) of the active potassium carbonate on the expression $(1 - x)/x$ for different partial pressures of sulfur dioxide (p_{SO_2}) and two partial pressures of water vapour (p_{H_2O}). For designation of points see Fig. 1

$$k't = \ln (1 - x)^{-1} - x \tag{5}$$

The numerical values of k' obtained either from Eq. (*4*) or (*5*) formed a basis for all further calculations to find a general algebraic expression of the dependence of k' on the partial pressures p_{SO_2} and p_{H_2O}.

In this case, the same general approach as in the original papers[6,9] was used, based on theoretical principles first applied by Langmuir and Hinshellwood on treating adsorption and desorption processes on the surface of solids. This approach is also evident from the form of Eq. (*1*). However, the behaviour of the active potash system turned out to be considerably more complicated than the active soda system. The characteristics and differences can be described as follows:

a) The reactivity of the anhydrous potassium carbonate with the dry gaseous mixture is not zero or negligible as in the case of the active soda system. At comparable conditions, this reactivity is by about 1.5 orders of magnitude lower than with the moist gaseous mixture (see also Figs 1, 2, 4, empty points, and Fig. 5, curve I).

b) The reactivity dependence on the partial pressure of water vapour shows in the case of active potash a distinct maximum in the range of 0 – 400 Pa. The reactivity of the active soda system increases monotonously over the whole range of water vapour pressures, reaching asymptotically a constant value (saturation region).

c) After reaching the maximum reactivity between 65 – 130 Pa of water vapour pressure the reaction rate of the active potash decreases achieving for $p_{H_2O} > 400$ Pa more or less constant or only slightly increasing values.

d) At a constant value of the water vapour pressure both alkaline carbonate systems behave practically analogously, i.e. on increasing p_{SO_2}, the reaction rate first monotonously increases, reaching asymptotically a constant value (saturation region).

With respect to the purely mathematical or formal description, the mentioned behaviour of the K_2CO_3(s)–SO_2(g)–H_2O(g) system resembles closely the rate dependences obtained with some catalytic reactions of organic compounds, e.g. with the catalytic isomerization of 2-buten-1-ol (crotyl alcohol) to butanal (butyraldehyde) (Pt and Fe on alkalized silica gel[20]) or eventually of 2-propen-1-ol (allyl alcohol) to propanal (propionaldehyde) (Pd on active carbon[21]), both in presence or in absence of hydrogen. Here, 2-buten-1-ol and 2-propen-1-ol correspond formally to the system K_2CO_3(s)–SO_2(g) and hydrogen to water vapour. Both hydrogen and water do not figure in the overall reactions. The isomerization of 2-buten-1-ol proceeds also in absence of hydrogen at non negligible rate, whereas the isomerization of 2-propen-1-ol does not. However, in both systems the presence of hydrogen in low concentrations causes a steep increase of the isomerization rate which after passing a maximum decreases to reach finally constant or only slightly increasing values. The isomerization in the 2-buten-1-ol system is most similar to the system studied in this paper, the only differences being the much lower contribution to the total rate in the absence of the gaseous catalyst than in the case of the active potash system. This fact cannot explain the relatively high and significantly constant rate values at water vapour pressures above 400 Pa. Therefore, it was necessary to postulate the existence of a third reaction mechanism, which seems to be most probably identical with the reaction mechanism found for the reaction of active soda with sulfur dioxide[6,9].

The principal approach and the relevant mathematical description of the application of the classical Langmuir–Hinshellwood adsorption and desorption theory to heterogeneous chemical processes will be ommited in this paper because it is more or less similar for most systems including $K_2CO_3(s)–SO_2(g)–H_2O(g)$ and can be found in many contemporary monographies[22–25].

With respect to the quality of adsorption centers and in accordance with references[6,9] it is assumed that sulfur dioxide and water molecules are adsorbed on the two qualitatively different adsorption centers without dissociation. The influence of the gaseous carbon dioxide as a reaction product will be neglected for the same reasons as in the active soda system[6,9], especially for its low concentration. Further, it is assumed that the rates of the adsorption and desorption processes are much higher than the rate of the chemical reaction (rate determining step).

Under these assumption one can formulate the resulting kinetic equation and calculate the relevant rate adsorption equilibrium constants. This will be accomplished in two steps: (i) in the absence of water vapour and (ii) in the presence of water vapour.

(i) *Evaluation in the absence of water vapour*. In this case, the following relation can be applied in order to express the relevant effective rate constant k' in Eqs (*4*) and (*5*), denoted here as k_I referring to mechanism I

$$k' \equiv k_I' = k_I \frac{K_{SO_2}\, p_{SO_2}}{(1 + K_{SO_2}\, p_{SO_2})} \quad , \tag{6}$$

where k_I is the true rate constant and K_{SO_2} is the equilibrium adsorption constant for sulfur dioxide. In this equation, k_I' values were obtained from the differential rate data as the slope of the r versus $(1 - x)/x$ dependences (see Fig. 4, empty points and Eq. (*4*)) or from the integral kinetic data with the use of Eq. (*5*) in a similar way. The unknown constants in Eq. (*6*), k_I and K_{SO_2}, may be obtained from the k_I'/p_{SO_2} versus k_I' dependence constructed from the whole set of 18 experiments performed in the absence of water vapour. According to the rewritten form (*7*) of Eq. (*6*), the dependence should assume a linear function

$$k_I'/p_{SO_2} = k_I\, K_{SO_2} - k_I'\, K_{SO_2} \quad . \tag{7}$$

Here K_{SO_2} represents the slope and $k'_I K_{SO_2}$ the intercept on the y axis, from which k_I can be easily obtained. Every kinetic run (experiment) provides one pair of values for the integral data and one pair of values for the differential data. Thus, two sets of 18 pairs were used in our calculations. The method of least squares was applied, yielding the following values: $k_I = 0.271 \,.\, 10^{-4}\ s^{-1}$ and $K_{SO_2} = 1.64 \,.\, 10^{-2}\ Pa^{-1}$ from the set of integral data and $k_I = 0.241 \,.\, 10^{-4}\ s^{-1}$ and $K_{SO_2} = 0.84 \,.\, 10^{-2}\ Pa^{-1}$ from the set of differential data. Their average values $k_I = 0.256 \,.\, 10^{-4}\ s^{-1}$ and $K_{SO_2} = 1.24 \,.\, 10^{-2}\ Pa^{-1}$ were used in all further calculations. It was assumed that the conversion of the carbonate to the sulfite proceeds by mechanism I (with the same rate) also in the presence of water vapour with the unchanged value of K_{SO_2}.

(ii) *Evaluation in the presence of water vapour*. The first step consists in the qualitative analysis of the obtained experimental dependences on the water vapour pressure. Partly this was done already in points *b*), *c*) and *d*) (see page 2363) of this chapter. Based on this considerations one can intuitively assume that the form of the relevant kinetic equation valid for the whole range of p_{H_2O} can be written in the form (*8*)

$$k' = k_I \frac{K_{SO_2} p_{SO_2}}{(1 + K_{SO_2} p_{SO_2})} + k_{II} \frac{K_{SO_2} p_{SO_2} K_{H_2O} p_{H_2O}}{(1 + K_{SO_2} p_{SO_2})(1 + K_{H_2O} p_{H_2O})^2} +$$

$$+ k_{III} \frac{K_{SO_2} p_{SO_2} K_{H_2O} p_{H_2O}}{(1 + K_{SO_2} p_{SO_2})(1 + K_{H_2O} p_{H_2O})} \quad . \tag{8}$$

In this equation, the first term on the right hand side corresponds to the contribution (k'_I) to the overall rate constant k' which can be ascribed to mechanism I (absence of water vapour as the catalyst). The second term can be ascribed to mechanism II which causes the occurrence of the maximum reaction rate at lower p_{H_2O} values (denoted as k'_{II}). Its contribution decreases rather steeply for $p_{H_2O} > 400$ Pa. The third term (denoted as k'_{III} is algebraically identical with the complete form of the effective rate constant in Eq. (*1*) valid for active soda. Mechanism III causes the gradual increase of the effective rate constant in the whole range of p_{H_2O}. Thus Eq. (*8*) can be simply expressed as relation (*9*)

$$k' = k'_I + k'_{II} + k'_{III} \quad , \tag{9}$$

which indicates that the overall reaction rate consists of the additive contributions due to mechanisms I, II and III. However, Eq. (*8*) can be also rewritten as Eq. (*10*) where the term in square brackets depending only on the partial pressure of water vapour p_{H_2O} is denoted as $k(p_{H_2O})$ and analogously the other term as $k(p_{SO_2})$.

$$k' = \frac{K_{SO_2}\, p_{SO_2}}{(1 + K_{SO_2}\, p_{SO_2})} \left[k_I + k_{II} \frac{K_{H_2O}\, p_{H_2O}}{(1 + K_{H_2O}\, p_{H_2O})^2} + k_{III} \frac{K_{H_2O}\, p_{H_2O}}{(1 + K_{H_2O}\, p_{H_2O})} \right] \qquad (10)$$

Shortly, Eqs (*8*) and (*10*) can therefore be rewritten to the relation (*11*)

$$k' = k(p_{SO_2})\, k(p_{H_2O}) \quad . \qquad (11)$$

It should be noted that the form of Eq. (*11*) is the consequence of the assumption that the adsorption of SO_2 and H_2O takes place on qualitatively different centers. In the case of identical adsorption centers for SO_2 and H_2O, the general form of Eq. (*11*) may not be expressed as the product of two separate functions of p_{SO_2} and p_{H_2O}. In this case Eq. (*3*) with $f(p_{SO_2}, p_{H_2O})$ would be valid.

Because the constants K_{SO_2} and k_I in Eqs (*8*) and (*10*) are already known, it is necessary to find only the optimum value of k_{H_2O}, k_{II} and k_{III}.

The number of these constants can be lowered by one (k_{III}) by introducing further assumptions, namely that the contribution of mechanism II to the overall rate of conversion may be neglected for high water vapour pressures (p_{H_2O} > 2 070 Pa). This enables to evaluate the relation between K_{H_2O} and k_{III} by using kinetic data obtained only at water vapour pressures of 2 070 Pa (see Fig. 5, curve II). The relevant procedure yielded this relation in a graphical form. It was thereafter used in treating the kinetic data obtained in the whole range of partial pressure of water vapour, of course with the exception of $p_{H_2O} = 0$.

The schematically described calculation algorithm was accomplished by a regression analysis with the goal to obtain such a pair of k_{II} and K_{H_2O} values (and thus also of k_{III}) which would fit experimental data in the best possible way. Thereby, the method of

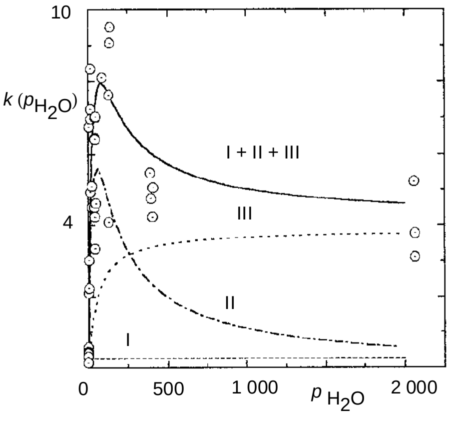

FIG. 5

Dependence of $k(p_{H_2O})$ (see Eqs (*10*) and (*11*)) on the p_{H_2O} (Pa). The points denote $[k(p_{H_2O})]_{exp}$, the full line the calculated $[k(p_{H_2O})]_{cor}$ by Eqs (*10*) and (*11*), using k_I, k_{II}, k_{III} and K_{H_2O} values obtained by the regression procedure. Curves I, II and III represent contributions of mechanisms I, II and III to the total $k(p_{H_2O})_{cor}$ (full line) least squares was used to find the optimum value of k_{II}. The input consisted of 26 experimental sets of three single k'_{exp}, p_{SO_2} and p_{H_2O} values, where k'_{exp} denotes the experimentally obtained value of k'. The resulting comparison between k'_{exp} and the correlated value of k'_{cor} is shown in Fig. 6, whereby k'_{cor} was calculated for given experimental values of p_{SO_2} and p_{H_2O} from Eq. (*8*), using k_I, k_{II}, k_{III}, K_{SO_2}, and K_{H_2O} values obtained by the correlation procedure. It can be seen that the average error of k'_{exp} with respect to k'_{cor} lies in the interval of ± 30.4 per cent with the standard deviation σ equal to ± 27.8 per cent.

Based on the performed calculations it is therefore possible to formulate the final form of the kinetic equation. The corresponding valid relations are formed by Eq. (*4*) for the differential form and by Eq. (*5*) for the integral form in which the effective rate constant k' corresponds to Eq. (*8*) or Eq. (*10*). The relevant constants have the following values

$$K_{SO_2} = 1.24 \;.\; 10^{-2}\ \text{Pa}^{-1} \qquad k_I = 0.26 \;.\; 10^{-4}\ \text{s}^{-1}$$
$$K_{H_2O} = 1.83 \;.\; 10^{-2}\ \text{Pa}^{-1} \qquad k_{II} = 22.4 \;.\; 10^{-4}\ \text{s}^{-1}$$
$$k_{III} = 3.9 \;.\; 10^{-4}\ \text{s}^{-1} \;.$$

DISCUSSION

The dependence of the reaction rate of the active sodium carbonate on the variables x, p_{SO_2}, and p_{H_2O} was initially found by a semiempirical procedure[6,9]. Later, the derived equation was based on exact theoretical considerations[11,13]. In the case of the active potassium carbonate, a more or less empirical or intuitive way has been applied. The accuracy of the obtained experimental data even excluded at the moment any other procedure for finding the final rate equation. This statement concerns especially data in

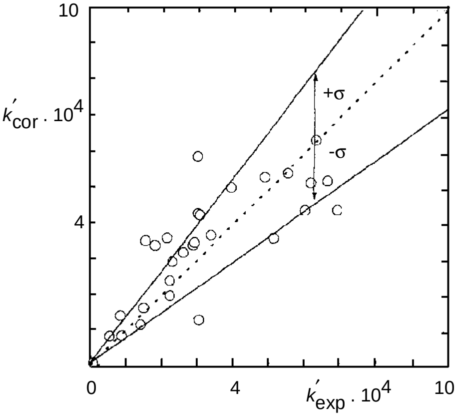

FIG. 6

Comparison of experimental effective rate constant k'_{exp} with the corresponding k'_{cor} calculated from Eq. (*8*), using k_I, k_{II}, k_{III}, K_{SO_2} and K_{H_2O} values obtained by the regression procedure. The average deviation is ±30.4 per cent, σ denotes the standard deviation expressed also in per cent (±27.8 per cent) the range of p_{H_2O} between 0 and 400 Pa, where a rather sharp maximum in the reaction rate was observed. Nevertheless, the reaction rate dependences with respect to the degree of conversion x of the form $r = dx/dt = k'(1 - x)/x$ is absolutely justified and satisfying. It indicates that the reaction rate is directly proportional to the ratio of the unreacted carbonate $(1 - x)$ and inversely proportional to the ratio of the product formed (sulfite) x. In other words, the rate of the conversion of the carbonate to the sulfite is directly proportional to the immediate ratio of the present amounts of the carbonate to the sulfite: $r(t) = k'n(K_2CO_3)\ (t)/\ n(K_2SO_3)\ \ (t)$. Comparison of the terms with the variable x (conversion of the solid) in Eq. (*1*) for the active soda and in Eq. (*4*) for the active potash shows immediately that the general form of the term can be written as $x^a(1 - x)^b$, whereby $a = 1/2$, $b = 3/2$ is valid for active soda and $a = -1$, $b = 1$ for active potash.

The dependences in Figs 2 and 3 indicate that the studied system belongs to the type of gas–solid reactions where the initial velocity has a maximum value[19]. This fact reveals that the nucleation rate, which represents an inevitable initial process of any heterogeneous reaction, proceeds at an infinite rate. In other words, all the potential nucleation sites are instanteneously changed into growth centers with the ability of further growth (i.e. the so called instanteneous nucleation). Further, it can be concluded that these potential nucleation and growth centers cover the surface of the solid potassium carbonate in very dense arrays. Therefore, at the start of the reaction the surface of the reaction interface is practically identical with the overall surface of the solid carbonate. With respect to the experimental conditions and to the fact that with increasing time (and thus with increasing degree of conversion) the area of the carbonate–sulfite interface must decrease it is clear, that the corresponding trend must be also found in the overall experimentally observed reaction rate. This considerations include of course the assumption that the rate determining step of the whole reaction process is the chemical reaction on the surface of the solid.

From the form of Eqs (*8*) and (*9*) it can be concluded that a relatively simple way was found to express the reaction rate in dependence on the partial pressure of both active gaseous components. The procedure of interpreting experimental results by the Langmuir–Hinshellwood model is analogous to the original papers on the active soda system[6,9]. Identical in both carbonate systems is the catalytic influence of water vapour. However, in the case of the active soda it is significantly more pronounced. This is shown in Table I which illustrates differences in the numerical values of the reaction rates for both solid systems under otherwise identical conditions. It can be seen that the reaction rate of the active soda is in average by the half to one order of magnitude higher than that of the active potash, except for very low degrees of conversion, where the reaction rate of potassium carbonate is even higher ($x = 0.0 - 0.10$). However, the reaction of the active potassium carbonate with sulfur dioxide proceeds also in the absence of water vapour which is not the case with the active sodium carbonate.

Principially different from the active sodium carbonate is the dependence of the reaction rate of the active potassium carbonate on the partial pressure of water vapour in the range of 70 – 133 Pa. Here, a significant reaction rate maximum is observed. With respect to the scattering of experimental rate data, it is preferable to determine the position of the maximum more exactly, by derivating the expression for the effective rate constant (Eq. (*8*) or Eq. (*9*)) with respect to p_{H_2O} and setting the resulting relation equal to zero. This procedure leads to the following relation (*12*) for $(p_{H_2O})_{max}$.

$$(p_{H_2O})_{max} = \frac{k_{II} + k_{III}}{K_{H_2O}\,(k_{II} - k_{III})} \qquad (12)$$

After substituting the constants k_{II}, k_{III} and K_{H_2O} by their actual values, we get $(p_{H_2O})_{max}$ = 77 Pa. This is in very good agreement with the experimental situation (see Fig. 5) and confirms also the validity of the applied correlation procedure.

From Eq. (*12*) it is evident that the position of the maximum is independent of the partial pressure of sulfur dioxide, p_{SO_2}. This is again the consequence of the justified assumption that water and sulfur dioxide molecules are adsorbed on qualitatively different sites. The position of the maximum can be best illustrated by multiplying the values of k'_{exp} and k'_{cor} (Eqs (*8*) and (*10*)) by the corresponding value of the expression $(1 + K_{SO_2}\, p_{SO_2})/K_{SO_2}\, p_{SO_2}$. The dependence of obtained values of $k(p_{H_2O})_{exp}$ and $k(p_{H_2O})_{cor}$ on p_{H_2O} is shown in Fig. 5. The region of the maximum reactivity and also the relatively constant values of the experimental and correlated values of $k(p_{H_2O})$ for p_{H_2O} > 400 Pa can be clearly recognized.

TABLE I

Comparison of the rates of the reaction of the active sodium carbonate, $r_{Na_2CO_3}$ (s^{-1}), and of the active potassium carbonate, $r_{K_2CO_3}$ (s^{-1}), with sulfur dioxide for different degrees of conversion *x* under otherwise identical conditions (temperature 423 K (150 °C), p_{SO_2} = 133 Pa, p_{H_2O} = 200 Pa)

x	$r_{Na_2CO_3} \cdot 10^4$	$r_{K_2CO_3} \cdot 10^4$	R^a
0.05	43.5	54.4	0.8
0.10	54.0	25.8	2.1
0.20	64.0	11.4	5.6
0.25	65.0	8.6	7.6
0.50	50.0	2.9	17.2
0.80	16.0	0.7	22.5
0.90	6.0	0.3	18.8

[a] $R = r_{Na_2CO_3}/r_{K_2CO_3}$.

Somewhat more complicated is the construction of a plausible hypothesis explaining the occurrence of the maximum reactivity. Assuming that the nucleation sites are situated on the carbonate surface in very dense arrays and that the nucleation and subsequent growth process are initiated (started) immediately on all potential nucleation centres instanteneously after the first contact of the carbonate surface with sulfur dioxide (both in the presence and absence of water vapour), it is possible to make the following consideration.

The necessary condition for the reaction to take place according to mechanism II is the presence and simultaneous contact of one SO_2 and one H_2O molecules. Thus the H_2O molecule needs one more vacant site in order that the reaction can take place. This statement should of course agree with the mathematical form of the term k_{II} in Eq. (*8*), which again should reflect the real physico-chemical background of the actual surface processes of mechanism II. Therefore, it is necessary to assume a certain optimum location of the adsorbed and reacting molecules on the carbonate surface which ensures, that the reaction proceeds at a maximum rate. This will be possible under following conditions: (i) Only when the carbonate surface will not be excessively blocked by adsorbed water molecules, because a sufficient ratio of the surface area must remain free for the adsorption of SO_2 molecules. Otherwise mechanism III will predominate. (ii) Only when the carbonate surface will not be excessively blocked by the adsorbed SO_2 molecules, because a sufficient ratio of the surface area must remain free for the adsorption of water molecules. Otherwise mechanisms I will predominate.

It should be again emphasized that the nucleation and growth centres are identical with the adsorption centres for SO_2 and that they are situated on the surface in very dense arrays. The same condition concerning the dense location of the adsorption centres must be valid for water molecules with respect to their catalytic activity. During the occupation of the carbonate surface by SO_2 and H_2O molecules, a certain competition can be expected because of the mutual steric hindrance. The independent variable is of course the partial pressure of water vapour. This will determine whether the carbonate surface is occupied by water molecules to an extend which will cause the reaction rate to reach the maximum.

In the region of higher partial pressures of water vapour, the carbonate surface will be occupied by adsorbed water molecules to such an extend that the reaction path according to mechanism II will contribute to the total degree of conversion much less than the reaction path via mechanism III. However, even the last mentioned mechanism shows equally decreasing increments in the reaction rate with the increase of the water vapour pressure, which become asymptotically negligible, and the total reaction rate acquires therefore a constant value. This situation is probably given by the fact that the carbonate surface is almost totally occupied by water molecules and a further increase in p_{H_2O} at a given constant value of p_{SO_2} is without effect on the total reaction rate.

When compared to the most catalytic or adsorption situations, the above problem should not be understood in a static sense (especially in connection with the more or less unchanging quality of the solid surface), but rather in a dynamic sense, with the solid surface in a continual state of change, which is of course of chemical nature as a consequence of the progressing interface area due to the conversion of one solid to another i.e. the carbonate to the sulfite.

CONCLUSIONS

Based on performed kinetic experiments, it can be stated that a suitable rate equation which would describe the reaction of solid anhydrous potassium carbonate, prepared from potassium hydrogen carbonate, with gaseous sulfur dioxide has been found. It was derived on a more or less empirical and intuitive basis. This is in contrast with the previously studied active soda system where the rate equation was derived with respect to the degree of conversion x at first on a semiempirical basis[6,9], later confirmed also on a theoretical *ab initio* level[11,13]. The theoretically based derivation of the rate equation for the system K_2CO_3(s)–SO_2(g)–H_2O(g) should therefore become the subject of further considerations, especially with respect to the degree of conversion of the solid, x (Eq. (*4*)).

Remarkable is the considerable difference in the kinetic behaviour of the system K_2CO_3(s)–SO_2(g)–H_2O(g) and Na_2CO_3(s)–SO_2(g)–H_2O(g), with respect to both the conversion degree x and the dependence on the partial pressures of the active gaseous components (p_{SO_2},p_{H_2O}). The first system belongs to the type of gas–solid reactions with a maximum initial reaction rate, the second system to those with a zero initial reaction rate. Here, the maximum is reached at conversions of about 25 per cent. In the case of the active potash system it is probable that the reaction rate dependence on x may also describe the role of water vapour, with the occurrence of a maximum reaction rate at about p_{H_2O} = 80 Pa. Simple considerations indicate that this maximum seems to corroborate a very dense array of adsorption, nucleation, and thus also growth sites, with respect to SO_2 and H_2O. However, the whole problem should deserve a more exact treatment.

Surprising in the behaviour of the K_2CO_3(s)–SO_2(g)–H_2O(g) system is its formal resemblance to some heterogeneously catalyzed reactions, such as e.g. isomerization of unsaturated alcohols (2-buten-1-ol, 2-propen-1-ol) where the components formally not participating in the reaction cause a more or less sharp reactivity maximum by their presence at low concentrations and a decrease of the reactivity at higher concentrations[20,21]. It is questionable whether this similarity is only of purely formal or mathematical nature or whether it is based on analogous behaviour of the active components adsorbed on the surface of the corresponding solids (the carbonate or the catalyst). The respective dependences in terms of the effective rate constants are more similar between each other than between the active soda and the active potash.

The present work does not report the dependence of the studied system on temperature. Generally, the temperature dependence of the individual mechanisms I, II, and III need not change in the same way. A detailed investigation of this problem could contribute considerably to the elucidation of the nature of these mechanism.

With respect to the high sensitivity of the studied system towards the partial pressure of water vapour (at lower values) which made the installation of a special mixing apparatus necessary, it was sometimes impossible to maintain a hydrodynamic steady state at very low p_{H_2O} values during the whole experimental run as would have been desired. This fact is responsible for the rather high scattering of the obtained experimental results (see Fig. 5). The complete dependence of the reactivity on the partial pressure of water vapour is nevertheless well recognizable. The accuracy of the experimental effective rate constant k' determination in comparison to the values obtained from the correlation procedure lies in the range of ±30 per cent, whereas the usual accuracy known from experimental chemical kinetics is about ±15 per cent.

With respect to the properties of the studied system one may not exclude in future some special areas of application. However, because of the higher prices and lower reactivity of potassium salts than in the case of the active soda system, these practical applications are less probable, especially in a large production scale.

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SYMBOLS

Φf	an average multiplying factor resulting from the affine transformation procedure; for details see ref.[19]
K_{H_2O}	equilibrium constant for the adsorption of water vapour on the solid carbonate surface, Pa^{-1}
K_{SO_2}	equilibrium constant for the adsorption of sulfur dioxide on the solid carbonate surface, Pa^{-1}
k_0	true rate constant in Eq. (*1*) for the reaction between solid anhydrous sodium carbonate and sulfur dioxide, s^{-1}
k_I	true rate constant in Eqs (*6*), (*7*), (*8*) and (*10*) for reaction mechanism I between solid anhydrous potassium carbonate and sulfur dioxide, s^{-1}
k_{II}	true rate constant in Eqs (*8*) and (*10*) for reaction mechanism II between solid anhydrous potassium carbonate and sulfur dioxide, s^{-1}
k_{III}	true rate constant in Eqs (*8*) and (*10*) for reaction mechanism III between solid anhydrous potassium carbonate and sulfur dioxide, s^{-1}
$k(p_{H_2O})$	rate factor defined by Eqs (*10*) and (*11*) dependent only on the partial pressure of water vapour p_{H_2O}
$k(p_{SO_2})$	rate factor defined by Eqs (*10*) and (*11*) dependent only on the partial pressure of sulfur dioxide p_{SO_2}
k'_0	effective rate constant in Eq. (*2*) for the reaction between solid anhydrous sodium carbonate and sulfur dioxide, s^{-1}

k'	effective rate constant in Eqs (*4*), (*5*), (*6*), (*8*), (*9*), (*10*) and (*11*) for the reaction of solid anhydrous potassium carbonate with sulfur dioxide, s^{-1}
k'_I	effective rate constant in Eqs (*6*), (*7*), (*8*), (*9*) and (*10*) for reaction mechanism I between solid anhydrous potassium carbonate and sulfur dioxide, s^{-1}
k'_{II}	effective rate constant in Eqs (*8*), (*9*) and (*10*) for reaction mechanism II between solid anhydrous potassium carbonate and sulfur dioxide, s^{-1}
k_{III}	effective rate constant in Eqs (*8*), (*9*) and (*10*) for reaction mechanism III between solid anhydrous potassium carbonate and sulfur dioxide, s^{-1}
p_{H_2O}	partial pressure of water vapour in the reacting gaseous mixture, Pa
p_{SO_2}	partial pressure of sulfur dioxide in the reacting gaseous mixture, Pa
r	reaction rate defined as dx/dt, s^{-1}
t	reaction time, s
x	degree of conversion of the solid carbonate to solid sulfite; defined as the ratio of the number of molecules (moles) of carbonate changed at a given time t to sulfite to the number of molecules (moles) of carbonate initially present in the reaction system
σ	standard deviation of the experimentally determined values of the effective rate constants from the values calculated from Eq. (*8*) or (*10*) obtained by the correlation procedure

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