Inverse Method to Obtain Reaction Surface Area During Gas-Solid Reactions

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During noncatalytic gas-solid reactions, both the chemical composition, and the size and texture of the particle change simultaneously. A new inverse method allows to determine the influence of the reaction parameters (such as temperature) and changes in the specific reaction surface area with conversion. It can also establish the range of conversion, where constant reaction conditions are present at the reaction surface. This method is based on the mathematical treatment of experimental results which include the conversion vs. time together with the corresponding reaction parameters. This method consists of several well established mathematical procedures applicable to the specific situation at gas-solid reactions: variable conversion and reaction time are separated and inverted, respectively. The ratio of two reaction rates (of different experiments) at the same conversion provides information about the (only time-dependent) influence of the reaction parameter on the reaction rate. Finally, also the specific reaction surface area as a function of conversion is derived.

Introduction

Since the work of Yagi and Kunnii (1955) numerous particle structures have been looked at, such as the sharp interface model. (Sahimi et al. (1990) gives a good review of models that allow to describe the solid structure of porous media.) The shrinking core model was described by Szekely et al. (1976) where the reaction is considered to proceed at the surface of an unreacted and geometrically well defined particle (core). The porous structure of a solid material can be described by a pore or grain model. Grain models are the application of the shrinking core model on a porous structure when the voids between the grains represent the pores. Grain models where the grains are of the same shape and size are proposed by Szekely et al. (1976), Levenspiel (1983), Reh (1977), Eddings and Sohn (1993), Friedrichs (1980), Tine (1985), Do (1982), Hartmann and Coughlin (1976), and others. Pore models consider the structure as an assembly of hollow spaces usually of cylindrical shape, whereas the solid is regarded as the continuous phase. Numerous pore models have been proposed over the years such as a single pore model by Ramachandran and Smith (1977) or more complex models such as random pore models (Petersen, 1957; Bhatia and Perlmutter, 1980, 1981; Gavalas, 1980; Sotirchos and Yu, 1985). To account for pore blocking, sinter effects or inaccessible porosity grain models and pore models were altered and extended (Delikouras and Perlmutter, 1991; Ranade and Harrison, 1979). In addition to these continuum models, statistical models based on percolation theory also have been used to account for the structure of porous materials where fragmentation and inaccessible pore spaces can also be described (Reyes and Jensen, 1987; Brown and Miles, 1995).

Aichinger (1997) proposed a new method where conventional grain and pore models are included. He pointed out how to determine the reaction surface area by a set of purely chemically controlled reactions. His method does not require a preliminary assumption of the geometry of the solid texture. From experiments, the connection between the reaction surface area S_v based on the initial surface area $S_{v,o}$ and the distance s given between the initial surface area and the reaction surface area at a conversion X is obtained. The function $S_v/S_{v,o}$ can be described by a geometry (sphere, plate, cylinder, and the thickness of a hollow cylinder) and its corresponding frequency distribution function. This method also allows to determine whether unclear reaction conditions were present at the beginning of the reaction: For each geometry, a frequency distribution function is defined to describe the maximum range of conversion vs. time. The distribution functions determined can be used to extrapolate towards conversion zero assuming that the number of elements of the frequency distribution did not change during the range of extrapolation. From these extrapolated curves, so-called "lag" times can be determined for each geometry. These lag times, together with the corresponding reaction parameters of the experiments, allow to restrict the type of geometry best suited for the description of the reaction surface area, and whether unclear reaction conditions were present at the beginning of the reaction.

An inverse method is presented here that allows to uncouple the chemical kinetics from the reaction surface area changing with conversion (Krammer, 1998). This method provides a test of the experiments with respect to the influence of the reaction history, and of an unclear reaction start on the reaction rate, respectively. Two simple gas-solid reaction systems are investigated and the proposed method is applied: The decomposition of limestone at different CO_2 partial pressures and temperatures, and the oxidation of graphite (C) with oxygen are investigated.

Principle of Inverse Method

For each experiment i, the conversion X vs. time t is given for a specific set of reaction parameters γ_i (such as, temperature, pressure). The conversion X is monotonously increasing with time t.

In general, the reaction rate can be expressed by an ordinary differential equation (see also Gavalas, 1980)

$$\frac{dX}{dt} = k_o K S_v \tag{1}$$

with the conversion X, the reaction time t, the reaction rate constant k_o, which is the same for an entire set of experiments, an expression K, and the specific reaction surface area S_v. Here, it is assumed that the reaction surface area S_v only depends on the conversion X and that K only depends on γ, which in turn can depend on the reaction time t. The expression K is assumed to be the same for an entire set of experiments.

Usually, the solid structure is complicated and, therefore, models are employed. Since the true geometry can hardly be described exactly, the models are based on more or less plausible hypothesis. Here, the interest is focused on the situation where the dependency of the surface area on the conversion is not known *a priori*. The specific surface area can be expressed as a function of the conversion X that implicitly depends on the reaction time t

$$S_v = S_v[X(t)] \tag{2}$$

The specific reaction surface area $S_v(X)$ is the same for an entire set of experiments.

At the beginning of the reaction ($t = 0$), starting conditions can be defined. (Usually, the material under investigation is characterized prior to the reaction to obtain well defined starting conditions.)

$$t = 0 \qquad \begin{cases} X = 0 \\ S_v = S_{v,o} \qquad \text{(BET surface area)} \\ \gamma = \gamma_o \end{cases} \tag{3}$$

Here, the constant k_o, the expression K, and the specific reaction surface area S_v are subject to the investigation. The specific reaction surface area represents the actual available (accessible) reaction surface area, which cannot always be directly measured when, for example, a product layer is present.

The determination of the expression $K(\gamma)$, k_o, and finally $S_v(X)$ from a set of experiments is trivial when the initial conditions ($S_{v,o}$ and the reaction parameters γ_o) are known, respectively.

However, a more realistic situation is given when experiments are performed at different reaction parameters which are not known at any time of the experiment due to an unclear reaction start.

When the reaction parameters γ are only known for a restricted period of the reaction time t, the influence of one reaction parameter on the reaction rate can still be determined. (For reasons of simplicity, only one parameter is changed such as temperature.) Also, the reaction surface area $S_v(X)$ can be derived, but only for the time period where the reaction parameters that are present at the reaction surface area are known at least from one experiment.

Again, the results of a number of experiments n must be available. Each experiment i is performed at conditions where the magnitude of one reaction parameter is changed. Due to an unclear reaction start, the presumed reaction parameters (that is, operating conditions) are not available instantaneously at the reaction surface. However, as the reaction proceeds, they are eventually achieved. During the nonstationary period, knowledge about the reaction parameters that are actually present at the reaction surface are hardly available, but the reaction parameters are known once they have become constant.

The method that is proposed here allows to determine the range where constant reaction parameters are achieved. Once this reaction period is determined, the expression $K(\gamma)$ and its constants can also be determined by a curve fit. Finally, the reaction surface as a function of the conversion X can also be derived.

(1) A plot is created where the reaction rate of experiment j is plotted vs. the reaction rate of the experiment i at the same conversion X (see Figure 1).

The slopes of the lines between the origin and each point of this curve can be determined, and they are given by

$$\frac{\left.\frac{dX}{dt}\right|_i}{\left.\frac{dX}{dt}\right|_j} = \frac{S_{v,i} K_i k_o}{S_{v,j} K_j k_o} \qquad \text{at the same conversion } X \tag{4}$$

$$\text{with } i \le j \qquad i, j = 1, \ldots, n$$

$$\text{at} \qquad i = j \qquad \rightarrow \frac{\left.\frac{dX}{dt}\right|_i}{\left.\frac{dX}{dt}\right|_j} = \frac{S_{v,i} K_i k_o}{S_{v,j} K_j k_o} = 1 \tag{5}$$

with the total number of experiments n and the numbered experiments i and j performed at different conditions.

(2) If the reaction surface area depends only upon the conversion X, the specific reaction surface areas $S_{v,i}$ and $S_{v,j}$

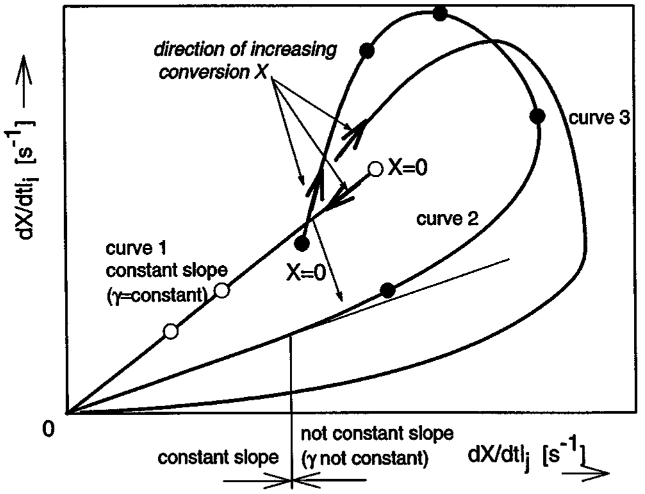

Figure 1. Reaction rate of experiment *i* vs. the reaction rate of experiment *j* at the corresponding conversion *X*.

Three different situations can be distinguished: the reaction parameter γ is constant throughout the reaction (curve 1); the reaction parameter is constant, but only for the final stage of the reaction (curve 2); the reaction parameter is not constant during the entire reaction (curve 3).

cancel out in Eq. 4, because they are the same at the same conversion X. Of course, the constant k_o also cancels out, because it is independent from the conversion X and the changed reaction parameter. Consequently, Eq. 4 becomes

$$\frac{\left.\frac{dX}{dt}\right|_i}{\left.\frac{dX}{dt}\right|_j} = \frac{K_i}{K_j} \tag{6}$$

(3) For the range of conversion X where no constant slope can be found, the presumed reaction conditions γ_i and γ_j are temporarily possibly different. Moreover, the assumptions do not hold that the specific surface area and/or the expression K are the same for the entire set of experiments.

In order to determine the function K and its constants, it is advisable to concentrate first on the conversion range where a constant slope can be defined. For the range of the conversion X where the absolute value of the derivative of the slope is below an acceptable limit a, the slope can be regarded to be constant

$$\frac{d\left(\frac{\left.\frac{dX}{dt}\right|_i}{\left.\frac{dX}{dt}\right|_j}\right)}{dX} \equiv \left|\frac{d\left(\frac{K_i}{K_j}\right)}{dX}\right| \leq a \tag{7}$$

(4) When there are n experiments, only N independent equations of the type (Eq. 4) and curves are possible which is given by

$$N = \sum_{k=1}^{n} (k-1) \tag{8}$$

When only one reaction parameter is changed, a plot can be created where the ratio of K_i and K_j (from the constant range) is plotted vs. γ_i at constant γ_j, respectively. (Here γ_i and γ_j denote one changing reaction parameter (such as temperature), respectively.)

(5) If the slope is found to be constant, it can be assumed that the expressions K_i and K_j are of the same type with the same constants. The type of function K, which may best represent the results, can be derived by a three-dimensional surface fit. In order to obtain the best constants of the function, an error minimization procedure must be employed. For a specific reaction system, the type of function is possibly available from literature. On the other hand, the type of function may also be chosen freely.

(6) Once the function K and its constants are known, the changes of reaction surface area with conversion can be determined, but only for the range where the reaction parameters at the reaction surface are known

$$\frac{1}{K}\frac{dX}{dt} \alpha S_{v,o}.$$

Only when the reaction parameters are known at any time during the reaction, the reaction rate constant k_o and the entire function of the reaction surface $S_v(X)$ can also be determined with the initial condition.

Examples

Two different reaction systems were investigated by Aichinger (1997), and his data are used to show the applicability of the proposed method. All experimental were performed by means of the same thermogravimetic analyzer. Details of the experimental setup are given by Aichinger (1997). The composition and the structural data of the materials used in this study are given in Table 1.

Decomposition of limestone

The decomposition of limestone at a constant temperature and different CO_2 partial pressures was investigated by Khinast et al. (1996). Whereas the decomposition of limestone at different temperatures in nitrogen was investigated by Aichinger (1997). The total pressure P was kept constant at ambient pressure. At a high temperature, CO_2 is released and CaO is formed

$$CaCO_3 \Rightarrow CaO + CO_2 \tag{9}$$

The data of limestone are given in Table 1.

Figure 2 gives the conversion profiles vs. reaction time obtained for the decomposition reaction of limestone at differ-

Table 1. True Particle Density, Fraction of Inert, Particle Size, and the BET Surface Area of the Materials

	True Particle Density (kg/m^3)	Inert Fraction (wt. %)	Particle Size (μm)	BET Surface Area (m^2/g)
Bad Ischler Limestone	2,710	2.1–3.7	50–63	1.36
Graphite	2,230	0.01	1–30	8.73

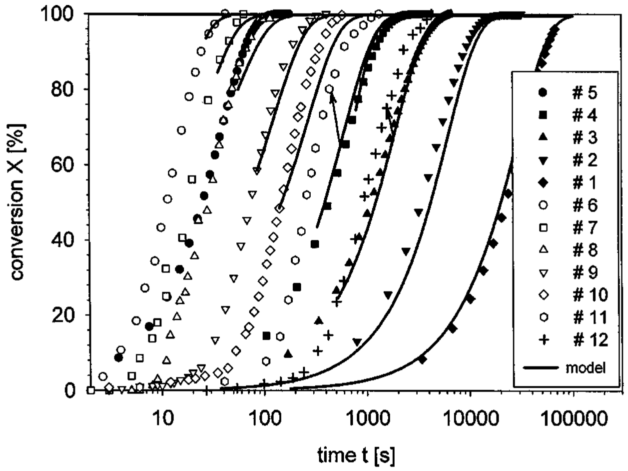

Figure 2. Experimental results and model calculations of the conversion vs. reaction time of the decomposition of limestone at different CO_2 concentrations (Khinast et al., 1996) and temperatures (Aichinger, 1997).

Numbers in the figure legend refer to Table 2.

ent CO_2 partial pressures in nitrogen and temperatures, respectively. In this figure the solid lines indicate the modeling results, given only for the range where a constant slope can be defined (see Table 2).

The link between the reaction rate and the CO_2 partial pressure and the temperature is investigated by the proposed method. First, the influence of the CO_2 partial pressure is investigated, and, afterwards, the influence of the temperature on the reaction rate together with the corresponding reaction surface area are determined.

The rate of the decomposition reaction can be expressed by Eq. 1. Here, K is a function of the CO_2 partial pressure p_{CO_2}, the temperature T, the equilibrium pressure $p^o_{CO_2}$, and the reaction time t, respectively.

$$K = K\left[p_{CO_2}, T, p^o_{CO_2}(T), t\right] \tag{10}$$

Table 2. Experimental Number, Partial Pressure of CO_2, Reaction Temperature, Lower Range of Conversion X_{low} where a constant slope is defined and the corresponding reaction time t_{low}, error e*

No.	p_{CO_2} [Pa]	T [K]	X_{low} [%]	t_{low} [s]	e
1	0	795	0	0	−0.09
2	0	837	0	0	0.19
3	0	864	85	2,733	0.17
4	0	913	75	798	−0.29
5	0	1,023	90	65	−0.19
6	0	1,053	94	26	0.20
7	1×10^3	1,053	85	35	−0.21
8	2×10^3	1,053	81	53	0.20
9	3×10^3	1,053	59	90	0.24
10	4×10^3	1,053	49	149	0.57
11	5×10^3	1,053	44	239	0.82
12	6.5×10^3	1,053	20–25‡	445	0.49

*The total pressure is $P = 1\cdot10^5$ [Pa]. (‡ extrapolated value).

The reaction surface area S_v is given as the sum of the external and internal surface area that is accessible for a gas-solid reaction; at the beginning of the reaction, this surface area is given by the BET surface area (see Table 1).

According to the definition given in Eq. 7, the conversion range (lower and upper limit) is defined where a constant slope can be obtained (here $a = 4\cdot10^{-4}$): Table 2 gives the lower range (conversion X_{low} and corresponding reaction time t_{low}) of each experiment. The upper range is given at total conversion ($X_{upp} = 100$).

The error e is defined by

$$\left| \frac{1}{n} \sum_{i=1}^{n} \frac{\left.\dfrac{dX}{dt}\right|_{\text{calculated}}}{\left.\dfrac{dX}{dt}\right|_{\text{experiment}}} (1+e) - 1 \right| \rightarrow \text{minimum} \tag{11}$$

The calculated reaction rate and the reaction rate determined from the experiments are related to the same conversion X; n denotes the number of data points of one experiment. The error e is a measure of the average deviation from the experimental values obtained by a conventional error minimization technique.

In Figure 3 the slope (= ratio of K_i and K_j) is plotted vs. p_{i,CO_2} at constant values of p_{j,CO_2} (and temperature). The data points (x_j = constant) can best be described by an exponential function, which is chosen empirically. Consequently, also, the reaction rate depends exponentially on the partial pressure. A rapid decay of the reaction rate with an increasing partial pressure of CO_2 was also reported by Hyatt et al. (1958) who described the reaction by a two step mechanism

$$\frac{dX}{dt} = k_1 S_v \exp(-a_1 p_{CO_2}) \qquad \text{with} \qquad a_1 = 0.07519\ [\text{Pa}^{-1}] \tag{12}$$

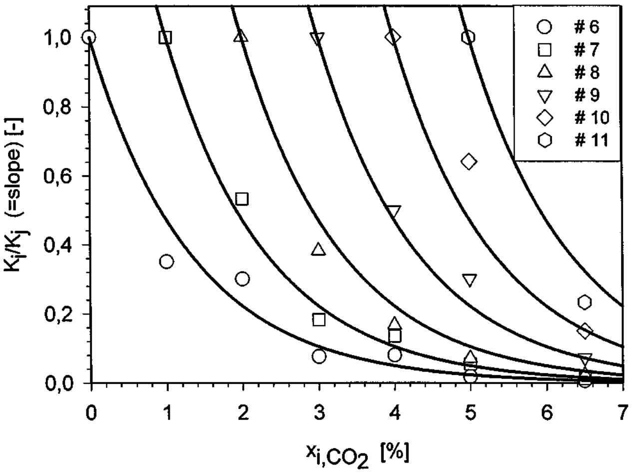

Figure 3. Slope vs. molar ratios of the decomposition of limestone (operating conditions).

Lines indicate model calculations. Numbers in figure legend refer to Table 2.

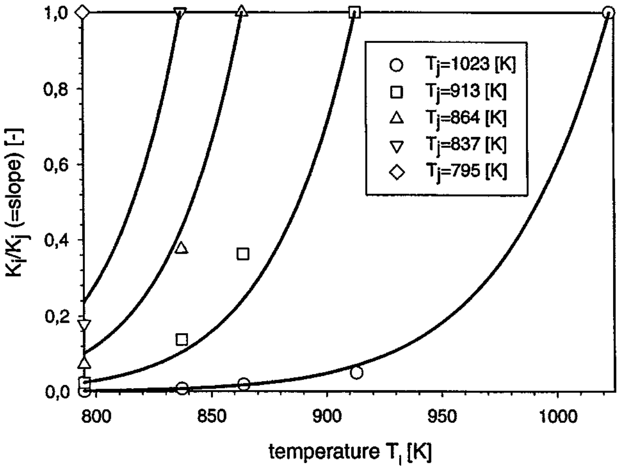

Figure 4. Slope vs. temperature of the decomposition of limestone (operating conditions).

Lines indicate model calculations.

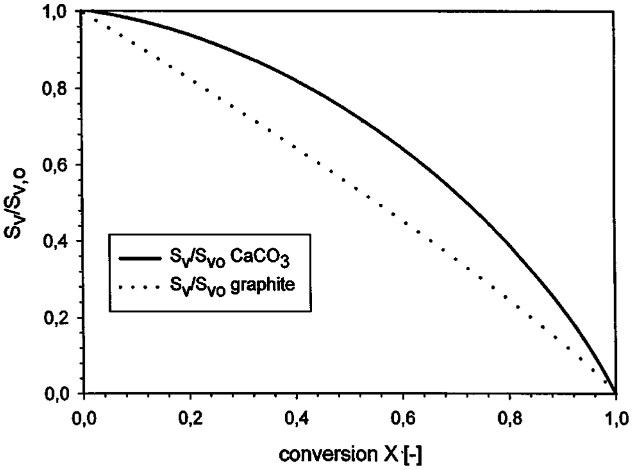

Figure 5. Dimensionless reaction surface area is plotted vs. conversion for the decomposition of limestone, and the oxidation of graphite.

In Figure 4, the slope (= ratio of K_i and K_j) is plotted vs. the temperature T_i at constant values of T_j (and molar ratio of $x_{CO_2} = 0$).

Assuming the validity of the Arrhenius law for the temperature dependency, it follows

$$\frac{dX}{dt} = k_2 S_v \exp\left(-\frac{a_2}{T}\right) \quad \text{with} \quad a_2 = 24{,}804.8\ [\mathrm{K}] \quad \text{and } k_2 = 236.5\ [\mathrm{m/s}] \tag{13}$$

When the equilibrium pressure $p^o_{CO_2}$ during the decomposition of limestone is also taken into account (which depends upon the temperature), it gives

$$\frac{dX}{dt} = k_3 S_v p^o_{CO_2} \exp\left(-\frac{a_3}{T}\right) \tag{14}$$

Knowing the reaction surface area at the beginning, the initial reaction rate constant k_s can be determined, since the slope of the ratio of the reaction rates of the experiments at 564°C and 522°C is constant.

Consequently, the reaction rate is given by

$$\frac{dX}{dt} = k_s S_v \frac{p^o_{CO_2}}{P} \exp\left(-\frac{E_a}{\Re T}\right) \exp\left(-a_1 p_{CO_2}\right)$$
$$\text{with } k_s = 9.73 \cdot 10^{-6}\ [\mathrm{m/s}], \qquad E_a = 39{,}746\ [\mathrm{J/mol}] \tag{15}$$

with the temperature T and p_{CO_2} denoted as the partial pressure of CO_2 and $\Re$ the ideal gas constant. Figure 5 shows the dimensionless reaction surface area vs. conversion.

The description of the specific surface area by means of the modified random pore model does not seem to account for the changing reaction surface area (Khinast et al., 1996), which is also noted by Aichinger (1997).

The initial reaction rate determined here is certainly larger than the value ($k_s = 7.48 \cdot 10^{-9}$ [m/s] given by Khinast et al. (1996), because the reaction rate is retarded at the beginning not by the features of the specific surface area, but by the nonstationary initial reaction conditions which was pointed out by Aichinger (1997).

The inverse model showed that the solid particles did not experience constant operating conditions from the reaction start. The dependency of the reaction rate on the partial pressure of CO_2 and the temperature was determined, respectively.

Oxidation of graphite

The oxidation of graphite was performed at different temperatures between 753 and 1,022 K in air. Table 1 lists the characteristic data of the material. During the oxidation of graphite carbon dioxide is formed.

$$C + O_2 \Rightarrow CO_2 \tag{16}$$

Figure 6 gives the conversion profiles vs. reaction time obtained for the oxidation reaction at different temperatures. In this figure the solid lines indicate the modeling results. The link between the reaction rate and the temperature is investigated by the proposed method. In Figure 7 the slope is plotted vs. the temperature T_i. Again the data points (T_j = constant) can best be described by an Arrhenius type law.

$$\frac{dX}{dt} = k_s S_v \exp\left(-\frac{E_a}{\Re T}\right) \quad \text{with}$$
$$k_s = 0.00512\ [\mathrm{m/s}], \qquad E_a = 139{,}869\ [\mathrm{J/mol}] \tag{17}$$

Figure 5 shows the corresponding dimensionless reaction surface area vs. conversion.

The results show that, for all experiments except the one performed at 923 K, operating conditions were instantaneously present at the beginning. Therefore, with the reaction surface area as a function of conversion, the initial reaction rate constant, and the function and its parameters that describe the dependency of the reaction rate on the temperature, can easily be determined.

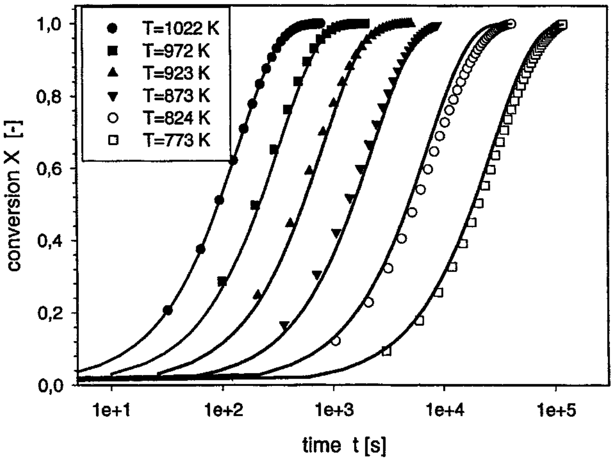

Figure 6. Experimental results and model calculations of the conversion vs. reaction time of the oxidation of graphite at different temperatures (Aichinger, 1997).

Restrictions and Opportunities of the Method

This method is restricted to experimental results where the conversion is monotonously increasing with time. This restriction is important to solve the inverse problem of reaction time t to conversion X unambiguously since the reaction rate dX/dt is plotted vs. conversion X.

In order to be able to determine the reaction surface area at least two experiments must be available where the variables reaction time t and conversion X can clearly be separated between the expression $K = K[\gamma(t)]$ and the surface area $S_v = S_v[X(t)]$, respectively.

The method fails when the reaction conditions i and j are not constant but change in a manner that the changes do not become obvious when the ratio of the two reaction rates is formed; this is, however, very unlikely.

When the reaction parameters summarized by γ are only constant during a fraction of the reaction time, the period of nonstationary reaction conditions can have an impact on the proceeding reaction (memory). Therefore, the slopes between the origin and the curve in the plot of the reaction rates can be different although the reaction parameters are already constant. This can be due to different specific reaction surface areas at the same conversion, because of the different history. The impact of the different history on the proceeding reaction can also be determined by this method when the reaction rates of different experiments are plotted against each other at the same conversion. In the range where the reaction parameters are constant, the deviation of the slope from a constant value is a measure for the impact of the previously different conditions on the reaction. Finally, when a constant slope can be defined, it can be assumed that in this range previously different reaction conditions have no impact on the proceeding reaction.

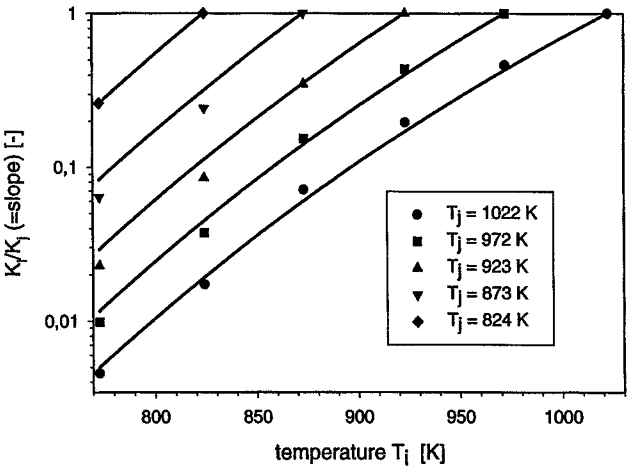

Figure 7. Slope vs. temperature of the oxidation of graphite (operating conditions).

Lines indicate model calculations.

This method was presented for the case when only one reaction parameter of the set of parameters γ is changed. Of course, more reaction parameters can be changed simultaneously, which is suggested by Box et al. (1978) mainly to limit the number of experiments. However, the determination of the according expression K gets increasingly complicated. (The change of two different reaction parameters expressed by γ_1 and γ_2 requires already a three-dimensional surface fit when the ratios of the reaction rates are plotted vs. $\gamma_{1,i}$ and $\gamma_{2,i}$.)

In this article it is assumed that the reaction rates can be determined from experiments which give the conversion X vs. the reaction time t. Of course, large errors can be associated with the determination of the derivative (dX/dt), which is not tackled here. When the analytical expression for the reaction rate is integrated and the results are compared with the original database, the deviation should be small. In order to minimize the overall error, a mathematical routine should be employed that allows parameter identification.

The expression K describes the influence of the reaction parameters on the reaction rate. This expression K is only an overall (empirical) rate expression where a complex reaction system (such as different reaction steps, intermediate products, byproducts, adsorption and desorption, and nucleation effects), the thermodynamic equilibrium conditions, and the stoichiometry of the reaction are included.

Conclusions

From a set of experiments (at least two experiments) with one changing reaction parameter, the results conversion vs. time is available. An analysis of the results requires the determination of the changing reaction surface area and the impact of the reaction parameter on the reaction rate.

The reaction parameter can change during the reaction (time-dependent). When information is available on the magnitude of the reaction parameter at any time of the reaction and on how the reaction parameter changes with time, the reaction surface area and an empirical expression K that accounts for the influence of the reaction parameter on the reaction rate can readily be derived.

However, information on how the reaction parameter changes with time is very often not available during the entire reaction period. Information on the magnitude of the reaction parameter is hardly available especially at the beginning of the reaction: Gas-solid reactions need some time to get stationary conditions throughout the particle.

A method is proposed where reaction rates obtained at different conditions are compared at the same conversion, although information on the reaction parameter is only available during a restricted reaction period.

- This method allows to determine the range of the experiment where stationary conditions are present.
- Based on a set of experiments, this method allows to determine the influence of a changing parameter on the reaction rate. The according function K can be derived by data fitting when the type of expression K does not depend upon the reaction conditions γ.
- Furthermore, the reaction surface area is determined as a function of conversion without a predefinition of a textural model only when the reaction surface area does not depend upon the reaction conditions γ.

Two different examples of gas-solid reactions are investigated, which show the applicability of the proposed method.

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