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Kinetics of Reduction of Iron Catalysts for Ammonia Synthesis

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The reduction of industrial iron synthetic ammonia catalysts by a stoichiometric mixture of hydrogen and nitrogen has been investigated. The reduction was studied in the temperature range 450–550°C and for several grain sizes using a spring microbalance in a flow system. It was found that the results satisfy the Seth and Ross kinetic equation for a mixed-control mechanism in which neither the surface reaction nor the diffusion determines the reaction rate. The parameters of the Seth and Ross equation were calculated by a least squares method.

INTRODUCTION

Industrial catalysts for ammonia synthesis are usually obtained by reducing the oxides of iron, most frequently magnetite containing the appropriate promoters. It is a well-known fact that the conditions in which the reduction is carried out strongly influence the activity of the reduced catalyst. Consequently the process of reduction is considered as one of the important steps in the formation of the catalyst. Despite this the kinetics of the reduction have not yet been fully worked out.

Various kinetic curves have been published in the literature (*1–7*). Analyzing four of them, Skarchenko *et al.* (*4*) suggested that the reaction was first order. Hall, Tarn and Anderson (*1*) found that their results were best described by an equation derived for spherical particles assuming that the reduction proceeds uniformly inward from the external surface and that the rate is proportional to area of the sphere of unreduced catalyst. The remaining authors did not discuss the kinetics at all and the data given in their papers are not suitable for reinterpretation.

In recent years several equations of mixed-control type (*8–11*) have been proposed to describe the kinetics of the reduction of metal oxides. All those equations, in the derivation of which two or more rate-influencing steps were postulated, are based on similar assumptions. In all cases the reaction rate at the product–reactant interface and the diffusion rate through the product layer are taken into account.

Seth and Ross derived (*8*) the equation:

$$\alpha t = \beta[1 - (1 - R)^{1/3}] + \left[\frac{1}{2} - \frac{R}{3} - \frac{(1 - R)^{2/3}}{2}\right], \quad (1)$$

where

$$\alpha = \frac{K_d}{d_0 r_0^2}(C_0 - C_{\mathrm{eq}}), \quad (1a)$$

$$\beta = \frac{K_d}{K_p r_0} \quad (1b)$$

and R is the reduction degree,

$$R = \frac{\text{wt of oxygen removed from the pellet}}{\text{wt of oxygen removable from the pellet}}$$

For the sake of convenience the degree of reduction was also expressed as the percentage of reduction.

The meaning of the remaining symbols is as follows: t = time of reaction, K_d = diffusion constant, K_p = reaction rate constant of the reaction at the oxide–metal interface, d_0 = initial density of the pellet, r_0 = initial radius of the spherical pellet,

C_0 = concentration of the reducing agent in the gaseous phase and C_{eq} = concentration of the reducing agent inside the pellet, if hypothetical equilibrium is established at the oxide–metal interface. This equation can (with some approximation) be derived from the equalities:

$$K_p 4\pi r_i^2 (C_i - C_{eq}) = K_d 4\pi r_x^2 \frac{C_0 - C_i}{r_0 - r_i} = 4\pi r_i^2 \frac{dr_i}{dt}$$

where C_i is the concentration of hydrogen in the interface oxide–metal at time t and r_i is the radius of the nonreduced oxide nucleus in the pellet at the same time t. The second term is an estimate of the diffusion rate through the product layer and r_x is taken as $r_x = (r_0 \cdot r_i)^{1/2}$. It is convenient to write Eq. (1) in a linear form:

$$\frac{t}{1 - (1 - R)^{1/3}} = \frac{\beta}{\alpha} + \frac{1}{6\alpha}[1 - (1 - R)^{1/3}][2(1 - R)^{1/3} + 1]. \quad (2)$$

It is seen that a plot of

$$\frac{t}{1 - (1 - R)^{1/3}}$$

versus

$$\frac{1}{6}[1 - (1 - R)^{1/3}][2(1 - R)^{1/3} + 1],$$

should yield a straight line with the slope $1/\alpha$ and the intercept β/α.

The Seth and Ross equation has been successfully applied to describe the kinetics of iron oxide reduction (*12*). The aim of the present research was to study the applicability of this equation to the reduction of iron catalysts for ammonia synthesis.

EXPERIMENTAL METHODS

Materials

For most of the experiments the Danish catalyst Topsøe KM I was used. Either grains of a well-defined size or small cubes cut out of larger grains and polished with an accuracy up to 0.1 mm were applied. In some experiments the reduction of an industrial spherical catalyst which we shall designate with the symbol P was also studied. KM I catalyst contained 34.27% FeO and 58.20% of Fe_2O_3 (*19*). For catalyst P these values were 28.86% and 62.08%, respectively.

Apparatus

The reduction of the catalyst was carried out in a flow system with a stoichiometric mixture of hydrogen and nitrogen (3:1). The mixture was obtained by catalytic decomposition of dry ammonia at 650°C. Traces of moisture were removed using calcium chloride and traces of ammonia using concentrated sulphuric acid. Traces of oxygen were removed with the help of the BTS catalyst kindly supplied by Badische Anilin und Soda Fabrik, Ludwigshafen, West Germany. The purified gas was then introduced into the spring microbalance.

The molybdenum spiral of the balance was suspended in a vertical glass tube surrounded by a water jacket through which water from a thermostat was circulated. The glass tube was coupled with a quartz tube (ϕ = 31 mm), by means of a cooled joint. The latter tube was inserted into a tubular furnace installed vertically. The sample (0.03 to 0.2 g) was held in a platinum wire basket and suspended in the quartz tube by a quartz thread attached to the spring. The elongation of the spring was measured with a movable microscope which observed the shift of a scale fastened to the thread. It was possible to measure mass changes with an accuracy of 2×10^{-5} g. The temperature, measured by a thermocouple close to the sample, was kept constant to ±1°C. A second thermocouple between the furnace core and the reaction tube served to control the furnace temperature. Ford and Walker (*21*) who investigated the reduction of iron oxides by hydrogen-carbon monoxide found that at 1000°C the difference between the temperature of the sample and that of the reducing gas due to cooling of the sample by the reaction amounted to 30°C. In our experiments carried out at about 500°C this effect should be much less. Approximate calculations based on the equation given by Hougen *et al.* [cited in (*22*)] show that in our conditions the real temperature of the sample should not deviate more than 1°C from the temperature of the surrounding gas.

The flow rate of the reducing gas was measured with a rotameter.

Procedure

The sample was always preheated in a nitrogen stream. When the desired temperature was attained the reducing gas was passed through. After completing the experiment nitrogen was reintroduced and the sample was cooled.

Changes of mass were measured every 2 min at the beginning of the experiment and at increasing intervals up to 30 min toward the end.

RESULTS

Five series of measurements were carried out, denoted below as I–V. Examples of kinetic curves showing the degree of reduction as a function of reacting time are given in Fig. 1.

In Series I the effect of sample weight and of flow rate were investigated using KM I catalyst in the form of cubes (edge length about 1.9 mm). The reduction was carried out at 500°C and at flow rates of the reactant gas of 98 and 150 liters/hr (linear flow rates 5 and 7 cm/sec, respectively). The results are given in Table 1.

The effect of the cube size on the reduction velocity was studied in Series II. KM I cubes with an edge ranging from 1.4 to 3.3 mm were investigated. Reduction was carried out at 500°C and the flow rate was 98 liters/hr. The results of this series are given in Table 2.

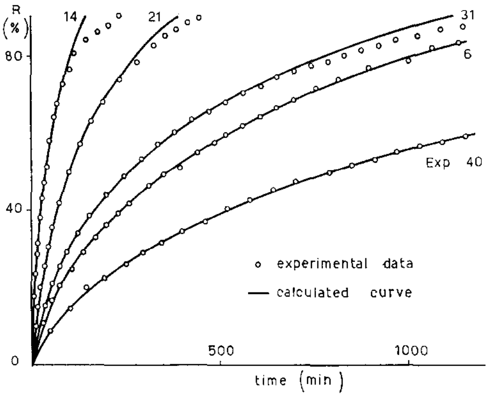

FIG. 1. Kinetic curves for reduction of iron catalysts.

In Series III the dependence of the reduction rate on temperature was investigated. KM I cubes of edge length 2.3 mm were used for this purpose. The flow rate was 98 liters/hr. Results at 450, 475, 525, and 550°C are given in Table 3.

The temperature dependence of the reduction was also studied in Series IV Spherical pellets of the industrial catalyst P were selected for these experiments, with a diameter ranging from 2.5 to 3 mm and an average radius of 1.37 mm. Five pellets were taken for each run. The measurements were carried out at 500, 525 and 550°C. The flow rate of the reducing gas was again 98 liters/hr. The results of the measurements are given in Table 4.

In Table 5 the results obtained for Series V are given. In this Series irregular grains

TABLE 1
REDUCTION OF KM I CUBES (EDGE LENGTH ~1.9 mm)

Expt. no.	R final (%)	Sample wt (g)	Flow rate (liters/hr)	K_p (cm sec^{-1})	dK_p (%)	$K_d \times 10^2$ (cm^2 sec^{-1})	dK_d (%)
20	77.4	0.0733	98	9.2	2.9	8.4	1.7
21	93.5	0.0741	98	10.5	2.4	11.2	1.5
22	91.2	0.0722	150	11.6	1.2	7.7	0.6
23	60.3	0.0361	98	7.9	6.6	7.5	4.0
24	81.7	0.0368	98	4.5	8.3	9.2	5.4
25	90.3	0.0365	150	13.0	6.1	7.4	2.5
26	58.0	0.0737	150	7.6	4.7	7.0	2.8
27	57.5	0.0369	150	6.6	5.5	7.8	3.6

TABLE 2
Reduction of KM I Cubes of Various Sizes

Expt. no.	R final (%)	Sample wt (g)	Cube edge (mm)	K_p (cm sec^{-1})	dK_p (%)	$K_d \times 10^2$ (cm^2 sec^{-1})	dK_d (%)
28	92.2	0.0392	1.4	7.2	3.5	5.8	2.0
29	82.7	0.0388	1.4	6.7	2.9	3.8	1.4
30	71.3	0.0643	2.3	8.0	1.3	4.0	0.5
31	91.5	0.0643	2.3	8.6	2.7	4.6	1.0
32	94.2	0.1081	2.8	3.9	0.8	4.6	0.4
33	70.6	0.1122	2.8	11.2	3.8	3.3	0.7
34	90.8	0.1852	3.3	4.3	1.0	4.2	0.4
35	73.1	0.1897	3.3	5.1	1.1	5.3	0.5
36	86.6	0.0334	1.9	7.9	2.3	5.6	1.1
37	71.0	0.0332	1.9	6.3	4.0	4.3	2.0

TABLE 3
Reduction of KM I Cubes at Various Temperatures[a]

Expt. no.	R final (%)	Temp (°C)	K_p (cm sec^{-1})	dK_p (%)	$K_d \times 10^2$ (cm^2 sec^{-1})	dK_d (%)
40	85.8	450	2.8	1.3	1.7	0.5
41	71.1	450	4.9	1.4	2.4	0.5
44	60.7	475	4.1	2.4	2.4	1.0
45	87.6	475	3.9	2.5	1.8	0.8
42	92.4	525	8.8	1.6	6.6	0.7
43	70.8	525	5.5	1.4	5.3	0.8
38	93.2	550	8.7	3.8	8.6	2.0
39	70.6	550	11.8	3.1	5.1	1.0

[a] Sample wt, 0.0645–0.0619 g.

TABLE 4
Reduction of Pellets of Catalyst P[a]

Expt. no.	R final (%)	Temp (°C)	K_p (cm sec^{-1})	dK_p (%)	$K_d \times 10^2$ (cm^2 sec^{-1})	dK_d (%)
1	77.1	550	14.7	3.1	7.0	1.1
2	95.4	550	13.9	1.8	7.8	0.7
3	94.0	550	11.4	4.0	4.9	1.4
4	92.0	550	8.4	4.1	5.4	1.6
6	93.0	500	4.6	3.9	3.3	1.6
7	87.1	500	5.2	3.4	3.7	1.6
9	87.0	525	10.9	3.0	5.2	1.1
10	50.4	525	6.7	3.5	3.2	1.6
11	50.7	525	6.4	3.8	3.0	1.7
12	50.4	525	8.6	4.7	5.1	2.4
13a	80.0	500	6.4	2.3	2.8	0.8
5	96.0	500	16.2	1.2	6.0	1.1

[a] Sample wt 0.2640–0.2124 g; sample wt for Expt. 13a, 0.1857 g.

TABLE 5

Reduction of Grains of Catalyst KM I[a]

Expt. no.	R final (%)	K_p[b] (cm sec^{-1})	$K_d \times 10^{2b}$ (cm^2 sec^{-1})	K_p[c] (cm sec^{-1})	$K_d \times 10^{2c}$ (cm^2 sec^{-1})	dK_p[d] (%)	dK_d[d] (%)
13	91.0	14.5	8.6	9.9	4.0	3.2	2.0
14	93.6	14.3	7.4	10.3	3.8	6.7	4.3
15	75.6	14.2	7.3	10.2	3.8	7.7	4.7
16	93.9	12.2	7.9	8.4	3.7	1.8	0.4
17	91.8	10.5	7.2	7.2	3.4	3.8	2.4
18	84.4	10.2	6.4	6.9	3.0	4.4	2.6
19	72.8	9.8	8.4	6.7	3.9	2.9	1.9

[a] Sample wt in Expts. 13, 16–19 for 9 grains: 0.0506–0.0492 g; sample wt in Expts. 14, 15 for 5 grains: 0.0223–0.0225 g; flow rate in Expts. 13–16: 98 liters/hr; flow rate in Expts. 17–19: 150 liters/hr.

[b] K_p and K_d calculated with r_0 estimated from a sphere containing the same amount of catalyst as the average grain.

[c] K_p and K_d calculated with r_0 estimated using geometric mean.

[d] Relative standard deviations of K_p and K_d are independent of the way of estimating r_0.

of KM I catalyst of sieve mesh within the range of 0.75–1.02 mm were investigated at 500°C. The reduction was carried out at flow rates of 98 and 150 liters/hr.

Discussion

General

In the analysis of our results the linearized form of the Seth and Ross Equation (2) was used. The coefficients α and β were calculated with the least squares method. An ODRA-1204 computer was used for this purpose.

It is known (*8*) that the Seth and Ross equation may not be valid for a reduction degree R close to 1. Also at the beginning of the process deviations from linearity may occur. Figures 1 and 2 illustrate graphically the results of run No. 21. For the sake of clarity in Fig. 1 only some of the experimental points are shown. The number of readings was much greater and in particular runs reached 80–100. Fig. 1 shows the plot of R against t, Fig. 2 the plot of

$$\frac{t}{1-(1-R)^{1/3}} \text{ against}$$

$$\frac{1}{6}[1-(1-R)^{1/3}][2(1-R)^{1/3}+1],$$

corresponding to the linearized form of the Seth and Ross Eq. (2). It follows from Fig. 2 that the Seth and Ross equation is satisfied for reduction degrees ranging from about $R = 0.05$ to 0.76. In general the lower limit of the applicability of the equation varied from $R = 0.05$ to 0.10 and the upper one from $R = 0.70$ to 0.80.

When calculating the parameters of the Seth and Ross equation we made use of experimental results obtained for one of the two ranges of R: 10–70% and 10–80%. From the two ranges that one was chosen which finally yielded smaller standard deviations of the α and β values. In the cases when the measurements were interrupted before the reduction degree R reached a value higher than 0.70 the R range for which the calculations were

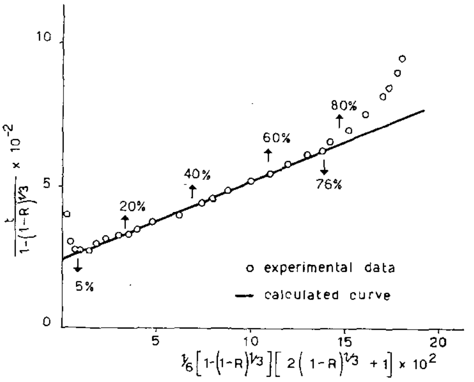

Fig. 2. The kinetic curve of reduction in the linearized coordinate system for Expt. No. 21.

TABLE 6

DIFFERENCES BETWEEN THE CALCULATED AND OBSERVED DEGREES OF REDUCTION

Reduction degree (%)	10	20	30	40	50	60	70	80	90
No. of investigated curves	45	45	45	45	45	40	38	27	18
Mean value ($R_{\text{exp}} - R_{\text{calc}}$) (%)	0.42	0.24	0.32	0.40	0.34	0.31	0.36	1.27	2.75
Largest value of ($R_{\text{exp}} - R_{\text{calc}}$) (%)	1.6	1.4	0.8	1.6	1.2	1.0	1.9	2.0	5.0

carried out was correspondingly narrower.

From the known values of α and β the detailed dependence of R on t was calculated for particular runs. From the differences between the calculated and the observed R value the mean and maximum deviations were estimated (Table 6). The comparison was carried out for several values of R differing between themselves by 10%. It follows from the table that for values up to 70% the deviations are small. Thus it could be assumed that the Seth and Ross equation describes the reduction of the catalyst well enough to be a good starting point for a discussion.

The superiority in our case of the Seth and Ross equation over other equations in which the existence of a well-defined rate-determining step is assumed may be demonstrated by using the following argument (*8*). If the interface reaction were to determine the overall reaction rate, the second term of Eq. (1) would be equal to zero and the plot of $\beta[1 - (1 - R)^{1/3}]$ against time would be linear. If, however, the diffusion were rate determining, the first term would vanish and linearity of $\{(1/2) - (R/3) - [(1 - R)^{2/3}/2]\}$ against time would be expected. In fact neither the linearity of the first term, nor of the second one was observed. The fact that also the plot of log $(1 - R)$ versus t was not linear proved additionally that, in contrast with the results given by Skarchenko *et al.* (*4*), the kinetics of reduction did not follow the first order law.

The constants K_p and K_d were calculated from α and β in accordance with Eq. (1a) and (1b). To calculate these constants we required a knowledge of d_0, r_0 and $C_0 - C_{\text{eq}}$.

The density d_0 of the catalyst was calculated from its composition (*1*, *13*). It was found for KM I that $d_0 = 4.98$ g/cm^3, and with catalyst P $d_0 = 4.91$ g/cm^3. Correction due to the change of temperature was neglected.

The calculation of the radius r_0 is certainly open to discussion. The basic question is whether the Seth and Ross equation is indeed applicable to systems which have no spherical symmetry. In investigating the cubes we assumed for r_0 a value which would yield the same amount of the catalyst in spherical form.*

For Series V where irregular grains of KM I catalyst were used their effective radius r_0 was estimated in two different ways. Either the radius of a sphere corresponding to the average weight of grain or half the geometric mean value of the sieve mesh size was taken (denoted as r_z in Fig. 4).

The difference of concentrations $C_0 - C_{\text{eq}}$ was evaluated thermodynamically. C_0 is here the experimental concentration of hydrogen in the gas phase. In order to find C_{eq} let us note that in the temperature range from 450 to 550°C the reduction of magnetite proceeds directly to iron (*14*).

Therefore we decided to estimate the value of C_{eq} from the equilibrium condition defined after Tatievskaya (*15*)

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* The Seth and Ross equation can also be derived on the assumption that the unreduced core preserves the form of a cube during the whole time of the reaction. The appropriate formula can be obtained from Eq. (1) by multiplying the left side by 2 and by replacing r_0 by the edge length a_0. Also the K_p and K_d constants must now be replaced by K_p^a and K_d^a, where $K_p^a = 0.81\ K_p$ and $K_d^a = 1.28\ K_d$. However, the reaction at the edges of the cube will certainly be faster than at its surface. Thus the shape of the oxide will continuously change from a cube into a sphere. Therefore such a modification is somewhat disputable.

$$K = \frac{C_{(\mathrm{H_2O})}{}^{\mathrm{eq}}}{C_{(\mathrm{H_2})}{}^{\mathrm{eq}}} \overset{\text{ass}}{\approx} \frac{C_0 - C_{(\mathrm{H_2})}{}^{\mathrm{eq}}}{C_{(\mathrm{H_2})}{}^{\mathrm{eq}}} \qquad (3)$$

where K is the equilibrium constant of the reaction:

$$\mathrm{Fe_3O_4 + 4H_2 = 3Fe + 4H_2O}.$$

The required values of K were obtained by interpolating the data published in the literature *(15)*.

The calculated K_p and K_d constants and their relative standard deviations (%) are given in Tables 1–5.

A Detailed Analysis of the Series

It is known *(12)* that Schenk and Schultz' results for Kiruna magnetite cubes *(16)* satisfy the equation derived by Seth and Ross. Making use of this property we have investigated the KM I catalyst in the cube form in the experimental Series I–III.

The purpose of Series I of the measurements was to investigate the influence of the sample weight and of the flow rate of the reducing gas on K_p and K_d. According to the date of Table 1 the experiment is of 2^2 factorial type *(17)*.

The analysis of variance *(18)* was carried out for these data. It follows from this analysis that there is a negligible influence of the sample weight and of the flow rate on K_p and K_d: the calculated value of the F statistics do not exceed the critical value at the 0.05 significance level. This result is an indication that the outer diffusion does not play any role in our experiments.

In Series II the effect of the grain size was investigated in detail. The results are illustrated in Fig. 3 which shows the graph of log t_R against log r_0, where t_R is the time required by the cubes to reach the given degree of reduction R. According to the Seth and Ross theory the dependence should be linear and the slope should change with R from 1 to 2 *(8)*. For small R values the surface reaction should be rate determining and the slope should be close to 1. For large values of R, on the other hand, the diffusion is expected to play the most significant role. Thus the slope should now be close to 2. As follows from Fig. 3 the dependence is approximately linear. However, the calculated slopes are slightly higher than those reported by Seth and Ross *(8)*. It seems to us that the role of diffusion was apparently more significant in our experiments than in theirs.

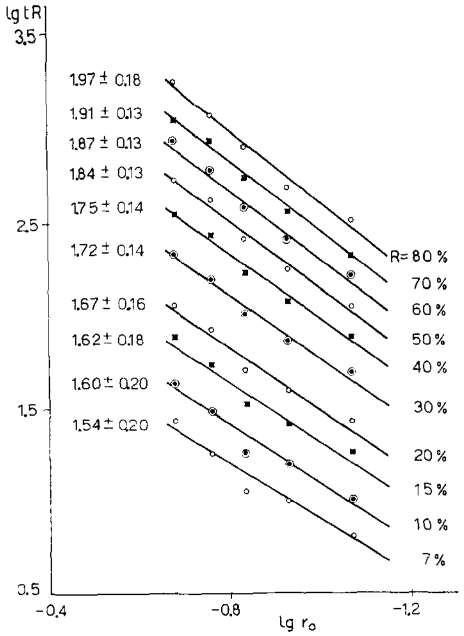

FIG. 3. The plot of log t_R versus log r_0 for several reduction degrees: (left) the slopes of the lines and their standard deviations.

The slopes which have been found for a given R value using least squares method show quite a large dispersion (Fig. 3). As follows from the figure the slopes seem to increase with R. To find if this trend is significant we have applied the 2 $(N)^{1/2}$ test *(20)* at the significance level 0.05. The result confirmed such an assumption.

The values of K_p and K_d do not depend on r_0 just as expected. This conclusion follows directly from an inspection of the data of Table 2.

The purpose of Series III of the measurements was to investigate the effect of temperature on the reduction rate. The results are given in Table 3. They correspond to the KM I catalyst in the form of cubes. In accordance with the data both K_p and K_d increase with temperature.

The activation energy calculated from the Arrhenius equation by the least squares method for the value K_p was 12.5 ± 3.6 kcal/mole. Because of the relatively large dispersion of K_d values [for Series I $K_d \times 10^2 = 8.5 \pm 1.2$ cm^2/sec; for Series II $K_d \times 10^2 = 4.6 \pm 0.6$ cm^2/sec], the activation energy of the diffusion process could not be obtained with satisfactory accuracy. Rejecting the results of Series I one would obtain about 16 kcal/mole for this energy. This is certainly too large a value for the diffusion of a gas. Such an increased value of the activation energy is likely to be caused by a change of the texture of the catalyst with temperature. In fact Hall, Tarn and Anderson (*1*) found a distinct change of the porous structure with the temperature of reduction in the case of the fused iron catalysts D 3001 and D 3006. With D 3001 the average radius of the pore was 371 Å after reduction at 450°C and 917 Å after reduction at 550°C. The corresponding values for the other catalyst were 366 and 800 Å increasing even up to 2420 Å for the reduction temperature of 650°C. However, the discrepancy between the results of Series I and II still remains unexplained. Perhaps a simultaneous measurement of the reduction rate and the determination of the texture could settle the point. From Series IV with catalyst P, K_p and K_d were calculated at different temperatures. Their values are slightly lower than those for KM I but they are more scattered and the activation energies are therefore not given here. More detailed investigations on this point are required.

As already said the Seth and Ross equation was derived for spherical pellets. Commonly, however, the shape of a reduced grain of the oxide is not regular. The effect of such an irregularity was analyzed in the experimental Series V. In this series K_p and K_d were determined for irregular grains, the results being compared with those obtained for cubes. As mentioned already the K_p and K_d constants were evaluated in two ways in this series differing in the estimate of the radius.

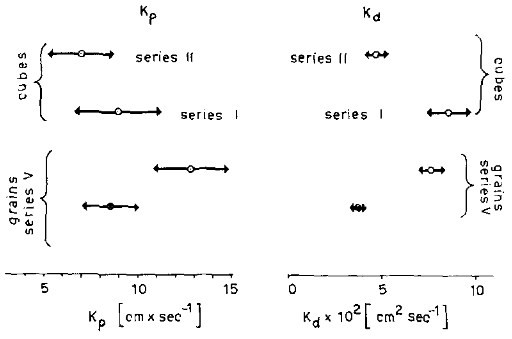

FIG. 4. 95% confidence intervals of K_p and K_d for the KM I catalyst corresponding to 500°C: values which follow from r_z are denoted by ⊗.

The mean values of K_p and K_d found in Series I, II and V are shown in Fig. 4 together with the calculated 95% confidence intervals. As follows from the figure, the values of the constants are comparable although the confidence intervals do not always overlap. The confidence intervals are smaller if the geometric mean value is used for calculating r_0. Also the overlap of the confidence intervals for K_p is better in this case. However, the overlap of the confidence intervals for K_d is now worse, the dispersion probably being caused by the discrepancy between the results of Series I and II.

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