

## KINETICS OF CATALYZED REACTION OF METHANOL WITH WATER VAPOUR

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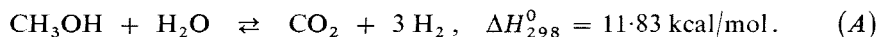
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Kinetics of methanol conversion with water vapour on a low-temperature catalyst of the composition  $\text{CuO-ZnO-Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  was studied at 1 atm, at temperatures 220–250°C and at different  $\text{CH}_3\text{OH} : \text{H}_2\text{O}$  ratios. The reaction course can be expressed by a kinetic equation in the form  $r = k p_A^{0.4} p_B^{0.6}$ , where  $p_A$  and  $p_B$  are partial pressures of methanol and water vapour, respectively. This relation can be simplified with satisfactory accuracy to the form  $r = k(p_A p_B)^{0.5}$ . Of the relations, based on the Langmuir-Hinshelwood concepts, the equation  $r = k K_1 K_2 p_A p_B : (1 + K_1 p_A + K_2 p_B)^2$  was found to be suitable which was derived under the assumption that the rate controlling process is the surface reaction  $\text{CH}_3\text{OHn} + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 (\text{g}) + \text{CO}_2 (\text{g}) + 2 \text{n}$ .

One of the possible ways of preparation of hydrogen for oxygen-hydrogen fuel cells is the catalytic conversion of methanol with water vapour. This procedure has been the subject of several studies<sup>1-11</sup>. Most of these works, however, are concerned with practical problems connected with the application of the conversion reaction and they deal above all with the preparation and application possibilities of suitable catalysts. However, detailed data on the kinetics of this reaction are so far lacking. This question has been dealt with only in papers<sup>5,6,9,10</sup> in which the composition of the inlet gas and the formation of by-products is studied.

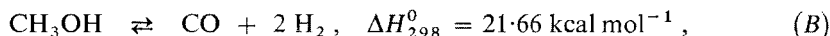
The aim of the present paper was to determine the principal kinetic data of the conversion reaction on a selected low-temperature catalyst which could serve in designing the reaction conditions for the above-mentioned method of the preparation of hydrogen and at the same time could be a basis for the concepts on the course of the reaction itself.

Conversion of methanol by water vapour can be described by the over-all equation



According to this equation, the outlet gas should contain, at total conversion of methanol after condensation of water vapour, which is always used in excess, 25%  $\text{CO}_2$  and 75%  $\text{H}_2$ . However, the mixture after conversion contains always also carbon monoxide. Thus it is evident that the reaction proceeds *via* a complex mechanism

and can be, in the first approximation, considered to consist of two consecutive reactions, the first step being the decomposition of methanol to hydrogen and carbon monoxide which in the second step reacts with water vapour



In addition to these main reactions, several side reactions can of course proceed in this system whose products are methane, higher hydrocarbons, alcohols and formaldehyde<sup>9-12</sup>. The course of these side reactions can be minimalized by a suitably chosen catalyst and by reaction conditions so that the study can then be limited to the analysis of the mentioned two reactions.

These partial reactions, particularly that of carbon monoxide with water vapour, were the subject of a number of studies. Reaction (B) was investigated mainly from the standpoint of methanol synthesis<sup>12,15</sup>. A review of works on the shift reactions of carbon monoxide with water vapour is given in papers<sup>13,14</sup>. From this survey it is clear that so far no accordance has been attained as to the course of even this most simple reaction; on the contrary, the results of different authors are often contradictory.

Conversion of methanol by water vapour is possible to assume to consist of two steps, according to Eqs (B) and (C). The equilibrium constants of the decomposition of methanol,  $K'_2$ , and of conversion of carbon monoxide by water vapour,  $K'_3$ , are given by the expressions

$$K'_2 = \frac{(x - y) \cdot (2x + y)^2}{(1 + 2x + a)^2 (1 - x)} \cdot P^2, \quad (1)$$

$$K'_3 = y(2x + y)/(x - y)(a - y), \quad (2)$$

where  $x$  is the conversion of  $\text{CH}_3\text{OH}$  in mol,  $y$  is the conversion of  $\text{CO}$  in mol,  $a$  is the number of mol of water vapour,  $P$  is the total pressure. The values of thermodynamic quantities necessary for determining the equilibrium constants and for calculating the equilibrium composition were taken from the literature<sup>16</sup>.

By simultaneous solution of Eqs (1) and (2) we obtained the values of  $x$  and  $y$  from which the equilibrium composition of the mixture at various temperatures could be calculated, as shown in Table I. From the values presented it is clear that at the given temperatures methanol can almost completely decompose to carbon monoxide and hydrogen. Actually, also this reaction proceeds, for kinetic reasons, only to a certain degree and it is possible to calculate the equilibrium content of  $\text{CO}$  in the reaction mixture after condensation of the non-reacted water vapour which

corresponds to a certain degree of methanol decomposition. These equilibrium values of CO are presented in Table II.

From the practical point of view it is desirable that the content of CO<sub>2</sub> in the gaseous mixture might be as low as possible and the total conversion of CH<sub>3</sub>OH as high as possible. The attainable content of CO is the smaller the lower is the conversion temperature and the lower is the degree of methanol decomposition according to Eq. (B). Increase in pressure results in a shift of the equilibrium to the higher degree of decomposition, however, even at 10 atm, the equilibrium is shifted rather to the right and the pressure dependence in this range of pressures is not too much manifested. The equilibrium is also shifted owing to the fact that CO is immediately consumed in reaction (C). The decrease of the CO content can therefore be realized in two ways, either by lowering the temperature or by using excess of water. A great excess of water is of course not advantageous. Lowering of temperature is limited by the activity of the catalyst used.

### EXPERIMENTAL AND RESULTS

*Apparatus.* The course of the reaction was followed in an isothermal integral reactor, schematically shown in Fig. 1. A solution of methanol and water is continuously fed by a piston micropump

TABLE I

Dependence of Equilibrium Values of  $x$  and  $y$  and of Equilibrium Content of CO after Condensation of Water Vapour on Temperature and on Molar Ratio CH<sub>3</sub>OH : H<sub>2</sub>O

CH <sub>3</sub> OH : H <sub>2</sub> O	°C	$x$	$y$	CO eq. %
1 : 1	200	0.9988	0.8932	2.72
	230	0.9995	0.8643	3.50
	250	0.9997	0.8368	4.25
	300	0.9999	0.7706	6.08
1 : 1.2	200	0.9994	0.9503	1.24
	230	0.9998	0.9264	1.87
	250	0.9999	0.9017	2.52
	300	0.9999	0.8380	4.22
1 : 1.5	200	0.9998	0.9756	0.61
	230	0.9999	0.9608	1.00
	250	0.9999	0.9439	1.42
	300	1.0000	0.8946	2.71
1 : 2	200	0.9999	0.9872	0.32
	230	0.9999	0.9788	0.53
	250	1.0000	0.9688	0.79
	300	1.0000	0.9363	1.62

TABLE II

Values of CO Content in Dependence on Methanol Decomposition, Temperature and Molar Ratio  $\text{CH}_3\text{OH} : \text{H}_2\text{O}$  after Condensation of Water Vapour

Molar ratio $\text{CH}_3\text{OH} : \text{H}_2\text{O}$	$x$	% CO			
		200°C	230°C	250°C	300°C
1 : 1	0.9	1.66	2.36	3.05	4.70
	0.7	0.63	1.01	1.44	2.68
	0.5	0.26	0.42	0.63	1.29
	0.3	0.09	0.15	0.22	0.48
1 : 1.2	0.9	0.84	1.32	1.84	3.31
	0.7	0.40	0.65	0.96	1.90
	0.5	0.18	0.31	0.46	0.97
	0.3	0.07	0.12	0.17	0.38
1 : 1.5	0.9	0.46	0.75	1.09	2.16
	0.7	0.25	0.42	0.63	1.30
	0.5	0.13	0.22	0.33	0.70
	0.3	0.05	0.09	0.13	0.28
1 : 2	0.9	0.26	0.43	0.64	1.33
	0.7	0.16	0.26	0.40	0.84
	0.5	0.09	0.15	0.22	0.48
	0.3	0.04	0.06	0.09	0.20

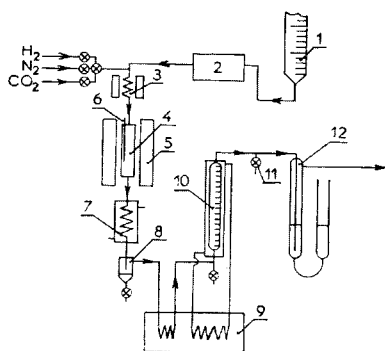


FIG. 1

Scheme of the Apparatus  
For description see text.

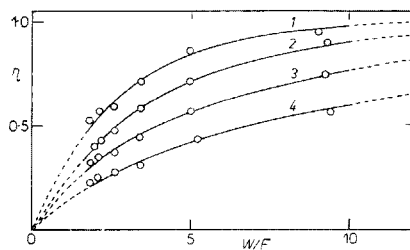


FIG. 2

Kinetic Isotherms for Molar Ratio  $\text{CH}_3\text{OH} : \text{H}_2\text{O} 1 : 1.5$

Pressure 1 atm. Temperature: 1 250°C,  
2 240°C, 3 230°C, 4 220°C.  $W/F$  is given  
in  $\text{g h mol}^{-1}$ .

2 from a measuring burette 1 into preheater 3, heated to 120°C. Here the solution is evaporated and the gaseous mixture proceeds into reactor 4, placed in a block oven 5 with controlled heating. Temperature within the reactor was measured by means of a Fe-Constantan thermocouple, placed in the bed of catalyst 6. The catalyst was coated in the reactor on a support made of sintered glass. The converted gas is led from the reactor into the cooler 7 where the unreacted portions of water and methanol are condensed and caught in the separator 8. The gas is then led through thermostat 9 into the thermostated flowmeter 10. Constant pressure in the apparatus was maintained by means of manostat 12. Gas samples for analysis were taken before manostat 11. The determination of CO<sub>2</sub> was carried out in an Orsat apparatus, CO was determined using gas chromatograph Chrom 3-I (Laboratorní přístroje, Prague). In the place, where methanol is fed in, an inlet is attached, allowing to dose the inert gas or the reaction products into the reaction mixture and also to feed the H<sub>2</sub>-N<sub>2</sub> mixture for the reduction of the catalyst.

*The catalyst used.* On the basis of preliminary experiments a low-temperature catalyst of the type CuO-ZnO-Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> was chosen. The catalyst used, prepared in the laboratory,

TABLE III  
Constants of the Interpolated Polynomials

CH <sub>3</sub> OH : H <sub>2</sub> O	°C	$a_0$ g h mol <sup>-1</sup>	$a_1$ g h mol <sup>-1</sup>	$a_2$ g h mol <sup>-1</sup>	$a_3$ g h mol <sup>-1</sup>
1 : 1	220	0.005	10.335	28.510	
	230	0.023	7.032	10.441	
	240	0.043	2.702	11.502	
	250	0.059	-1.475	12.649	
1 : 1.1	220	-0.005	10.591	28.577	
	230	0.050	5.754	13.874	
	240	0.021	3.239	10.580	
	250	0.033	1.656	9.763	
1 : 1.3	220	-0.009	6.414	25.333	
	230	-0.005	3.450	19.547	
	240	0.017	2.861	8.797	
	250	-0.006	11.315	-25.762	24.693
1 : 1.5	220	0.003	2.1512	26.428	
	230	-0.005	-0.327	16.972	
	240	-0.003	9.782	-21.470	24.483
	250	0.026	-4.220	13.341	
1 : 2	220	-0.044	3.780	21.357	
	230	0.017	-3.103	20.671	
	240	0.028	-3.958	14.235	
	250	-0.002	28.891	-77.909	58.3855

had the following composition: 22.3% CuO, 17.5% Al<sub>2</sub>O<sub>3</sub>, 24.2% ZnO and 22.5% Cr<sub>2</sub>O<sub>3</sub>. Loss by ignition was 14.5% bulk weight 0.573 g/cm<sup>3</sup>, total surface area of the catalyst in non-reduced state 262 m<sup>2</sup>/g. For kinetic studies 4 g of the catalyst were used of the grain size 0.8–1.0 mm. The catalyst was mixed with crushed glass of the same grain size in the 4 : 1 ratio. Preliminary measurements have shown that at the given grain size the reaction proceeds in the kinetic region. Prior to measurement, the catalyst was reduced in the reactor in a nitrogen–hydrogen mixture (3% H<sub>2</sub>) at 170–240°C and at a flow rate of 3.75 l/g h.

Kinetic isotherms (dependence of conversion on the feed rate) were determined at 220, 230, 240 and 250°C, with feed 0.35–2.3 mol of the mixture per g and at molar ratios CH<sub>3</sub>OH : H<sub>2</sub>O 1 : 1, 1 : 1.1, 1 : 1.3, 1 : 1.5 and 1 : 2. An example of the course of kinetic isotherms is shown in Fig. 2.

*Evaluation of data.* The total degree of conversion was calculated from the measured values of the flow rate of the converted gas, from the content of CO<sub>2</sub> and of CO, according to the relation

$$\eta = v(\% \text{CO}_2 + \% \text{CO})/22.4Fn_0 \quad (3)$$

and the degree of conversion to CO<sub>2</sub> according to Eq. (4)

$$\eta(\text{CO}_2) = v(\% \text{CO}_2)/22.4Fn_0, \quad (4)$$

where  $v$  is the flow rate of the gaseous mixture in Nl/h,  $F$  is the total feed of the solution in mol/h,  $n_0$  is the mole fraction of methanol in the solution, (% CO<sub>2</sub>) and (% CO) are the contents of the respective components in the gaseous mixture.

The reaction rate can be derived from the dependence of the conversion on the quantity  $W/F$ , where  $W$  is the amount of catalyst in g and  $F$  is the feed of the solution in mol/h, according to the relation

$$r = n_0 \, d\eta/d(W/F). \quad (5)$$

The determination of reaction rates was carried out both by graphical derivation of the individual kinetic isotherms in the respective points of  $\eta_1$  and by numerical derivation. In the latter case, the kinetic isotherms or their inversion functions were interpolated by a polynomial of the 2nd or 3rd order

$$W/F = a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 \quad (6)$$

and the values of derivation of Eq. (6) by  $\eta$  were calculated. The reaction rate, as defined by Eq. (5) is then given by the expression

$$r = n_0(a_1 + 2a_2\eta + 3a_3\eta^2). \quad (7)$$

The values of reaction rates, obtained by the two methods, were compared and evaluated. It turned out that the differences lie within the limits of 5% maximum which

means that with respect to the experimental errors of the kinetic measurements the agreement is fairly good. Nevertheless, the numerical method of determining the values of reaction rates from the measured kinetic isotherms appears to be more suitable, first of all because it is not charged with errors, arising from the graphical construction of tangents and also because the numerical method can easily be adapted for computing which makes the evaluation easier, especially when a great set of data is available. The values of constants of the respective polynomials (6) for kinetic isotherms, as obtained by the method of least squares, are summarized in Table III.

*Determination of the effect of reverse reaction.* To ascertain the effect of reverse reaction conversions of methanol were followed in the presence of higher concentrations of the reaction products, *i.e.* hydrogen and carbon dioxide. The presence of both components was found to have no effect on the reaction course in the measured temperature range and concentration range and thus the effect of reverse reaction is negligible.

## DISCUSSION

The main products of the conversion reaction are carbon dioxide and hydrogen which corresponds to the over-all reaction (A). In all cases the converted gas contains also carbon monoxide. In accordance with the theoretical analysis its content is the lower, the higher is the excess of water vapour and the lower is the conversion temperature. However, the experimentally found content of CO was in most cases lower than that derived by theoretical calculations for the respective degree of methanol conversion, assuming the two-step course of the reaction. The same conclusion was also made

TABLE IV  
Values of Constants of Eq. (8) in Dependence on Temperature and Their Statistical Test

$t, ^\circ\text{C}$	$k_1$ (mol CH <sub>3</sub> OH)g <sup>-1</sup> h <sup>-1</sup> atm <sup>-(m+n)</sup>	$\sigma_k \cdot t_{\pm}^a$	$m$	$\sigma_m \cdot t_{\pm}^a$	$n$	$\sigma_n \cdot t_{\pm}^a$	$\overline{\Delta r}_r^b$ %
220	0.0742	0.0003	0.49	0.020	0.48	0.024	4.1
230	0.1418	0.0003	0.41	0.005	0.61	0.009	3.8
240	0.2308	0.0010	0.41	0.005	0.60	0.009	3.0
250	0.3849	0.0035	0.36	0.004	0.74	0.006	2.0
<i>Average</i>			0.42		0.60		

<sup>a</sup>  $\sigma_i \cdot t_{\pm}$  Product of scattering of the respective constant and of the critical value of  $t_{\pm}$  for the determination of the reliability interval<sup>17</sup>. <sup>b</sup>  $\overline{\Delta r}_r$  Mean relative deviation of the reaction rate.

by Prigent and coworkers<sup>5</sup>. This fact can be explained so that a part of CO is consumed in parallel proceeding reactions, yielding higher alcohols, acetic acid and formaldehyde which were found in small amounts in the condensed product.

The content of carbon monoxide, however, is small in all cases so that the difference between the total conversion and the conversion to carbon dioxide is only small, and consequently also the reaction rate of total conversion of methanol differs only little from that of conversion to carbon dioxide. At the content of 0.6% CO the difference in the reaction rates is about 5%, at 1.4% CO the error is about 14.5%. With respect to the fact that in most cases the content of CO is lower than 0.6%, only total reaction rates of methanol conversion were determined for simplicity sake and these values were used for further deductions and discussions on the reaction course.

In the first step the measured data were correlated with the empirical kinetic equation in the power form

$$r = k p_A^m p_B^n p_C^2 p_D^s \quad (8)$$

(A = CH<sub>3</sub>OH, B = H<sub>2</sub>O, C = CO<sub>2</sub>, D = H<sub>2</sub>).

Since it was experimentally found that the reaction rate does not depend, in the studied region, on partial pressures of carbon dioxide and of hydrogen, the equation can be written in the simplified form

$$r = k_1 p_A^m p_B^n \quad (9)$$

The values of constants  $k_1$ ,  $m$  and  $n$  were obtained by the method of linear regression using the computer Tesla 200. The results are presented in Table IV. From these results it follows that the equation of the reaction rate of conversion can be written in the form

TABLE V

Dependence of the Values of Rate Constant  $k_2$  in Eq. (11) on Temperature and Their Statistical Test

°C	$k_3$ (mol CH <sub>3</sub> OH) g <sup>-1</sup> h <sup>-1</sup> atm <sup>-1</sup>	$\sigma_{k_3} \cdot t \pm$	$\frac{\Delta r}{r}$ %
220	0.0760	0.00001	4.5
230	0.1433	0.00002	4.3
240	0.2368	0.00005	3.0
250	0.3591	0.00020	2.2



$$r = k_2 p_A^{0.4} p_B^{0.6}, \quad (10)$$

in which the reaction rate is described with an average error of 3.1%. When written in the simplified form

$$r = k_3 (p_A p_B)^{0.5}, \quad (11)$$

the equation still fits very well the reaction course with an average error 3.5% which still lies within the limits of experimental errors. The values of the rate constant  $k_3$  were then calculated for equation (11), using the method of linear regression. Their temperature dependence is shown in Table V. The dependence of the logarithm of the rate constant  $k_3$  on the reciprocal value of temperature,  $1/T$ , as shown in Fig. 3, was used to calculate the value of the apparent activation energy,  $E = 24.8 \text{ kcal mol}^{-1}$ .

The mentioned kinetic equation (11) allows a relatively easy calculation of reaction rates for different reaction conditions, as it is necessary *e.g.* for the calculation of the quantity of the catalyst for the conversion reactor, however, it does not provide any data for speculations on the possible reaction mechanism. However, the non-integer exponents indicate a complex character of the reaction.

In the second step it was attempted to derive and interpret the kinetic relations on the basis of Langmuir-Hinshelwood assumptions. A general derivation of an equation, including both the adsorption of all components and the sequence of elementary reactions, results in a relation of such complexity that its verification and interpretation becomes practically impossible, for the very reason of the great number

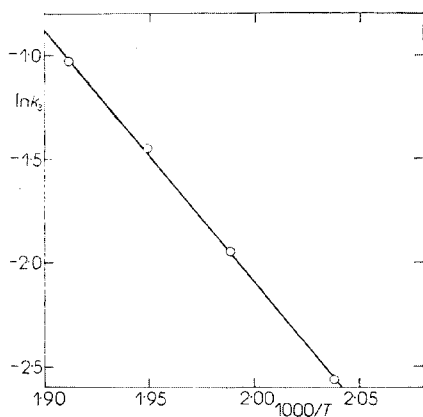


FIG. 3  
Dependence of  $\ln k_3$  on  $1/T$

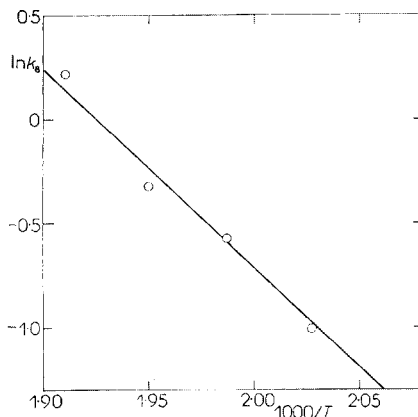
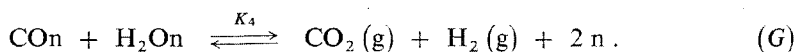
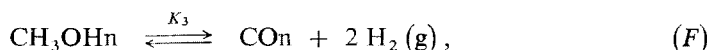
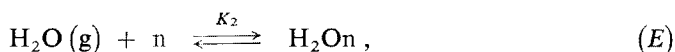
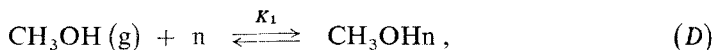


FIG. 4  
Dependence of  $k_3$  on  $1/T$

of constants. Therefore, only the simplified scheme and the irreversibility of the total reaction were considered in deriving the relations.

Let us now assume that the reaction course can be described by the following scheme



Kinetic relations are derived, assuming always one single controlling reaction in which the reverse reaction is neglected. The assumptions employed and the respective derived equations are summarized as follows:

a) The controlling step is the adsorption of methanol on one centre:

$$r = \frac{k_4 p_A}{1 + K_2 p_B + (K_2 K_4)^{-1} p_C p_D p_B^{-1} + (K_2 K_3 K_4)^{-1} p_C p_D^3 p_B^{-1}}. \quad (12)$$

b) The controlling step is the adsorption of water vapour on one centre:

$$r = \frac{k_5 p_B}{1 + K_1 p_A + K_1 K_3 p_A p_D^{-2} + (K_1 K_3 K_4)^{-1} p_C p_D^3 p_A^{-1}}. \quad (13)$$

c) The controlling step is the surface decomposition of methanol on one centre:

$$r = \frac{k_6 K_1 p_A}{1 + K_1 p_A + K_2 p_B + (K_2 K_4)^{-1} p_C p_D p_B^{-1}}. \quad (14)$$

d) The controlling step is the surface reaction of carbon monoxide with water vapour on two centres:

$$r = \frac{k_7 K_1 K_2 K_3 p_A p_B p_D^{-2}}{(1 + K_1 p_A + K_2 p_B + K_1 K_3 p_A p_D^{-2})^2}. \quad (15)$$

e) The controlling step is the surface conversion of methanol by water vapour on two centres:

$$r = \frac{k_8 K_1 K_2 p_A p_B}{(1 + K_1 p_A + K_2 p_B)^2} \quad (16)$$

The values of the individual constants for the suggested Eqs (12)–(16) were evaluated, similarly as for the power form of the equation, from the experimentally obtained reaction rates using the method of non-linear regression and the validity of the proposed relations was verified.

The found dependence of the reaction rate on concentration of the components in the feed indicates that the reaction rate depends on the partial pressure of methanol approximately in the same way as on the partial pressure of water vapour, which follows also from the power equation (11). However, Eqs (12)–(14) do not conform with this assumption. In numerical evaluation the constants of these equations can even attain negative values and the dependences of reaction rates derived from these equations do not agree with the experimentally found ones. This means that Eqs (12)–(14) do not provide an adequate description of the reaction course and their validity for this case is not satisfactory. Owing to the non-reality of the values of individual constants neither Eq. (15) can be applied to describe the kinetics of the system. An expression formally identical with Eq. (16) is also obtained from Eq. (15) which can be simplified under certain assumptions. The experimentally measured reaction rates in excess hydrogen revealed the independence of the reaction rate of  $p_D$ . In this case the partial pressure of hydrogen can be taken as constant and relation (15) is, after simplification, identical with Eq. (16), except for constant  $K_1$  which then represents a combination of the adsorption constant of methanol and of the equilibrium constant of the methanol decomposition. The values of the evaluated constants together with the testing of Eq. (16) are presented in Table VI. From the results found it follows that the form of Eq. (16) expressed the course of the studied reaction under the given experimental conditions with an average error 5.8%; as shown in Fig. 4. The value of the apparent activation energy, calculated from the plot  $\ln k_8$  vs  $1/T$ ,

TABLE VI

Dependence of the Values of Constants of Eq. (16) on Temperature and Their Statistical Test

°C	$k_8$ (mol CH <sub>3</sub> OH) g <sup>-1</sup> h <sup>-1</sup>	$\sigma_{k_8} \cdot t \pm$	$K_1$	$\sigma_{k_1} \cdot t \pm$	$K_2$	$\sigma_{k_2} \cdot t \pm$	$\overline{\Delta r_r}$ %
220	0.332	0.013	2.33	0.52	1.51	0.31	3.6
230	0.577	0.014	3.35	0.34	1.37	0.15	5.8
240	0.716	0.016	4.63	0.59	1.30	0.17	5.9
250	1.277	0.084	5.61	0.72	1.25	0.13	8.5

is  $E' = 18.9 \text{ kcal mol}^{-1}$ . Its numerical value is in this case lower in comparison with the value of the activation energy calculated from the temperature dependence of the rate constant  $k_2$  from Eq. (11). One explanation is that in Eq. (11) constant  $k_2$  represents the rate constant of the over-all reaction which includes further temperature-dependent parameters, whereas in Eq. (16) constant  $k_8$  is merely the rate constant of the rate limiting reaction and the temperature-dependent parameters  $K_1$  and  $K_2$  which would also affect the value of the total activation energy appear in Eq. (16) explicitly.

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