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**HEAT AND MASS TRANSFER  
IN HETEROGENEOUS CATALYSIS. XXII.\*****STUDY ON EFFECTS OF HEAT  
AND MASS TRANSFER BETWEEN THE EXTERNAL SURFACE  
OF CATALYST PARTICLE AND THE BULK  
OF REACTION MIXTURE ON REACTION RATE  
OF HYDROGEN WITH OXYGEN**

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A study was made on the effect of heat and mass transfer between the external surface of the catalyst particle and the bulk of the reaction mixture on the reaction rate of hydrogen with oxygen. In a flow reactor with one pellet of platinum catalyst were measured the reaction rate and the temperature difference between the pellet centre and the flowing reaction mixture at hydrogen concentrations in air from 0 to 3.9 vol. % and in the temperature range from  $-5$  to  $82^{\circ}\text{C}$ . It was proved that in a certain region of temperatures two stable steady states exist at the same concentration and temperature in the flowing reaction mixture. As consequence of these two steady states is the existence of hysteresis effects on the dependence of the reaction rate on concentration and on the dependence of the reaction rate on temperature.

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In the preceding paper<sup>1,4</sup> was studied on a mathematical model of a catalyst pellet the effect of heat and mass transfer between the external surface of the catalyst particle and the bulk of reaction mixture (the effect of external heat and mass transfer) on the reaction rate. From results of this study has followed that for strongly exothermic reactions it is possible to expect two stable steady states at the same concentration of the reactant and at the same temperature of the bulk of reaction mixture, the result of which is an overheating of the catalyst particle surface. Due to the existence of two steady states, the reaction rate is dependent on the reactant concentration and the reaction rate dependence on temperature is discontinuous and the hysteresis effects appear *i.e.* the reaction rate is different when the concentration or temperature is increasing than in the case when concentration or temperature is decreasing. The aim of this study is the experimental verification of the conclusions made on the basis of the above mentioned mathematical model studies.

As the model reaction was chosen the reaction of hydrogen with oxygen carried out in such a way that small amount of hydrogen was added to air in excess. This

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reaction is a suitable model reaction as it is at ordinary temperatures practically irreversible because it has no side-reactions and is strongly exothermic  $\Delta H_{298.1^{\circ}\text{K}} = -57.8$  kcal/mol hydrogen. From literature the reaction kinetics on the platinum catalyst may be in a narrow range of conditions expressed by the rate equation

$$r = k p_{\text{H}}^n \quad (1)$$

in which the reaction order  $n$  is mostly equal to one<sup>2</sup>.

## EXPERIMENTAL

### Catalyst

The catalyst was platinum (0.5 weight %) on alumina as a carrier; it was prepared by drying the alumina paste (size of particles from 0.05 to 0.08 mm) impregnated by water solution of the chloroplatinic acid (Safina, Vestec) at 95°C for 10 hours. After drying, the acid was decomposed by heating in the electric oven at 500°C for 5 hours in the air stream. The catalyst prepared in this way was tableted into pellets of 7.2 mm diameter times 7.1 mm height. The reduction of the catalyst was performed in the reactor by hydrogen (flow rate 10 l/h) at 300°C for 3 h. The reduced catalyst might be kept in contact with air but before the measurement its activation by active hydrogen was necessary (flow rate 10 l/h) at 180°C for 10 h.

### Apparatus

The measurement was made in a flow reactor at atmospheric pressure in the range of temperatures from -5 to 82°C and in the range of hydrogen concentrations in air from 0 to 3.9 vol.%. The complete arrangement of the apparatus is in Fig. 1. Hydrogen and oxygen as reactants were taken from pressure vessels and their volumetric flow rate was measured by capillary flow meters filled with evacuated silicon oil. The accuracy with which both the reactants were measured were  $\pm 1$  to 5 relative % of hydrogen and  $\pm 1$  relative % of air. Both components were purified from alkaline impurities on pellets of phosphorous pentoxide on kieselguhr. The traces of oxygen in hydrogen were removed by copper on kieselguhr as catalyst at 180°C. For drying of both components was used a molecular sieve (Calcit A4). After mixing the gases, the mixture passed through a heating coil into the reactor. The reactor was a tube of inside diameter 20 mm and 200 mm long, placed in an oil or water bath in which the temperature was kept constant with an accuracy  $\pm 1^{\circ}\text{C}$ . The measurement was made on a single pellet of the catalyst which was freely hanged in the reactor tube. The weight of the pellet was  $W = 0.3820$  g, the external surface of the pellet per unit of catalyst weight was  $a_m = 0.6335$  m<sup>2</sup>/kg. In the measurement the composition of the reacting mixture at the inlet and outlet of the reactor and the temperature difference between the center of the catalyst pellet and the bulk of the reaction mixture were measured.

### Analytical Method

The hydrogen concentration in the reacting mixture was determined by the use of a diffusion cell<sup>3</sup>. The principle of this analytical method is the recording of the resistance change of a platinum filament according to the heat evolved at combustion of hydrogen on the platinum black. The diffusive two-filament cell is arranged in such a way that the accuracy of the analytical method

is not affected if the flow rates of gases slightly fluctuate. Also a small content of water vapours in the reacting mixture is not affecting results of the analysis. For avoiding the necessity to calibrate the cell to the concentration of hydrogen in the reacting mixture, the reactor was arranged so that it was possible to calibrate the reacting mixture at the inlet and at the outlet of the reactor. During the measurement the flow rate of the reacting mixture through the combustion cell was kept constant at the rate 30 l/h. As the recording instrument was used the recorder EZ 4. The accuracy of determination of hydrogen conversion was  $\pm 0.8$  to 1 relative %. The reaction rate corresponding to this hydrogen conversion was determined on the basis of the assumption of validity of differential behaviour of the flow reactor. The hydrogen conversion was kept during the measurement within the range from 0 to 0.25 by selection of reacting conditions. The estimated error in determination of the reaction rate was then  $\pm 5$  relative %.

#### Measurements of the Catalyst Pellets Temperature

In the experiments, simultaneously with the reaction rate was measured the temperature in the center of the catalyst pellet and the temperature in the flowing reaction mixture. In some measurements also the temperature on the external surface of the pellet was measured by a thermocouple fixed directly to the cylindrical part of the pellet.

The temperature in the center of the pellet and in the flowing reaction mixture was measured by thermocouples (Fig. 2). The thermocouples were of the copper-constantan type for tempe-

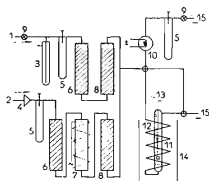


FIG. 1

#### Flow Sheet of Apparatus

1 Air inlet, 2 hydrogen inlet, 3 water manostat, 4 manostat (Research Workshop of Czechoslovak Academy of Sciences, Prague), 5 capillary flow meter, 6 column with pellets of phosphorous pentoxide on alumina, 7 column with copper catalyst on kieselguhr, 8 drying column, 9 needle valve, 10 combustion diffusion cell, 11 preheating coil, 12 reactor, 13 thermocouple, 14 bath of reactor, 15 gas outlet.

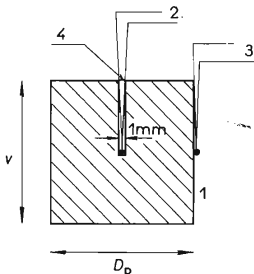


FIG. 2

#### Arrangement for Temperature Measurements in the Catalyst Pellet Centre

$v$  Pellet height,  $D_p$  pellet diameter, 1 pellet, 2 thermocouple for temperature measurement in the interior of pellet, 3 thermocouple for temperature measurement on external pellet surface 4 asbestos packing.

temperature measurements in the pellet center (the copper wire of 0.1 mm diameter was painted, the constantan one of diameter 0.08 mm had a teflon insulation 0.01 mm thick) and of platinum, gold, palladium-platinum, rhodium for temperature measurements of the flowing reaction mixture (the wires of composition 2% Pt, 49% Au, 49% Pd, or 90% Pt, 10% Rh were of 0.1 mm diameter with a teflon insulation 0.01 mm thick). The electromotive force of the thermocouple for measurement of temperature of the flowing reaction mixture fixed in the probe placed in the axial axis of the reactor was taken by a technical compensator Metra QTK, of the thermocouple for measurement of temperature in the pellet center by a recorder EZ 4. The accuracy of measurement of temperature differences between the pellet center and the bulk of the reaction mixture was estimated to be in the range of  $\pm 0.5^\circ\text{C}$ .

To check how reliable is the direct measurement of the temperature of the pellet surface by a thermocouple fixed to it, model measurements were made with a metal pellet electrically heated. As the metal pellet has a high thermal conductivity its surface should have the same temperature as its center. But from these experiments appeared that the thermocouple at the surface was not measuring exactly the surface temperature of the pellet but a temperature for about 15 to 20 rel. % less than was the difference between the exact surface temperature and the temperature of the flowing gases. At the chemical reaction was directly measured temperature difference between the pellet surface and the flowing gas about 15 to 30 rel. % of the temperature difference between the pellet center and the flowing gas, 15 rel. % in the range of strong external diffusion effect and 30 rel. % in the range where the effect of external heat and mass transfer is weak. From comparison with the results of model measurement it may be concluded, that at chemical reaction the

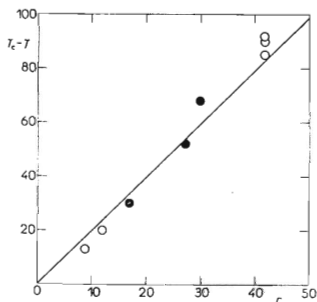


FIG. 3

Dependence of Temperature Difference ( $^\circ\text{C}$ ) between the Catalyst Pellet Centre and the Flowing Reaction Mixture on Reaction Rate  $r$  (mol/kg<sub>cat</sub> h)

Empty points denote values measured at constant partial pressure of hydrogen ( $p_{\text{H}} = 0.022$  atm), solid points values measured at constant temperature ( $82^\circ\text{C}$ ).

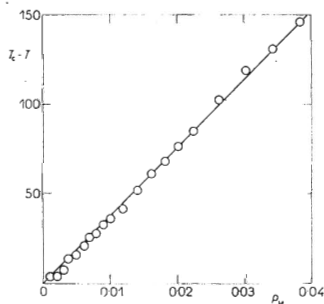


FIG. 4

Dependence of Temperature Difference ( $^\circ\text{C}$ ) between the Catalyst Pellet Centre and the Flowing Reaction Mixture on Partial Pressure of Hydrogen  $p_{\text{H}}$  (atm) for temperature  $82^\circ\text{C}$

actual temperature difference between the surface and center of the pellet is much less than actual difference between the pellet surface and the flowing gas. Therefore, for evaluation of data for the actual temperature difference between the pellet surface and the flowing gas was substituted the experimentally determined temperature difference between the pellet center and the flowing gas and not the experimentally determined temperature difference between the pellet surface and the flowing gas.

#### Measurement Procedure

At the beginning of each series of experiments the catalyst was activated for about 1 h in a stream of hydrogen. We did not succeed in some cases (at low temperatures) to keep the catalyst activity constant. It was slightly dependent on the preceding state of the catalyst *i.e.* on its preceding heating or cooling. More frequent periodic activation of the catalyst was therefore necessary. The measurement was performed at the constant volumetric flow rate of the reaction mixture through the reactor of 200 l/h (at 20°C). This flow rate corresponds to the Reynolds number defined by the relation

$$N_{Re} = G_0/a_v\varphi\mu \quad (2)$$

of approximately  $N_{Re} = 17.2$ .

At the given reaction conditions *i.e.* at the temperature and composition of the reaction mixture the measurement was made after reaching the steady state of the reactor. In all steady states the temperature difference was determined between the center of the catalyst pellet and the flowing reaction mixture, in some selected steady states also the reaction rate.

#### RESULTS AND DISCUSSION

To bring the regime of the catalyst pellet to a steady state, two conditions must be fulfilled. At first the rate of hydrogen transfer to the pellet surface must be equal to the reaction rate and further the heat evolved by chemical reaction must also be equal to the heat transferred from the pellet surface to the flowing gas. If we assume that the driving force of heat respective of mass transfer is the difference of temperature resp. of partial pressure of hydrogen these conditions may be written as relations

$$r = k_g a_m (p_H - p_{Hs}) \quad (3)$$

and

$$r(-\Delta H) = k_h a_m (T_s - T) \quad (4)$$

All kinetic measurements presented in this paper were carried out at constant flow rate of the reaction mixture. The individual experiments differ only by the hydrogen concentration and by the temperature of the flowing gas. It was calculated that neither the hydrogen concentration nor the temperature in region of the used reaction conditions practically affected the hydrodynamic conditions and physical quantities which were decisive for the magnitude of the heat and mass transfer coefficients. Therefore, it is possible to assume that the measured dependences of the reaction rate on hydrogen concentration and on temperature are determined at constant heat and mass

transfer coefficient values. Then according to Eq. (4) the temperature difference between the surface of the catalyst particle and the flowing reaction mixture should be proportional to the reaction rate in steady state. In Fig. 3 is given an example of the experimentally determined dependence of catalyst particle (pellet) overheating on the reaction rate. It is obvious that Eq. (4) fits the measured data. The deviations from the linear dependence are in the limits of accuracy with which the temperature difference between the particle surface and the flowing reaction mixture and with which the reaction rate values may be determined.

### *Dependence of the Reaction Rate on Partial Pressure of Hydrogen in the Reaction Mixture*

To prove experimentally if two steady states of the pellet may exist at the given partial pressure of hydrogen in the reaction mixture or if only one state may exist, two experiments at each partial pressure of hydrogen were carried out with different state of the pellet at the beginning of the experiment. In the first experiment the pellet

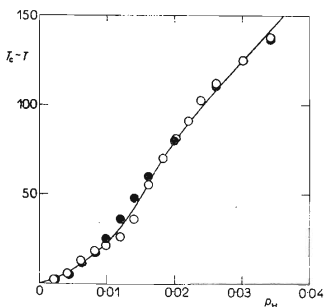


FIG. 5

Dependence of Temperature Difference ( $^{\circ}\text{C}$ ) between the Catalyst Pellet Centre and the Flowing Reaction Mixture on Partial Pressure of Hydrogen  $p_{\text{H}}(\text{atm})$  for Temperature  $44^{\circ}\text{C}$

Empty points denote values measured at successive increase of partial pressure of hydrogen, solid points at its successive decrease.

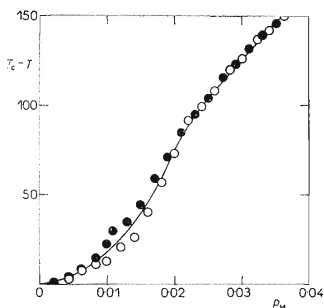


FIG. 6

Dependence of Temperature Difference ( $^{\circ}\text{C}$ ) between the Catalyst Pellet Centre and the Flowing Reaction Mixture on Partial Pressure of Hydrogen  $p_{\text{H}}(\text{atm})$  for Temperature  $22^{\circ}\text{C}$

Marking of points is the same as in Fig. 5.

was brought to the temperature of the flowing reaction mixture at zero partial pressure of hydrogen, then the required partial pressure of hydrogen was set up and the system was left to reach the steady state. In the second experiment the pellet was at first heated to a higher temperature by bringing it to a steady state at partial pressure of hydrogen 0.0380 atm and then the partial pressure of hydrogen was decreased to the value as in the first experiment. If two steady states of the pellet exist then the results of both experiments differ.

The experimentally determined dependence of the reaction rate on partial pressure of hydrogen for different temperatures is given in Figs 4 to 8. The result proves that in a certain region of partial pressures of hydrogen and temperatures two stable steady states of the pellet may exist. Due to the existence of two steady states is the dependence of the reaction rate on partial pressure of hydrogen discontinuous and consists of two branches (Figs 7 and 8). The branch connected with the point  $p_H = 0$  corresponds to the kinetic reaction regime. The second branch on which are situated the steady states with a high reaction rate corresponds to the regime of the external heat and mass transfer. The over-all rate of the process in states situated

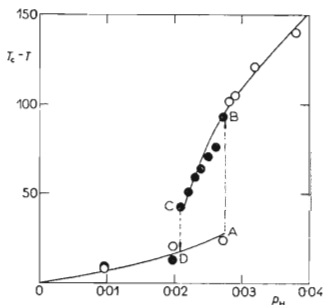


FIG. 7

Dependence of Temperature Difference ( $^{\circ}\text{C}$ ) between the Catalyst Pellet Centre and the Flowing Reaction Mixture on Partial Pressure of Hydrogen  $p_H$ (atm) for Temperature  $10^{\circ}\text{C}$

Points A and B denote the step transition of the catalyst pellet regime from kinetic to diffusion branch, points C and D step transition from diffusion to kinetic branch. Other marking is the same as in Fig. 5.

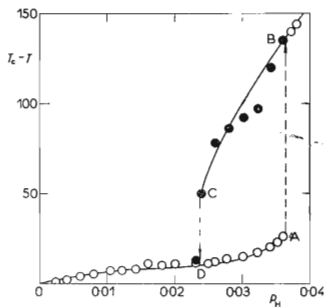


FIG. 8

Dependence of Temperature Difference ( $^{\circ}\text{C}$ ) between the Catalyst Pellet Centre and the Flowing Reaction Mixture on Partial Pressure of Hydrogen  $p_H$ (atm) for Temperature  $0^{\circ}\text{C}$

Marking of points is the same as in Fig. 7.

on this branch is determined mostly by the rate of external hydrogen transfer while the kinetic properties of the chemical reaction affect the rate of the process only insignificantly. With this conclusion is also in agreement the comparison of results measured at different temperatures. It is obvious that at low partial pressures of hydrogen and in states on the kinetic branch is the dependence of the reaction rate on partial pressure of hydrogen for different temperatures different while at higher partial pressures of hydrogen the steady states for all temperatures are on a common straight line passing through the origin. This straight line on which the steady states with the diffusive regime are placed (Eq. (3)) determines the highest reaction rate which may be reached at the given partial pressure of hydrogen and at the given hydrodynamic conditions.

From the analysis of the dependence of the reaction rate on partial pressure of hydrogen follows that by an increase of partial pressure the pellet regime is transformed gradually from the kinetic regime to the regime of external heat and mass transfer. The reason for this transformation is the difference in the temperature dependence of the reaction rate and of the heat and mass transfer coefficients. For the same reasons the region of partial pressure in which the rate of mass transfer is the determining operation is moved toward lower values of partial pressures with the increasing temperature. At higher temperatures (Figs 4 to 6) is the dependence of the reaction rate on partial pressure of hydrogen continuous and the transition of the kinetic regime to the regime of external heat and mass transfer is smooth. At lower temperatures (Figs 7 and 8) is the dependence of the reaction rate on partial pressure of hydrogen discontinuous and the transition from one regime to the other is a step change. This step transition from the kinetic regime to the diffusion takes place from point A to point B (Figs 7 and 8) and the transition from the diffusion regime to the kinetic one from point C to point D. The experimental results therefore confirm qualitatively the reached conclusions concerning the behaviour of the catalyst pellets by a study on a mathematical model.

### *Temperature Dependence of the Reaction Rate*

The dependence of the reaction rate on temperature of the flowing reaction mixture was determined at constant composition of the inlet reaction mixture (partial pressure of hydrogen in the reaction mixture was  $p_H = 0.022$  atm) in such a way that the temperature was at first gradually increased from temperature  $-5^\circ\text{C}$  to  $82^\circ\text{C}$  and then gradually decreased down to the temperature  $-5^\circ\text{C}$  (between the individual experiments the flow of hydrogen was not stopped so that the pellet has not cooled down). If in a certain region two steady states exist the hysteresis effect must appear (the hysteresis effect would appear only in the case when in the studied region of temperatures is situated at least the step transition point from the kinetic to the diffusion regime). The result is given in Fig. 9 and proves that in a certain region of temperatures



two stable steady states exist. The behaviour of the pellet at temperature changes is analogical to the behaviour at a change of partial pressure of hydrogen and will not be discussed in detail. In agreement with the experiments obtained by a study of the external heat and mass transfer effects on the temperature dependence of the reaction rate by the use of a mathematical model in the vicinity of the step transition from one regime to the other, the apparent activation energy is higher than the apparent activation energy in the kinetic region (*i.e.* the activation energy affected only by the internal heat and mass transfer). In the region of strong effect of the external heat and mass transfer is the apparent activation energy practically null which is in agreement with the assumption that the external mass transfer is the determining factor of the reaction rate.

#### *Verification of Validity of the Mathematical Model*

In the preceding papers<sup>1,4</sup> a model of a pellet catalyst affected by the external mass and heat transfer was presented. The dependence of the reaction rate on partial pressure of reactant and on temperature of the bulk of the reaction mixture is for the first order reaction expressed by the relation

$$R\beta\gamma = (P_A - R\beta\gamma\varphi_{nm}) \exp \left[ \tau_n \frac{R\beta\gamma\Omega_{mn} + \varphi_{mn}(\Delta T/T_n)}{1 + R\beta\gamma\varphi_{mn}\Omega_{mn} + (\Delta T/T_n)} \right] \quad (5)$$

(the meaning of the individual terms is not discussed as it is given in the preceding papers).

For calculation of parameters in relation (5) it is necessary to know the rate equation of the reaction on the given pellet of catalyst *i.e.* the equation describing the dependence of the reaction rate on partial pressure of hydrogen and on temperature of the reaction mixture when the external heat and mass transfer effects are eliminated but when the internal heat and mass transfer effects are included.

As the used experimental apparatus did not allow to work at so high flow rates so that in the whole range of partial pressure of hydrogen and temperature the effect of external heat and mass transfer would be eliminated, the following simplified procedure was used. From literature was used the information that the reaction was of the first order to hydrogen<sup>2</sup>. The value of the rate constant and of the activation energy were estimated from the reaction rates at low partial pressures of hydrogen and at low temperatures when the effect of external heat and mass transfer was very low. These values were then used for extrapolation in the whole range of partial pressures of hydrogen and temperature. The heat transfer coefficient was determined from Eq. (4) in which for  $(T_s - T)$  the measured temperature difference between the pellet center and the flowing reaction mixture was substituted. The mass transfer coefficient was determined from Eq. (3) in which the experimentally determined

reaction rate was substituted at conditions when the external transfer of hydrogen is the rate determining step. From the difference of partial pressures ( $p_H - p_{Hs}$ ) was substituted the total partial pressure of hydrogen. The summary of experimentally measured data is given in Table I.

From comparison of the dependence of the reaction rate on partial pressure of hydrogen calculated from Eq. (5) with the experimentally determined dependence is obvious that the agreement of the calculation and of the experiment is only qualitative. The deviations are of two types. First is for the calculated values the hysteresis region pushed toward the region of higher partial pressures of hydrogen and second the experimental curve has a slightly different shape than the calculated one. The hysteresis region is for the measured data wider and the distance between the transition points from the kinetic to the diffusion regime is much smaller than the distance calculated. The shift of the hysteresis region might be explained by inaccuracies in values of the rate constant and of the activation energy. The position of this region is namely very sensitive to the rate constant value.

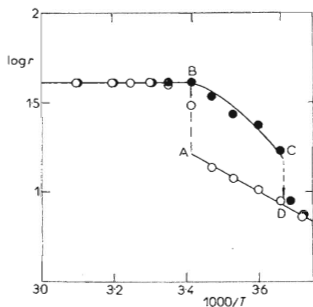


FIG. 9

Dependence of Reaction Rate  $r$  (mol/kg<sub>cat</sub> h) on Temperature (°K) at  $p_H = 0.022$  atm

Empty points denote values measured at successive increase of temperature of the flowing reaction mixture, solid points denote values measured at successive decrease of temperature. Points A and B denote the step transition of the catalyst pellet regime from kinetic to the diffusion branch, points C and D the step transition from diffusion to kinetic branch.

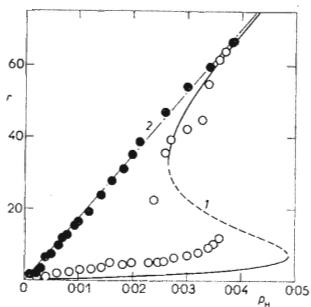


FIG. 10

Comparison of Measured and Calculated Dependence of Reaction Rate  $r$  (mol/kg<sub>cat</sub> h) on Partial Pressure of Hydrogen  $p_H$  (atm) for Temperature 0 and 82°C

Empty points denote values measured at 0°C, solid points at 82°C. 1 Calculated dependence for  $E = 11.5$  kcal/mol,  $r_{omn}(0^\circ\text{C}) = 1.922$  mol/kg<sub>cat</sub> h and temperature 0°C, 2 curve of the calculated dependence for temperature 82°C, resp. denoting the region of external heat and mass transfer.

TABLE I

Summary of Data Determined from Experimental Data

The errors in determination of quantities were estimated on basis of an analysis of possibilities to determine the concentration of the reactant and the temperature on the catalyst pellet surface.

Quantity	Value of quantity
$p_{H_2}$	0.0380 atm
$E$	5.1 $\pm$ 1 kcal/mol
$k(0^\circ\text{C})$	404.2 $\pm$ 80 mol/kg <sub>cat</sub> h atm
$k_g/k_h$	0.0664 $\pm$ 0.015 kg mol $^\circ\text{C}/\text{kcal atm}$
$k_g$	2.77 $\pm$ 0.6 kg mol/m <sup>2</sup> atm h

The kinetic data are necessarily affected by some uncertainty which is the result of difficulties in determination of the surface temperature of the catalyst pellet. In the region of conditions where the external heat and mass transfer are insignificant, the temperature difference inside the pellet is comparable to the outside temperature difference and the temperature measured in the center of the pellet is only a rough approximation of the temperature on the surface (the internal temperature difference is decreasing with increasing effect of the external mass and heat transfer; therefore this error is insignificant in the region of strong external mass and heat transfer effects). It is also possible to explain by the consequence of this effect why in the region of weak external mass and heat transfer effect the measured and calculated dependences of the reaction rate on partial pressure of hydrogen mutually differ.

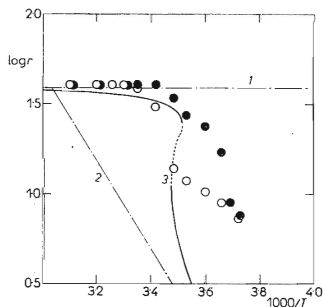


FIG. 11

Comparison of Measured and Calculated Dependence of the Reaction Rate  $r$  (mol/kg<sub>cat</sub> h) on Temperature ( $^\circ\text{K}$ )

1 Curve denoting region of the external heat and mass transfer, 2 curve denoting the kinetic region for  $E = 11.5$  kcal/mol, 3 calculated dependence for  $r_{\text{omn}}(0^\circ\text{C}) = 1.922$  mol/kg<sub>cat</sub> h and  $p_{H_2} = 0.022$  atm.

By change of value of the activation energy and of the rate constant in limits which would not be quite evident outside the limits of measurement errors it is not possible to get the width of the hysteresis region of the calculated and measured dependences to be the same. To obtain at least an approximate agreement it would be necessary to increase the activation energy value to 11 kcal/mol which is a value completely improbable (see Fig. 10).

The disagreement in the shape of the curve may be a result of invalidity of some assumption used for the assembling of the mathematical model. For example it is assumed that the kinetic equation determined at low temperature is valid in the whole range of temperatures on the surface of the catalyst pellet. The kinetic data are therefore extrapolated from temperature 0°C up to the temperatures of 150°C. It is not possible to rule out the possibility that the reaction order and the activation energy of the reaction may vary significantly. Other possible explanation is the influence of some other effects. For example at low temperatures the catalyst activity might be affected by a slow water condensation in the catalyst. Due to this condensation in certain regions, the apparent activation energy of the reaction could be increased which would lead to widening of the hysteresis region or the catalyst activity might be slightly dependent on temperature and on partial pressure of water on the catalyst surface in the previous experiment which might affect the shape of the hysteresis curve.

Another reason might be the non-isothermity of the flowing gas in the reactor. In the derived model it is assumed that the course of the reaction is affected only by the heat transfer between the surface of the catalyst particle and the isothermally flowing gas. In reality the course might be affected also by the heat transfer between the flowing gas and the bath in which is the reactor placed. Non-isothermity of the flowing gas may also affect the shape of measured dependences.

At the comparison of measured and calculated dependences of the reaction rate on temperature the calculated curves were chosen in such a way that they passed through the experimental point at 0°C temperature. Here, too, the qualitative agreement of the calculated and experimental data was confirmed, but a quantitative agreement was not satisfactory (Fig. 11).

#### LIST OF SYMBOLS

$a_m$	external particle surface per unit of catalyst weight
$a_v$	external particle surface per unit of catalyst volume
$D_p$	diameter of catalyst particle
$E$	activation energy of reaction
$G_0$	mass flow rate of reaction mixture per unit of cross-sectional area of the reactor
$k_g$	mass transfer coefficient
$k_h$	heat transfer coefficient
$k$	reaction rate constant related to the bulk temperature of the phase $T$
$k_n$	reaction rate constant related to the standard temperature of the bulk phase $T_n$

$n$	reaction order
$N_{Re} = G_0/a_v\varphi\mu$	Reynolds number
$p_H$	partial pressure of hydrogen in the bulk phase
$p_{Hm}$	standard partial pressure of hydrogen in the bulk phase
$p_{Hs}$	partial pressure of hydrogen on the catalyst surface
$P_A, P_H$	dimensionless partial pressure of the reactant A or hydrogen in the bulk phase
	$P_A = p_A/p_{Am}, P_H = p_H/p_{Hm}$
$r$	reaction rate
$r_0$	reaction rate at conditions when the external heat and mass transfer is eliminated
$r_{om}$	reaction rate $r_0$ related to the standard partial pressure
$r_{omn}$	reaction rate $r_0$ related to the standard partial pressure and standard temperature of the bulk phase
$R = r/r_0$	effectiveness factor of the external heat and mass transfer
$R$	gas constant
$T$	temperature of the bulk phase
$T_c$	temperature of the catalyst pellet center
$T_n$	standard temperature of the bulk phase
$T_s$	temperature of external surface of the catalyst particle
$v$	height of the catalyst pellet
$W$	catalyst weight
$\beta = r_0/r_{om}$	dimensionless parameter
$\gamma = k/k_n$	dimensionless quantity
$\Delta H$	heat of reaction
$\theta_n = E/RT_n$	dimensionless parameter
$\mu$	viscosity of reaction mixture
$\varphi$	shape factor of catalyst particle
$\varphi_{mn} = r_{omn}/k_g a_m p_{Am}$	dimensionless parameter
$\Omega_{mn} = (-\Delta H) p_{Am} k_g / (k_n T_n)$	dimensionless parameter

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