JOURNAL OF CATALYSIS 5, 476–483 (1966)

Temperature Profiles in Porous Catalysts at Exothermic Catalytic Gas Reactions

G. WURZBACHER

*From the Institut für Physikalische Chemie, Universität Münster (Westfalen), Germany**

Received September 6, 1965; revised December 12, 1965

Exothermic gas reactions occurring at porous catalysts may lead to high temperature gradients within the pellet.

An experimental arrangement is described which enables such temperature profiles to be investigated within a model catalyst pellet. For the case of the platinum- or silver-catalyzed H_2–O_2 reaction, profiles obtained at various experimental conditions have been measured and evaluated on the basis of a modified Damköhler relation.

Introduction

In heterogeneous gas reactions on porous catalysts transport processes within the catalyst pellet may have a considerable influence on the total conversion rate. If the reaction is nearly thermoneutral or if the catalyst has a sufficiently high thermal conductivity, the temperature gradients within the pellet are negligibly small. At these conditions, only the possible influence of mass transport within the pores ("pore diffusion") has to be taken into account. This special case has been studied since 1939 by Thiele (*1*), Zeldovich (*2*), Wagner (*3*), and others.

The situation is much more complicated, if the absolute value of the reaction enthalpy is relatively large and the thermal conductivity of the pellet relatively small so that appreciable temperature gradients are encountered. In this case, besides the mass balance

$$\operatorname{div} \mathbf{j}_i - \nu_i \cdot R(c_i) = 0 \qquad (1)$$

the energy balance

$$\operatorname{div} \mathbf{q} + \Delta H \cdot R(T, c_i) = 0 \qquad (2)$$

has to be taken into account (see List of Symbols, below). Because of the pronounced nonlinear temperature dependence of the reaction rate R, substantial difficulties arise in the calculation of concentration and temperature profiles, even in cases of simple kinetics. However, as demonstrated by Damköhler (*4*), concentration and temperature profiles are correlated by a simple expression

$$T - T_s = -\frac{\Delta H D_{\mathrm{eff}}^{(p)}}{\nu_i \lambda_{\mathrm{eff}}^{(p)}} (c_i - c_i^{(s)}) \qquad (3)$$

Several authors (*4–15*) since 1961 have carried out calculations of the profiles and of the averaged conversion rate within the pellet, partly with the use of electronic computers. An estimate on the basis of Eq. (3) shows that in nearly all practical cases the temperature difference is of the order of 1°C. Nevertheless, some of the calculations reported in the literature have been extended to cases of rather high temperature differences. As a result it turned out that at sufficiently large values of ΔH and of the activation energy of the reaction rate multiple solutions for the averaged conversion rate within the pellet and thus, multiple solutions for the temperature and concentration profiles should exist (*13*, *15*). In view of these predictions, experimental investigations of such systems appeared interesting.

As yet, measurements of the temperature profiles in porous catalysts have not been reported. It was the aim of the present work

* Present address: Battelle-Institute e.V., Frankfurt/Main, Germany, Wiesbadener Strasse.

to generate and examine such profiles in a model catalyst pellet at simple conditions for mass and heat transfer.

List of Symbols

c_{total}	Total molar gas concentration (mole cm^{-3})
c_i	Molar concentration of component i (mole cm^{-3})
$\mathbf{j}_i$	Molar flux of component i per unit area (mole cm^{-2} sec^{-1})
$\mathbf{q}$	heat flux per unit area (cal cm^{-2} sec^{-1})
x_i	Mole fraction of component i
$D_{eff}^{(p)}$, $D_{eff}^{(b)}$	Effective diffusivity within the pellet and in the gas boundary layer, respectively (cm^2 sec^{-1})
ΔH	Enthalpy of the reaction $\Sigma \nu_i A_i = 0$ (cal $mole^{-1}$)
$P^{(p)}$, $P^{(b)}$	Porosity of pellet and gas boundary layer, respectively
R	Reaction rate (mole cm^{-3} sec^{-1})
T	Absolute temperature (°K)
κ	Dimensionless number, defined by Eq. (7)
$\lambda_{eff}^{(p)}$, $\lambda_{eff}^{(b)}$	Thermal conductivity in the pellet and in the gas boundary layer, respectively (cal cm^{-1} sec^{-1} deg^{-1})
ν_i	Stoichiometric number; $\nu_i < 0$ for reactants, $\nu_i > 0$ for products

Affixes

b	Bulk gas stream
c	Pellet center
s	Pellet surface

Experimental

1. Apparatus

The apparatus used is depicted in Fig. 1. The model pellet K consisted of a parallel arrangement of closely packed thin porcelain tubes, length, 4.5 cm; outside diameter, 0.16 cm; wall thickness, 0.03 cm. The inside and outside surface of the tubes was coated with a thin layer of finely divided catalytically active metal.

The conversion of H_2–O_2 was chosen as the model reaction. In the first experiments, platinum served as the catalyst metal. As this metal turned out to be too active in the course of the experiments, it was replaced by silver.

On silver, the H_2–O_2 reaction occurs at temperatures between 60° and 150°C at easily measurable rates. Above a partial oxygen pressure of 5 mm Hg, it is of the zeroth order with respect to oxygen and has an activation energy of about 10 kcal $mole^{-1}$. Water vapor acts as inhibitor [cf. also ref. (*17*)].

The catalyst face directed to the gas stream was covered with an inert layer serving as diffusion and heat conduction boundary layer. In the first experiments, which were carried out on a platinum catalyst, this layer consisted of quartz wool; in the experiments on a silver catalyst it was made of porcelain tubes of the same type as the catalyst support.

The model pellet was placed in a cylindrical vessel consisting of Duran glass, which was surrounded by an electric furnace O. The furnace served to prevent heat losses to those sides of the pellet where no mass transfer took place. It consisted of five separate heating coils which were wound on a thin-walled ceramic cylinder. At the upper end of the furnace, a hollow brass ring was mounted through which a thermostated liquid was passed.

Inside the model pellet were placed two iron-constantan thermocouples (Th 1 and 2) of a wire thickness of 0.1 mm which were surrounded by very thin-walled glass capillaries. One of the thermocouples was axially movable for measuring the temperature profile. The position of the second thermocouple was fixed; its temperature was taken as a point of reference. A third thermocouple, also axially movable, was placed in a boring within the wall of the ceramic cylinder which carried the heating coils; it served to measure the temperature profile of the adiabatic furnace.

2. Procedure

The experiments were carried out with hydrogen-oxygen and—in the case of the

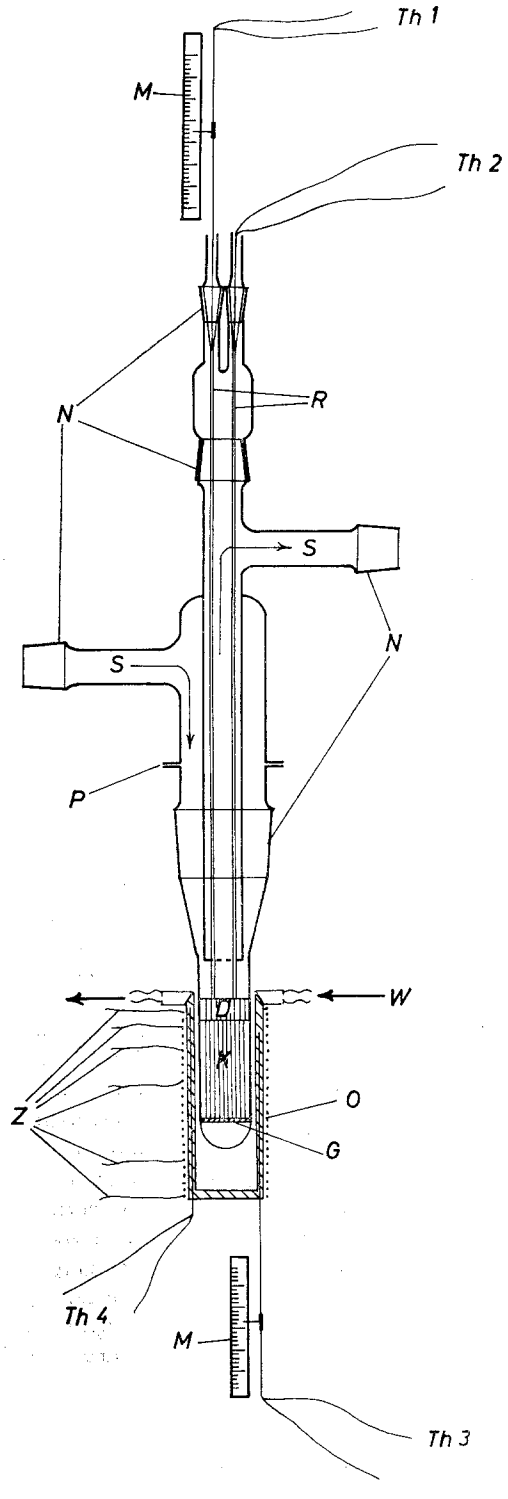

FIG. 1. Experimental arrangement for the investigation of temperature profiles in a model catalyst pellet: G, plane glass plate; K, model catalyst pellet; M, scales; N, standard glass joints; O, electric furnace; P, plane glass joint; R, glass capillaries; S, gas flow; Th, thermocouples; W, thermostated water; Z, electrical leads.

platinum catalyst—with hydrogen-air mixtures. The oxygen content amounted 2 to 8%, the flow rate was 300 cm³ NTP/sec.

Before the measurement, the catalyst was heated for 1 hr at 400°C in a slow hydrogen current. After having been cooled to room temperature, the desired oxygen or air content was adjusted in the hydrogen stream.

The platinum catalyst was active even at room temperature; in the experiments with a silver catalyst, which does not become sufficiently active below 80°C, the gas stream was preheated before entering the reaction vessel.

Subsequently the temperature profile of the furnace wall was closely adapted to that of the model catalyst pellet by variation of the electric current within the different heating coils. Figure 2 illustrates the stepwise adaptation of the two profiles, which generally was achieved up to a difference of less than 1°C.

RESULTS

Figure 3 illustrates the temperature profiles obtained with the platinum catalyst. In these experiments, the temperature already reaches its maximum value 5 mm behind the pellet surface. Because of the particularly high activity of the platinum catalyst, the deficient oxygen is completely consumed within a narrow marginal zone of the catalyst. Therefore, inside the pellet the temperature profile will be horizontal. Hence, maximum temperature raises are realized with a catalyst of this type; however, the reaction does not penetrate deeply into the catalyst.

With the silver catalyst the profiles of Figs. 4 and 5 were obtained. As do those of Fig. 3, the curves of Fig. 4 correspond to the case of limited penetration of the reaction into the pellet. However, because of the lower activity of the silver catalyst, the reaction zone is much broader.

The profiles of Figs. 3 and 4 vary in the

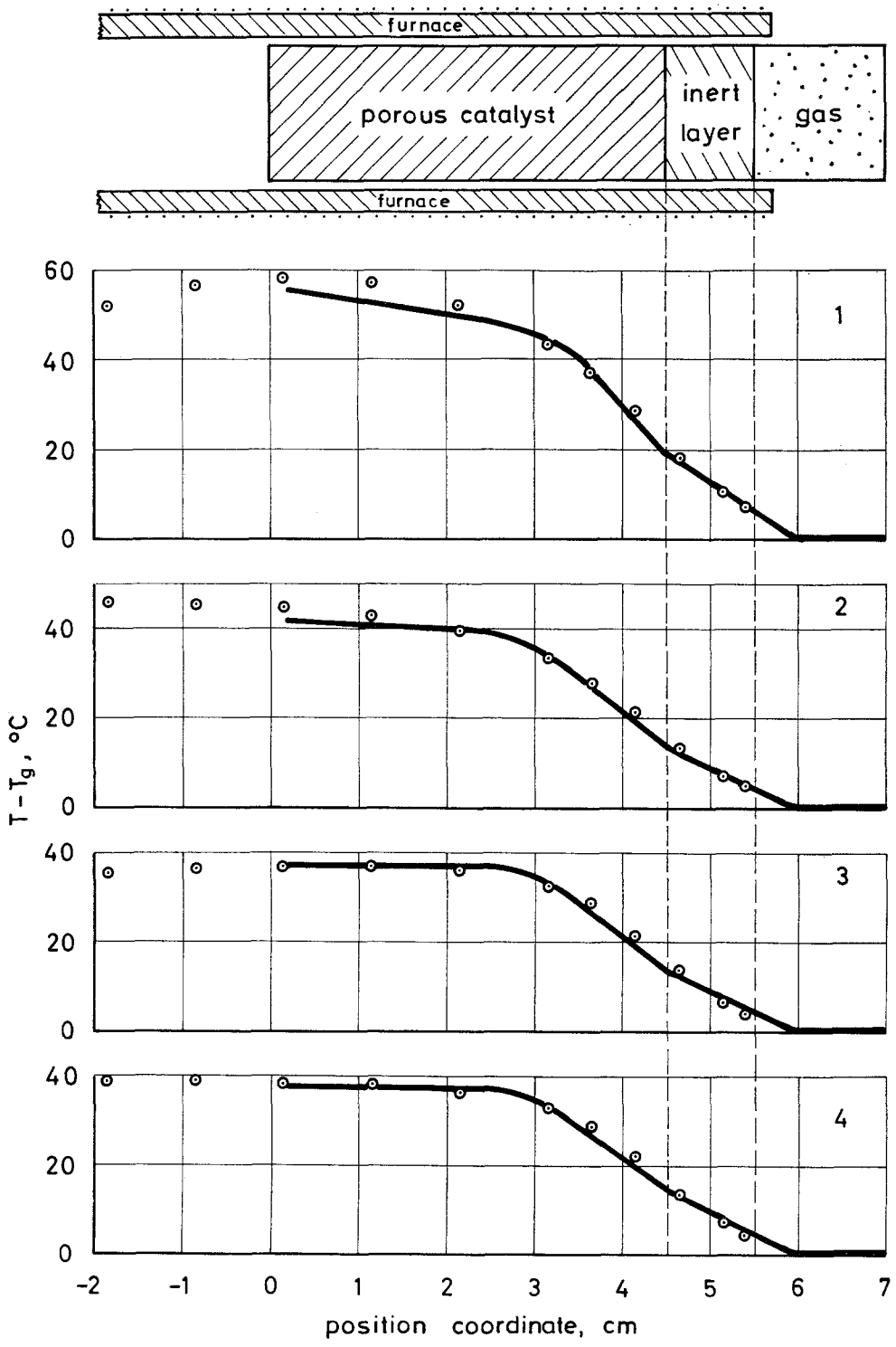

FIG. 2. Several stages of adaptation of the temperature profiles of furnace wall and model catalyst pellet: Solid line, profile in the catalyst pellet; open circles, profile in the furnace wall. The numbers indicate the consecutive order of the measurements.

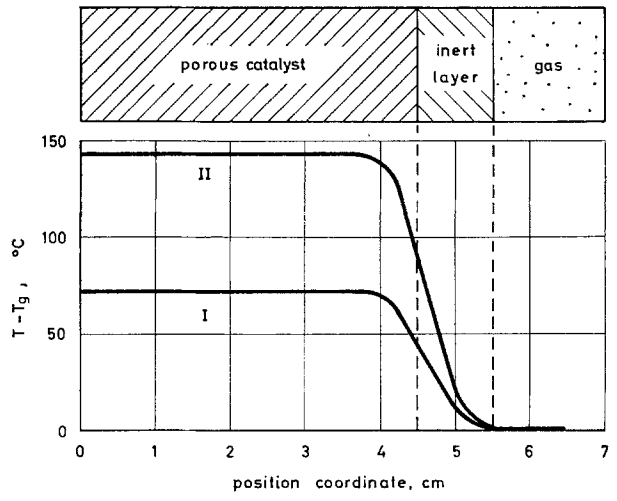

FIG. 3. Temperature profiles measured in the platinum catalyst pellet.

No.	x_{O_2}(b)	T_c (°C)	T_s (°C)	T_b (°C)
I	0.040	96	68	23
II	0.076	166	115	23

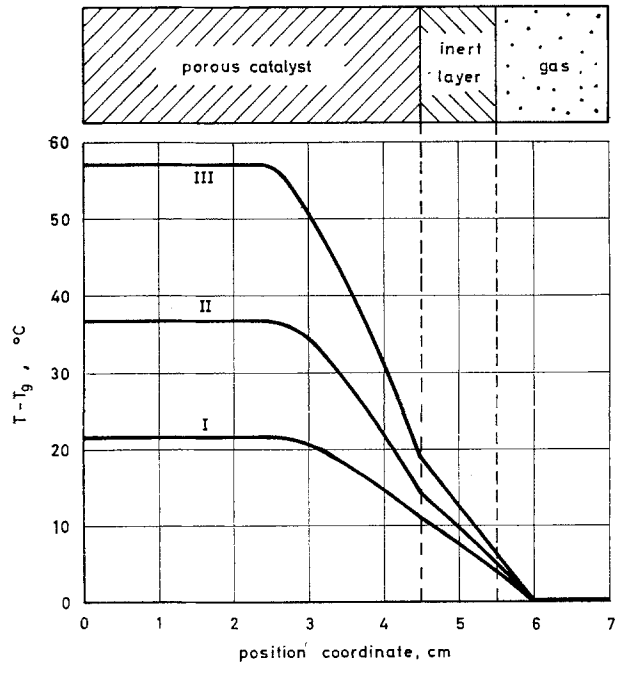

FIG. 4. Temperature profiles measured in the silver catalyst pellet.

No.	x_{O_2}(b)	T_c (°C)	T_s (°C)	T_b (°C)
I	0.020	98	87	76
II	0.035	116	93	79
III	0.058	132	94	75

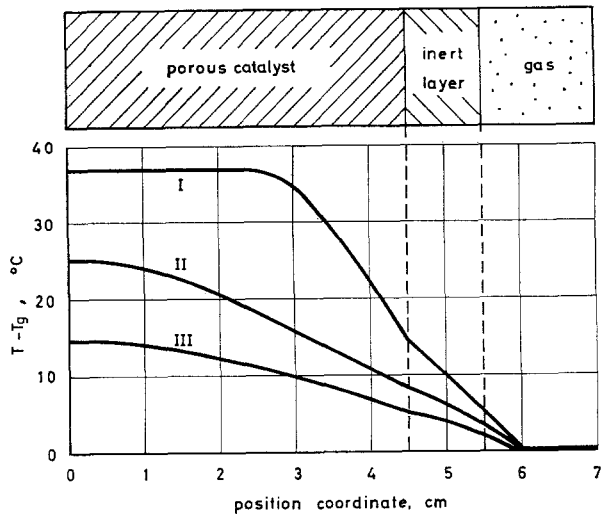

FIG. 5. Temperature profiles measured in the silver catalyst pellet.

No.	$x_{O_2}^{(b)}$	T_c (°C)	T_s (°C)	T_b (°C)
I	0.035	116	93	79
II	0.035	93	76	68
III	0.035	81.5	72	67

height of the temperature plateau inside the pellet, which is determined by the oxygen concentration of the gas mixture passing along the catalyst. In Fig. 5 profiles are summarized corresponding to a series of experiments in which the gas temperature was varied at constant gas composition. If the temperature is reduced, the reaction penetrates more deeply into the pellet and the profile is flattened.

If only axial heat flow is involved, the temperature gradients within the inert layer and the pellet at the boundary of both (Figs. 3 to 5) are inversely proportional to the respective thermal conductivities. In fact, in some of the curves the ratio of these gradients differs from the corresponding values of $\lambda_{eff}^{(p)}/\lambda_{eff}^{(b)}$, as given in the Table 1. This indicates that there is still some radial heat flow in the region of high-temperature gradients.

EVALUATION AND DISCUSSION

The horizontal part of the temperature profiles in Figs. 3 and 4 suggests that the oxygen concentration vanishes in the interior of the pellet so that the conversion comes to an end. In this case, Eq. (3) takes the form

$$\frac{\nu_{O_2}\lambda_{eff}^{(p)}}{\Delta H D_{eff}^{(p)}}(T_c - T_s) = c_{O_2}^{(s)} \qquad (4)$$

For the diffusion and heat conduction boundary layer the relation

$$-\frac{\nu_{O_2}\lambda_{eff}^{(b)}}{\Delta H D_{eff}^{(b)}}(T_s - T_b) = c_{O_2}^{(s)} - c_{O_2}^{(b)} \qquad (5)$$

which is analogous to Eq. (3), may be deduced. Subtraction of Eq. (5) from Eq. (4) and transformation yields

$$T_c - T_b + (\kappa - 1)(T_s - T_b) = \frac{\Delta H D_{eff}^{(p)} c_{total} x_{O_2}^{(b)}}{\nu_{O_2}\lambda_{eff}^{(p)}} \qquad (6)$$

where

$$\kappa = D_{eff}^{(p)}\lambda_{eff}^{(b)}/D_{eff}^{(b)}\lambda_{eff}^{(p)} \qquad (7)$$

Thus, the difference between the temperatures of the pellet center and of the bulk gas stream corrected by $(\kappa - 1)(T_s - T_b)$ is proportional to the mole fraction of oxygen in the bulk gas. The constant of propor-

TABLE 1
SUMMARY OF THE NUMERICAL VALUES USED IN THE CALCULATION[a]

Quantity	Value	Unit
$\Delta H/\nu_{O_2}$	1.150×10^5 [b]	cal mole^{-1}
c_{total}	3.05×10^{-5}	mole cm^{-3}
$P^{(p)}$	0.45	—
$D(O_2\text{–}H_2)$	1.36[b]	cm^2 sec^{-1}
$D_{eff}^{(p)}(O_2\text{–}H_2)$	0.61	cm^2 sec^{-1}
$\lambda(H_2)$	5.02×10^{-4} [b]	cal cm^{-1} sec^{-1} deg^{-1}
λ(porcelain)	4.2×10^{-3} [c]	cal cm^{-1} sec^{-1} deg^{-1}
λ(quartz glass)	3.5×10^{-3} [d]	cal cm^{-1} sec^{-1} deg^{-1}
$\lambda_{eff}^{(p)}$	2.5×10^{-3}	cal cm^{-1} sec^{-1} deg^{-1}
Boundary layer of quartz wool (Pt catalyst)		
$P^{(p)}$	0.93	—
$D_{eff}^{(p)}/D_{eff}^{(b)}$	0.48	—
$\lambda_{eff}^{(b)}$	7.0×10^{-4}	cal cm^{-1} sec^{-1} deg^{-1}
$\lambda_{eff}^{(p)}/\lambda_{eff}^{(b)}$	3.6	—
κ	0.133	—
Boundary layer of porcelain tubes (Ag catalyst)		
$P^{(b)}$	0.45	—
$D_{eff}^{(p)}/D_{eff}^{(b)}$	1	—
$\lambda_{eff}^{(b)}$	2.5×10^{-3}	cal cm^{-1} sec^{-1} deg^{-1}
$\lambda_{eff}^{(p)}/\lambda_{eff}^{(b)}$	1	—
κ	1	—

[a] The temperature dependence of the material and reaction constants has been neglected; the values used are based on an average temperature of 400°K.

[b] Calculated from data given in ref. (*18*).

[c] Value provided by the manufacturer.

[d] Ref. (*19*).

tionality is derived from the values given in the table

$$\frac{\Delta H D_{eff}^{(p)} c_{total}}{\nu_{O_2} \lambda_{eff}^{(p)}} = 860°$$

The numerical data necessary for the calculation of κ are also summarized in the table. The diffusivity within the pellet, $D_{eff}^{(p)}$, was calculated from the value for binary O_2–H_2 diffusion taking into account the reduction of the diffusional cross section owing to the presence of the closely packed tubes. The diffusivity ratio $D_{eff}^{(p)}/D_{eff}^{(b)}$ was assumed to be the ratio of the porosities of the pellet and the inert layer. The overall thermal conductivities of the pellet and inert layer consist of the contributions of the solid material and the gas within the pores, which was taken to be hydrogen.

The values thus obtained for the left-hand side of Eq. (6) have been plotted in Fig. 6 versus the mole fraction of oxygen $x_{O_2}^{(b)}$ (closed circles and squares). For comparison, the calculated curve, straight line with a slope of 860°C, is also plotted in the diagram. In view of the approximations used, experimental values and calculated curve agree satisfactorily.

The position of the points corresponding to the $(T_c - T_b)$ values without correction term (open squares in Fig. 6) shows that the latter may assume fairly large values.

The results demonstrate that the experimental arrangement yields profiles of relatively large values of $(T_c - T_s)$, generated by the exothermic catalytic reaction, and that the effect of the diffusion and the heat conduction boundary layer can be taken into account in a simple way. Further effort has to be directed towards the complete prevention of radial heat flow within the region of particularly large temperature gradients.

A more detailed analysis of the profiles, especially of those depicted in Fig. 5 where the maximum temperature rise is not attained, requires intimate knowledge of the kinetics of the reaction occurring on the catalyst.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Prof. Dr. E. Wicke for stimulation and encouragement during this work and to Dr. P. Hugo for valuable comments.

REFERENCES

1. THIELE, E. W., *Ind. Eng. Chem.* **31**, 916 (1939).
2. ZELDOVICH, J. B., *Acta Physicochim. URSS* **10**, 583 (1939).
3. WAGNER, C., *Z. Physik. Chem.* **A193**, 1 (1944).
4. DAMKÖHLER, G., *Z. Physik. Chem.* **A193**, 16 (1944).
5. SCHILSON, R. E., AND AMUNDSON, N. R., *Chem. Eng. Sci.* **13**, 226, 237 (1961).
6. MINGLE, J. O., AND SMITH, J. M., *A.I.Ch.E. J.* **7**, 243 (1961).
7. TINKLER, J. D., AND METZNER, A. B., *Ind. Eng. Chem.* **53**, 663 (1961).
8. TINKLER, J. D., AND PIGFORD, R. L., *Chem. Eng. Sci.* **15**, 326 (1961).

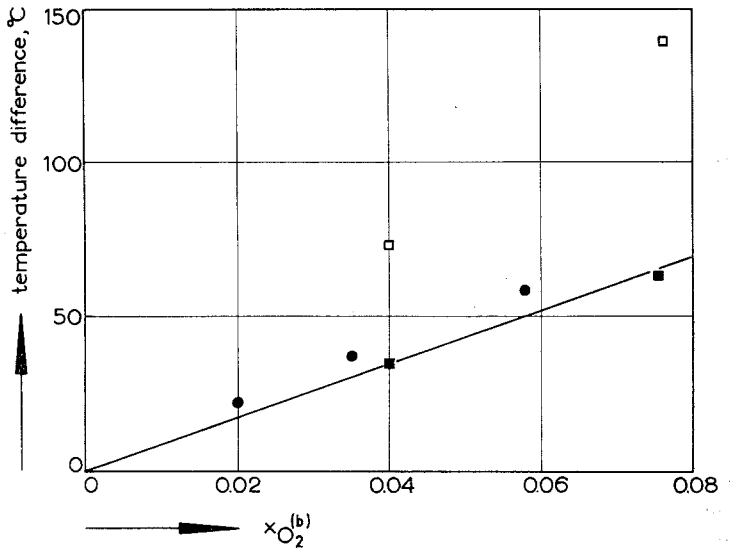

FIG. 6. Plot of experimental values of $T_c - T_b$ (circles and open squares) and $T_c - T_b + (\kappa -)(T_s - T_b)$ (circles and closed squares) versus $x_{O_2}^{(b)}$; □, ■, platinum catalyst; ●, silver catalyst. The straight line has the calculated slope of 860°.

9. BEEK, J., *A.I.Ch.E. J.* **7**, 357 (1961).
10. AKEHATA, T., NAMKOONG, S., KUBOTA, H., AND SHINDO, M., *Can. J. Chem. Eng.* **39**, 127 (1961).
11. CARBERRY, J. J., *A.I.Ch.E. J.* **7**, 350 (1961).
12. PETERSEN, E. E., *Chem. Eng. Sci.* **17**, 987 (1962).
13. WEISZ, P. B., AND HICKS, J. S., *Chem. Eng. Sci.* **17**, 265 (1962).
14. ANDERSON, J. B., *Chem. Eng. Sci.* **18**, 147 (1963).
15. ØSTERGAARD, K., *Chem. Eng. Sci.* **18**, 259 (1963).
16. WAGNER, C., *Chem. Technik* **18**, 1, 28 (1945).
17. BOND, G. C., "Catalysis by Metals," p. 448. Academic Press, London and New York, 1962.
18. International Critical Tables, Vol. V. McGraw-Hill, New York, 1926.
19. D'ANS, J., AND LAX, E., "Taschenbuch für Chemiker und Physiker," 2nd ed., p. 1128. Springer-Verlag, Berlin, 1949.