Table 1. Comparison of Helium Fugacities

Investigator	T, °K.	P, atm.	f, atm. Graphical	 Original R-K	 This modification
Michels and Wouters (*14*)	323.15	115.82	121.88	124.32	121.99
Holborn and Otto (*7*)	90.17	41.1	43.67	44.77	43.69

culated by the original Redlich-Kwong equation and by the modified version are also shown.

A detailed comparison of experimental compressibility factors with those calculated by the original and modified Redlich-Kwong equations will be included in a forthcoming Bureau of Mines Report of Investigations.

FUGACITY

The fugacity of helium was determined at two conditions using the original Redlich-Kwong equation, this modification, and graphical integration of PVT data. The results are given in Table 1.

The improvement in the fugacities is consonant with the improved compressibility factors. Kharakhorin (*10*) calculated a fugacity of 43.72 at 90.1° and 41.1 atm. with the Beattie-Bridgman equation of state.

SUMMARY

A modified, two-constant Redlich-Kwong (*19*) equation for helium has been presented which will calculate compressibility factors for 1,073 data points in the range from 30° to 1,473°K., with a mean deviation of 0.18% from the experimental data.

NOTATION

A = parameter of Redlich-Kwong equation
a = parameter of Redlich-Kwong equation
B = parameter of Redlich-Kwong equation
b = parameter of Redlich-Kwong equation
f = fugacity
h = BP/Z
K = Kelvin temperature
P = pressure
P_c = critical pressure
R = universal gas constant
R-K = Redlich-Kwong
T = temperature
T_c = critical temperature
V = molal volume
V_c = critical molal volume
Z = compressibility factor, PV/RT

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A New Method to Measure Reaction Rates for Highly Reactive Catalysts: Heat and Mass Transfer on Catalytic Surfaces

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In case of gaseous reactions catalyzed by solid particles, the reactants diffuse from the ambient gas stream to the surface of the catalyst. On the other hand, the products and also the heat of reaction are transferred from the surface to the ambient gas stream. As a result, there exist the differences of the concentrations of the reactants and of the products, and also the differences of the temperature between the ambient gas stream and the catalytic surface (*1*). Especially for a highly reactive catalyst, these differences are considerably large. For example, as shown later in the experimental results, this temperature difference becomes as much as 200°C.

The experiments of kinetic analyses of reactions catalyzed by solid particles have usually been performed by using differential reactors of packed beds. The rate of reaction has generally been determined from the gas anal-

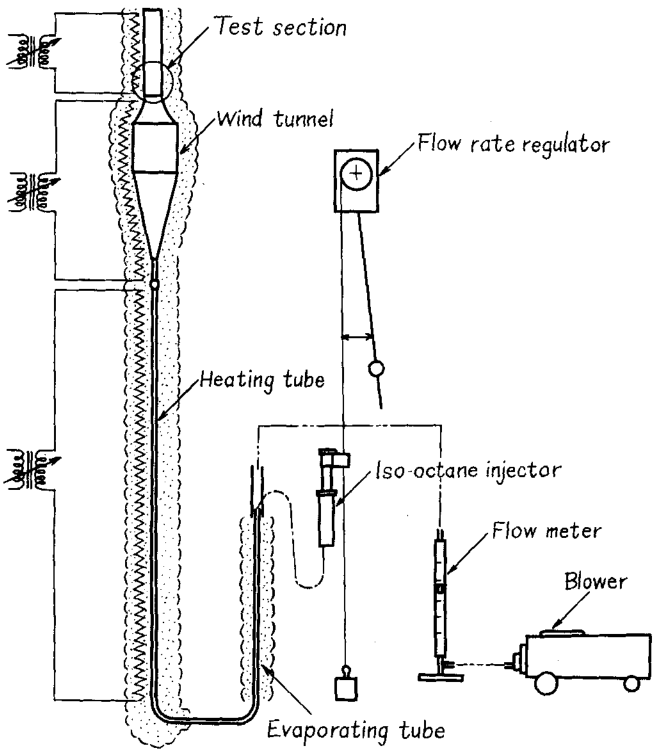

Fig. 1. Apparatus.

yses before and after the reactor.

Many examples appear in the literature where the large differences of temperature and concentration between the surface of the catalyst and the ambient stream have been neglected with consequent erroneous interpretation of the reaction model. In those cases, the differences of temperature and concentration have been regarded as causes of errors. By making positive use of the differences of temperature, the authors have developed a new experimental method to measure reaction rates for highly reactive catalysts.

This method is described as follows. The experimental apparatus is schematically shown in Figures 1 and 2. A single particle of catalyst is suspended in a reactive gas flow, and the temperatures of the particle and of the main flow are measured with thermocouples. The state of the reaction can be analyzed by the following procedure. From the measured temperature difference between the catalyst and the main gas flow, the heat flux at the surface of the catalyst can be calculated by using the heat transfer coefficient for a solid particle suspended in a forced flow. Dividing this heat flux by the heat of reaction, the reaction rate can be obtained. From this reaction rate and mass transfer coefficient for a solid particle suspended in a forced flow, the difference of concentration between the surface of the catalyst and the main flow can be calculated.

Compared with the usual methods, this new method has the following advantages: It is necessary only to measure the temperatures; it is much simpler than gas analysis. The coefficients of heat and mass transfer for a single particle have been measured more accurately than those of packed beds. Since the characteristics of a single particle are determined, fine differences of characteristics among each particle can be distinguished. Since the heat capacity of the apparatus is small, the system reaches a steady state in a moment. We can measure instantaneous changes of characteristics, for example, instantaneous damage of catalytic activity.

EXPERIMENTS

By the method proposed above, the reaction of the catalytic oxidation of iso-octane has been analyzed, because the authors have been interested in the catalytic oxidation of unburned gasoline in the exhaust gas of an automobile engine.

Apparatus

The experimental apparatus is shown in Figures 1 and 2. The measurements have been performed under the atmospheric pressure. A reactive gas of the desired air-fuel ratio is generated by evaporating iso-octane into air. The reactive gas is heated to the desired temperature, and sent to the test section through the streaming section of the wind tunnel. The standard flow rate of the reactive gas is 20 liters/min. at room temperature. The test section is 50 mm. wide and 30 mm. deep. The reactive gas flows upward in the test section. Five to seven cylindrical particles of catalyst which are 5 mm. in diameter and 5 mm. in length are skewered by a 0.2 mm.-diameter thermocouple wire. They form a somewhat long cylindrical catalyst as a whole, and are suspended in the test section across the reactive gas flow. The temperature T_c of the catalyst is measured by the skewering thermocouple at the center, and the temperature T_∞ of the main flow is measured by a thermocouple located at 15 mm. upstream. Because the radiative heat transfer is predominant especially at high temperature, the wall temperature of the test section is elaborately regulated so as to keep at the same temperature as the main flow.

In advance of the experiment, we insured that no self-reaction takes place in the reactive gas mixture itself at the temperature as high as 500°C.

REDUCTION OF DATA

The oxidation of iso-octane is written as

$$C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O - \Delta H \qquad (1)$$

where

$$-\Delta H = 1{,}219 \text{ kcal./mole}_{C_8H_{18}}$$

In the reduction of the data, it was assumed that the process on the catalysts studied here could be taken to be the complete combustion of Equation (1) and that there are no side reactions. This assumption is supported by Experiment III to a certain extent.

The heat flux q at the surface of the catalyst is calculated as

$$q = q_{\text{rad}} + q_{\text{conv}} \qquad (2)$$

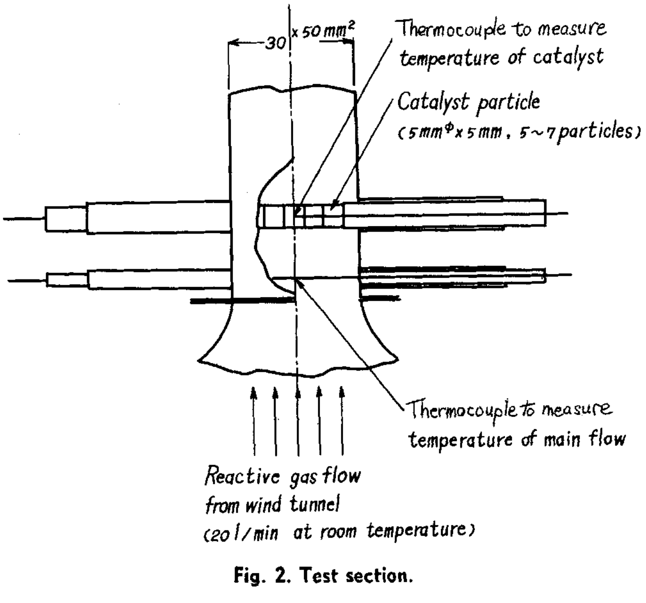

Fig. 2. Test section.

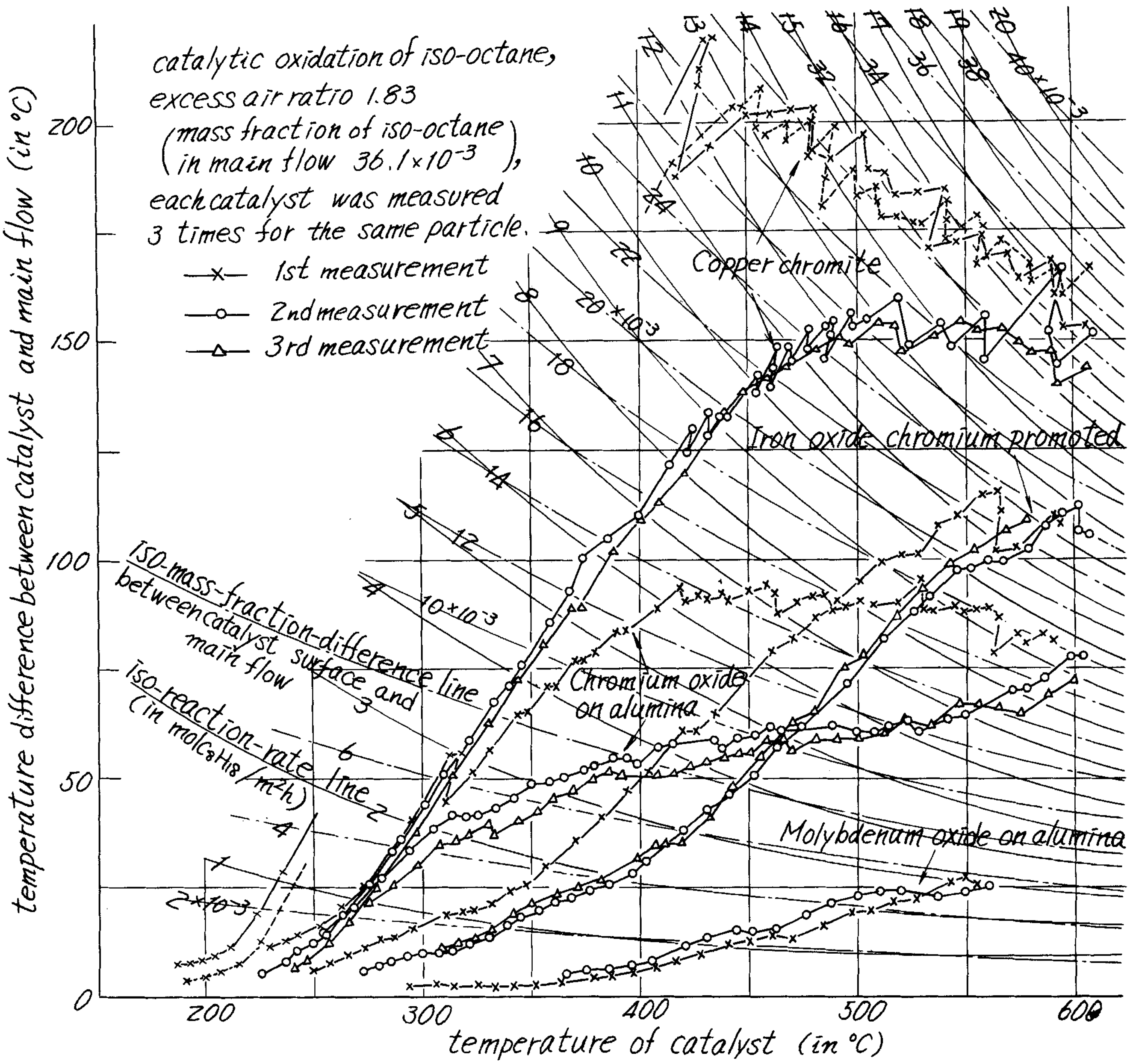

Fig. 3. Comparison of catalytic activity.

$$q_{\text{rad}} = 4.88\,\epsilon_c \left[\left(\frac{T_c}{100}\right)^4 - \left(\frac{T_w}{100}\right)^4 \right] \quad \text{(kcal./sq. m. hr.)} \qquad (3)$$

$$q_{\text{conv}} = h\,(T_c - T_\infty) \qquad (4)$$

where the catalytic particle is assumed to be completely enclosed by black walls of the test section, and, as mentioned before, the wall temperature T_w of the test section is taken the same as the main flow, that is, $T_w = T_\infty$. The emissivity of the surface of the catalyst is assumed to be 1.0 in the following calculation because the surface of the catalyst is considered porous. The heat transfer coefficient for a cylinder in the cross flow is calculated by (2)

$$N_{Nu} = 0.43 + 0.48\,N_{Re}^{0.5} \quad (1 < N_{Re} < 4{,}000)$$

$$N_{Nu} = \frac{hd}{\lambda_f}, \quad N_{Re} = \frac{Gd}{\mu_f} \qquad (5)$$

The range of the Reynolds number in the experiment is from 55 to 85.

The reaction rate r is calculated as

$$r = \frac{q}{-\Delta H} \qquad (6)$$

The difference Δw of the mass fraction of iso-octane between w_c at the surface of the catalyst and w_∞ in the main flow is

$$\Delta w = w_\infty - w_c = \frac{Mr}{\rho_f k} \qquad (7)$$

The mass transfer coefficient k is calculated by (2)

$$N_{Sh} = 0.43 + 0.533\,N_{Sc}^{0.31}\,N_{Re}^{0.5}, \quad N_{Sh} = \frac{kd}{D_f} \qquad (8)$$

The diffusion coefficient D_f of iso-octane is calculated by the equation of Fujita (3) since there is no measured value.

EXPERIMENT I: COMPARISON OF CATALYTIC ACTIVITY FOR VARIOUS CATALYSTS

The measurement was performed for four species of catalyst:

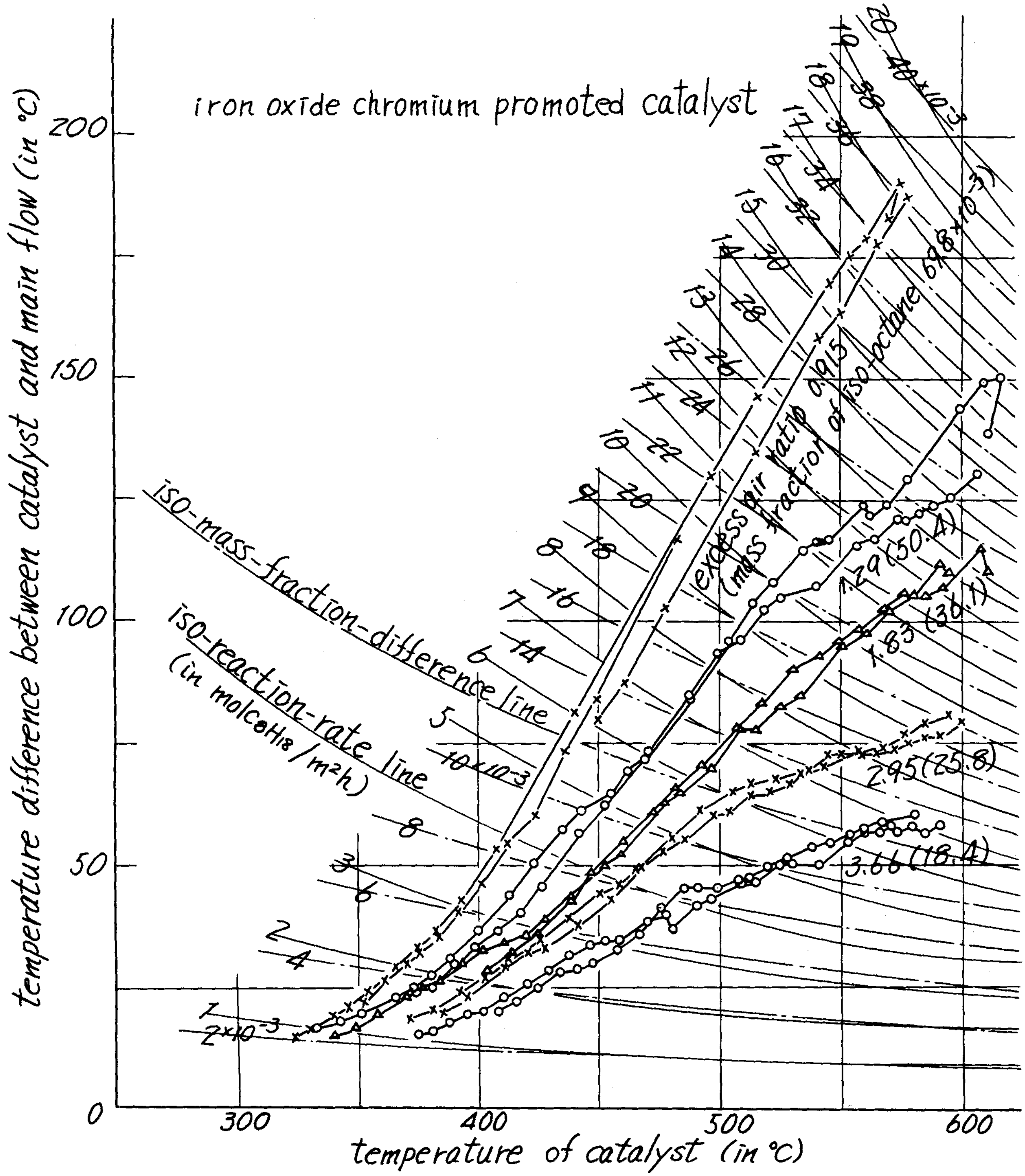

Fig. 4. Reaction rate analysis 1.

Copper chromite

CuO	30.9 ± 1.0%
Cr_2O_3	37.7 ± 1.0%
MnO_2	3.2 ± 0.2%
Kieselguhr	15.0 ± 1.0%
Graphite	5 ± 0.5%
Bulk density	1.16 ± 0.05 g./cc.

Iron oxide chromium promoted, carbon monoxide shift catalyst

Fe_2O_3	85 ± 2.0%
Cr_2O_3	7 ± 1.0%
Graphite	4 ± 0.5%
Bulk density	1.40 ± 0.1 g./cc.

Chromium oxide on alumina

Cr_2O_3	12.5 ± 0.5%
MgO	2.5 ± 0.5%
Alumina	82.5 ± 2.0%
Bulk density	1.0 ± 0.1 g./cc.

Molybdenum oxide on alumina

MoO_3	10 ± 0.5%
Alumina	90 ± 1.0%
Bulk density	1.0 ± 0.05 g./cc.

The method is to raise the temperature of the reactive gas under the constant air-fuel ratio. The measurement was repeated for three times on each particle. The catalytic activities were compared as shown in Figure 3, which gives the correlation of the temperature of the particle and the temperature difference between the particle and the main flow.

The reaction rate and the difference of mass fraction are calculated by the procedure mentioned above and are also plotted in Figure 3.

From the results the following assumptions can be made.

For every catalyst, the curve for the first measurement is much different from the curves for the second and third measurements, which interpret that the catalytic activity of a fresh particle fails in accordance with the temperature rise. The zigzag on the curve for the first measurement is considered to correspond to the instantaneous small damages of the activity.

The good agreement between the curves for the second and the third measurement interprets that once a virgin catalyst is heated up to some temperature, and once the activity of the catalyst fails, it fails no longer by repeated heating up to the same temperature. It seems that the catalyst reaches a steady state.

For the copper chromite catalyst, in addition to the previous series of measurements for one particle, the measurement for another fresh particle was made. The result is shown by the dotted line in Figure 3. The curves for the first measurement of both particles resemble each other, which may show that the drops of the activity take place not accidentally but somewhat regularly.

In this experiment, the excess air ratio of the main reactive gas flow is kept at 1.83, namely, the mass fraction of iso-octane is 0.0361. Therefore, the iso mass-fraction difference line of $\Delta w = 0.0361$ corresponds to the diffusionally controlled condition. It is observed that the reaction rate for a fresh particle of the copper chromite catalyst is almost controlled by only the diffusion process in the boundary layer around the particle.

EXPERIMENT II: RATE ANALYSIS FOR IRON OXIDE CHROMIUM PROMOTED CATALYST

For an iron oxide chromium promoted catalyst, the measurement was performed by varying both the temperature and the excess air ratio of the reactive gas. The result is shown in Figure 4.

The rate equation for this catalyst is assumed to be written by the Arrhenius type as

$$r = A \exp\left(-\frac{\Delta E}{RT}\right)(C_{C_8H_{18}})^n \qquad (9)$$

Figure 5 illustrates the determination of the order of the reaction for iso-octane. By smoothing the curves shown in Figure 4, the correlation between the reaction rates and the concentrations of iso-octane at the surface of the catalyst is obtained for a constant temperature of the catalyst. The results are plotted in Figure 5. The data show a good agreement with the straight lines of the gradient of ½. Thus the order of the reaction n is determined as

$$n = \frac{1}{2} \qquad (10)$$

From Figure 5, a straight line shown in Figure 6 is drawn. The gradient of the straight line gives

$$\frac{\Delta E}{R} = 6.81 \times 10^3 \text{ (deg.)} \qquad (11)$$

Therefore, the activation energy is

$$\Delta E = 13.55 \text{ (kcal./mole)} \qquad (12)$$

Finally the equation of the reaction rate r (mole/sq. m. hr.) is expressed as

$$r = 1.50 \times 10^5 \exp\left(-\frac{6.81 \times 10^3}{T}\right)(C_{C_8H_{18}})^{1/2} \qquad (13)$$

where T is the temperature of the catalyst (°K.) and $C_{C_8H_{18}}$ is the molar concentration of iso-octane (mole/cu. m.).

The molar concentration of oxygen at the surface of the catalyst is not constant but decreases in proportion to the increase of temperature and the increase of the reaction rate, owing to the thermal expansion of gas and the mass transfer of oxygen from the ambient stream to the surface of the catalyst. Therefore, if the reaction rate is affected by the oxygen concentration, Figures 5 and 6 have to be affected as the oxygen concentration is deviated. That is, in the range of the data in Figure 5, the oxygen concentration at the surface of the catalyst decreases at most 25% from the value in the ambient stream. Then, isotherms in Figure 5 can, at the same time, be regarded as iso-oxygen concentration lines, and the order of reaction for the oxygen concentration given by Equation (10) can be justified. Also, in the range of the data in Figure 6, the difference of the oxygen concentration due to thermal expansion is about 20%, and this effect may be negligible in determining the activation energy from Figure 6.

To complete the kinetic analysis, further considerations on heat and mass transfer inside the catalyst particle have to be made. Equation (13) is only an apparent equation of the reaction rate which includes the effects of pore diffusion and heat conduction inside the catalyst in addition to the actual characteristics of the catalyst (*4*).

In case the catalyst is so active that the differences of temperature and concentration due to the heat and mass transfer outside the catalyst particle become large, the thickness of the reacting layer due to the pore diffusion inside the apparent surface of the catalyst is sufficiently thin. Then the effects of pore diffusion and heat conduc-

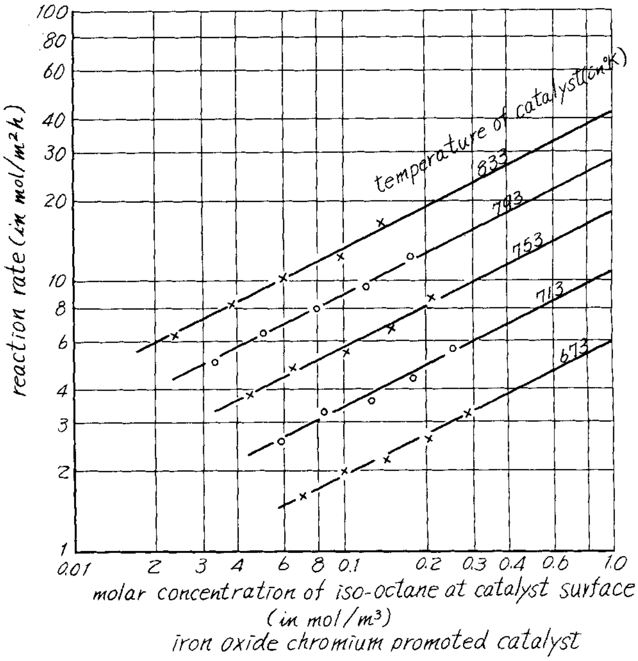

Fig. 5. Reaction rate analysis 2, determination of the order of reaction.

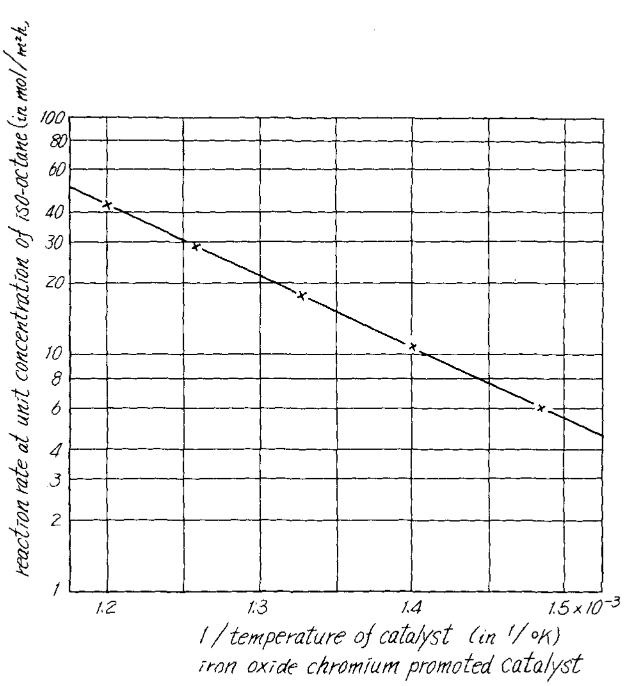

Fig. 6. Reaction rate analysis 3, determination of the activation energy.

tion inside the catalyst can be treated as one dimensional, and be analyzed somewhat easily. (In this experiment, the thickness of the reacting layer is calculated as thin as about 0.05 mm.) On account of the thinness of the reacting layer, the temperature difference across the reacting layer becomes very small, and the layer can be regarded as isothermal. (In this experiment, the temperature difference is calculated as small as within 0.2°C., compared with the difference of the temperature across the outer boundary layer being as large as 150°C.) Under these conditions, the reaction of the true order of n is observed as the reaction of the apparent order of $(n + 1)/2$. Also the activation energy is observed as one half of the true value (5). Then, from Equations (10) and (12), the true values of the order of the reaction and the activation energy are

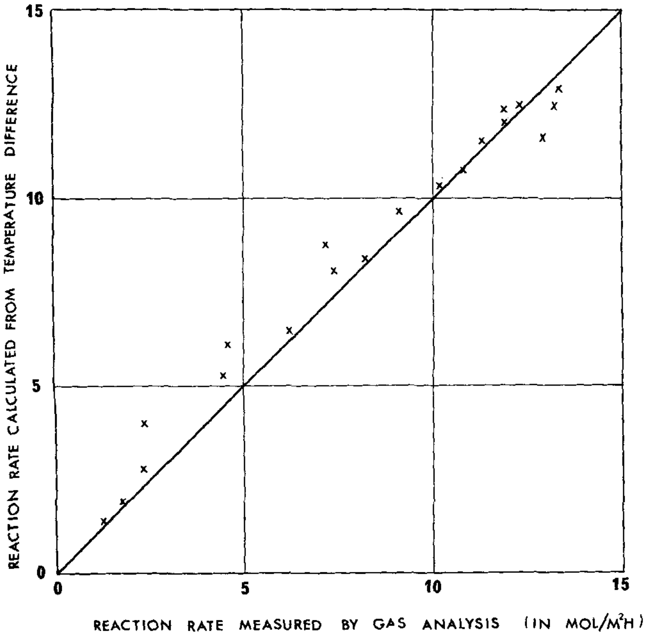

Fig. 7. Verification of accuracy.

$$n = 0 \tag{14}$$

$$\Delta E = 27.1 \text{ (kcal./mole)} \tag{15}$$

EXPERIMENT III: VERIFICATION OF THE ACCURACY OF THIS NEW METHOD

In order to verify the accuracy of the new method, the concentration of the carbon dioxide at the downstream of the test section was measured by using a gas-chromatographic analysis. The reaction rates calculated from this gas analysis are compared with the values obtained by this method, as shown in Figure 7. As the concentration is very small, the result of gas analysis is somewhat unreliable. But both values of the reaction rate show a fairly good agreement.

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NOTATION

C = molar concentration
D = diffusion coefficient
d = diameter of catalytic particle
ΔE = activation energy
G = mass velocity of reactive gas
$-\Delta H$ = heat of reaction
h = heat transfer coefficient
k = mass transfer coefficient
M = molecular weight
N_{Nu} = Nusselt number
N_{Re} = Reynolds number
N_{Sc} = Schmidt number
N_{Sh} = Sherwood number
n = order of reaction
q = heat flux
q_{conv} = heat flux by convection
q_{rad} = heat flux by radiation
R = gas constant
r = reaction rate
T = temperature
w = mass fraction

Greek Letters

Δ = difference
ϵ = emissivity
λ = thermal conductivity
μ = viscosity
ρ = density

Subscripts

c = catalyst
f = value at temperature, $T_f = \dfrac{T_c + T_\infty}{2}$
w = wall
∞ = main flow

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