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Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors

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The oxidation of glucose to gluconic acid in aqueous alkaline solution on a platinum-carbon catalyst was chosen as a model reaction to study the liquid-solid contacting efficiency in trickle-bed reactors. The global rates of dissipation of oxygen were measured for both liquid-full and trickle-bed reactors under conditions of negligible liquid-solid mass transfer effects. The liquid-solid contacting efficiency was evaluated from the rates for both reactors, which were measured under the same conditions of temperature, oxygen concentration and liquid flow rate using the same catalyst.

Under the range of experimental conditions used (catalyst particle sizes; 0.110 and 0.242 cm, superficial liquid velocity; 0.0236 to 0.337 cm/sec), the liquid-solid contacting efficiency was nearly constant. The average value was 0.91. Data were taken in a gas-continuous flow regime and showed no significant change in the rate of reaction with change in superficial gas (oxygen) velocity.

Keywords——trickle-bed reactor; contacting efficiency; oxidation; glucose; platinum on carbon catalyst; liquid-full reactor

The term trickle-bed reactor means a reactor in which a liquid phase and a gas phase flow concurrently downward through a fixed bed of catalyst particles while the reaction takes place. Trickle-bed reactors have usually been used in catalytic oxidation or hydrogenation reactions, which are important steps of chemical processing. For example, the synthesis of butynediol from gaseous acetylene and aqueous formaldehyde, the hydrogenation of glucose to sorbitol and the hydrogenation of an alkyl anthraquinone to hydroanthraquinone, which upon oxidation yields quinone and hydrogen peroxide.[2] Trickle-bed reactors have also been applied to biochemical reactions, for example, the oxidation of glucose to gluconic acid on immobilized glucose oxidase.[3] However, most of the published studies on industrial applications concern the processing with hydrogen of various petroleum fractions.[4]

To analyze trickle-bed reactor performance, it is necessary to determine the intrinsic reaction rate, interphase and intraparticle mass transfer resistances, liquid-solid contacting efficiency, *etc*., all of which affect the global rate of reaction in trickle-bed reactors. There is much information available about chemical kinetics and mass transfer coefficients, but the information about the liquid-solid contacting efficiency (the fraction of the particle surface covered by liquid) is fragmentary.[2,5-10] In these studies the liquid-solid contacting efficiency was found to be between about 0.6 and 1.0, but there was no consistency with the dependence of the superficial liquid velocity on the aforementioned fraction. In case of a low intrinsic

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[1] Location: *Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*
[2] C.N. Satterfield, *A.I. Ch. E. Journal*, **21**, 209 (1975).
[3] S. Fukushima, Y. Fujii, H. Miyagawa, and M. Nakano, The 41st Annual Meeting of the Society of Chemical Engineers of Japan, Sendai, April 1976, p. 596.
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rate constant, the global rate of reaction in trickle-bed reactors should be predominantly controlled by the liquid-solid contacting efficiency. Thus, to study the contacting efficiency, we chose as a model reaction the oxidation of glucose to gluconic acid in an aqueous alkaline solution on a platinum-carbon catalyst at 30° and under atmospheric pressure. The kinetics of this reaction are well known.[11)] Under these conditions, this slow and irreversible reaction is 0 th order in oxygen concentration, and proceeds with negligible side reactions.

Experimental

Chemicals——Reagent grade dextrose and reagent grade sodium hydroxide (with a stated purity of 95%) were used as supplied. For catalyst preparation, reagent grade chloroplatinic acid and granular activated carbon were used. All chemicals were purchased from Wako Pure Chemical Industries, Ltd.

Catalyst Preparation——Granular activated carbon (4 to 6 mesh) was crushed and sieved. Two average particle sizes were chosen for the catalyst support: $d_p=0.242$ cm (7 to 9.2 mesh) and $d_p=0.110$ cm (14 to 16 mesh). The particles were warmed with 0.2 N HNO_3 solution for 3 hr in order to remove contaminating metals as nitrates, then washed repeatedly with warm distilled water until the wash water became neutral. Next, 0.5 g of chloroplatinic acid was solved in 50 ml of distilled water and a calculated quantity of granular support was added. The mixture was warmed until the originally yellow solution became colorless, and was then left overnight at room temperature. The pH of the solution was adjusted to 8.0 by adding sodium carbonate, and 5 times the calculated quantity of formaldehyde was added dropwise with stirring. Subsequently the mixture was kept for 2 hr at 90°. After removing excess liquid and washing sufficiently with distilled water, the catalyst was stored in distilled water. The properties of the catalyst are shown in Table I.

TABLE I. Physical Properties of the Catalyst

Platinum content, wt%	1.0
Surface area, m^2/g	1200[a)]
Pore volume, cm^3/g	0.81[c)]
Solid phase density, g/cm^3	1.81[b)]
Particle density, g/cm^3	0.732[b)]
Bulk density, g/cm^3	0.380[b)]
Porosity of particles	0.60[c)]
Void fraction of bed	0.48[c)]

a) From Takeda Chemical Ind., Ltd.
b) Measured. *c*) Calculated.

Apparatus and Operating Procedure——Fig. 1 shows a schematic diagram of the apparatus. In a constant-temperature bath 5, 0.1 M aqueous glucose solution 3 and 0.25 M aqueous sodium hydroxide solution 4 were saturated with oxygen by continuous bubbling. The feed rates of glucose and sodium hydroxide solutions were adjusted to a ratio of 20 to 1. The mixed glucose-sodium hydroxide-oxygen solution and oxygen gas were introduced into the top of the reactor 1, the temperature of which was kept constant by circulation of water from the constant-temperature bath through the jacket.

The glass reactor was 2.1 cm i.d. and 27 cm long. For trickle-bed operation the liquid was introduced through a distributor consisting of three 0.1 cm i.d. and 1.0 cm long capillary tubes (stainless steel) placed across the reactor cross-section. The outlet of the tubes was located 0.5 cm above the top of the carbon prepacking. The bed as a whole consisted of three sections: a prepacking section of carbon particles, a catalyst section consisting of platinum on carbon particles, and an aftersection of carbon particles, all supported by a stainless steel screen placed 6 cm above the bottom of the reactor. The particle sizes and the lengths of these sections are given in Table II. On the basis of the criteria reported by Herskowitz *et al.*[12)] for uniform liquid distribution throughout the catalyst section, it was expected that with this arrangement radial dispersion would be negligible.

After passing through the reactor, the effluent was separated into gas and liquid phases. The gas was recycled through a flask 8. A part of the liquid was fed to a stripping column 7 for gas chromatographic analysis, and the rest was discharged.

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11) *a*) H.G.J. deWilt, Ph. D. thesis, Technische Hogeschool Eindhoven, 1969; *b*) K. Heyns and H. Paulsen, *Adv. in Carb. Chem.*, **17**, 169 (1962); *c*) M. Rottenberg and M. Thürkauf, *Helv. Chim. Acta*, **42**, 226 (1959).

12) M. Herskowitz and J.M. Smith, *A.I. Ch. E. Journal*, **24**, 439 (1978).

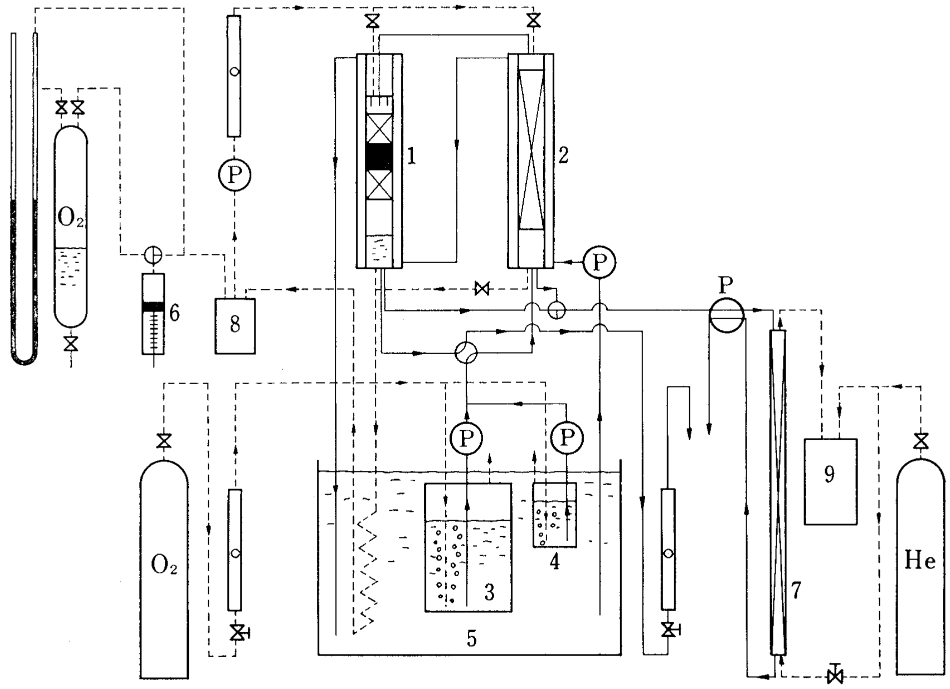

Fig. 1. Schematic Diagram of the Apparatus

------→------: gas flow line, ——→——: liquid flow line.
1: trickle-bed (or liquid-full) reactor, 2: absorber, 3: glucose aq. reservoir, 4: NaOH aq. reservoir, 5: constant temperature bath, 6: piston burette, 7: stripping column, 8: flask, 9: gas chromatograph, P: pump

Table II. Experimental Conditions

Particle diameter, d_p, cm	0.242	0.110
Depth of pre- and afterpacking sections, cm	1.6	1.3
Mass of catalyst in reactor, g	5.0	2.0
Depth of catalyst section, cm	0.95	0.39
Superficial liquid velocity, u_L, cm/sec	0.0248—0.337	0.0236—0.332
Superficial gas velocity,[a] u_G, cm/sec	2.9	0.94—4.9
Reaction temperature, °C	30	

[a] For trickle-bed operation.

For liquid-full operation, the mixed glucose-sodium hydroxide-oxygen solution was fed from the bottom of the reactor 1. The effluent was then introduced at the top of an absorber 2 which was a 1.5 cm i.d. and 25 cm long glass column packed with 2—3 mm glass beads. In the absorber the liquid was concurrently brought into contact with the circulating oxygen gas, so that most of the oxygen consumed in the liquid-full reactor was supplied from the flowing oxygen gas to the liquid. At the bottom of the absorber the effluent was separated into gas and liquid phases; the rest was the same as for trickle-bed operation.

The decrease in the concentration of dissolved oxygen after passage through the reactor was small (less than 30%) for both trickle-bed and liquid-full operations. As the concentrations of glucose and sodium hydroxide were much higher than the concentration of dissolved oxygen, these were essentially uniform throughout the reactor. Hence, the operations for both reactors were regarded as differential reactor ones.

Analytical Methods——The quantity of oxygen absorbed during a run was measured by means of a piston burette 6. A part of the effluent stream, separated at the bottom of the reactor (for trickle-bed operation) or of the absorber (for liquid-full operation), was diverted to the top of the stripping column, which was a 1.6 cm i.d. and 100 cm long glass column packed with 2—4 mm glass beads. Here helium was used to remove dissolved oxygen. The gas stream from the stripping column was sent to a gas chromatograph **9.** Oxygen was measured with a 100 cm long and 0.4 cm o.d. stainless steel column packed with 5A molecular sieve particles (80—100 mesh). The column was maintained at 50°.

The global rate of reaction, R [$\mathrm{mol\cdot g^{-1}\cdot sec^{-1}}$], was calculated from the amount of oxygen gas absorbed during a certain period, t [sec], and the difference between the concentrations of dissolved oxygen in the feed stream to the reactor, C_f [mol·cm^{-3}], and in the effluent stream from the gas–liquid separator, C_e [mol·cm^{-3}]. Then R may be written as

$$R = \frac{M_{O_2}}{mt} + \frac{(C_f - C_e)Q_L}{m} \tag{1}$$

where m [g] is the mass of the catalyst in the reactor, and Q_L [cm^3·sec^{-1}] is the volumetric feed rate of liquid. M_{O_2} [mol] was evaluated from the volume of gas supplied by the piston burette and the vapor pressure of water at room temperature.

Results and Discussion

The outer surface of the catalyst particles in a trickle-bed reactor is not covered completely with the flowing liquid. The fraction, f, of the particle surface covered with liquid is defined as the liquid-solid contacting efficiency. Assuming that no gas reaction occurs, the global rate of reaction in a trickle-bed reactor, R_{TB}[mol·g^{-1}·sec^{-1}], may be written as

$$R_{TB} = fR_C + (1-f)\,R_N \tag{2}$$

where R_C [mol·g^{-1}·sec^{-1}] and R_N [mol·g^{-1}·sec^{-1}] are the global rates of reaction on the catalyst covered and not covered with liquid, respectively. The catalyst surface which is not covered with the flowing liquid is wet to the naked eye. The catalyst pores under this surface must be filled with liquid by capillarity. Assuming that the liquid in these pores is not replaced by the flowing liquid, the contribution of the reaction occurring in these pores to the global rate of reaction may be negligible. Thus, equation (2) can be written as

$$R_{TB} = fR_C \tag{3}$$

For negligible liquid-solid mass transfer resistance, R_C may be identical to the global rate of reaction in a liquid-full reactor, R_{LF} [mol·g^{-1}·sec^{-1}]. Equation (3) then becomes

$$f = \frac{R_{TB}}{R_{LF}} \tag{4}$$

Therefore, the liquid-solid contacting efficiency can be obtained simply from the ratio of R_{TB} to R_{LF}, both measured under conditions of negligible gas phase reaction and negligible liquid-solid mass transfer resistance.

First, the deactivation of the catalyst was measured in the liquid-full reactor using particle sizes d_p=0.110 and 0.242 cm. The results are given in Fig.2. For each catalyst, a significant decrease in the global rate of reaction was observed at the beginning of the reaction time, but after about 50 hr conditioning the decrease became very slow. A similar kind of catalyst deactivation was observed by deWilt,[11a)] who studied kinetically the oxidation of glucose with

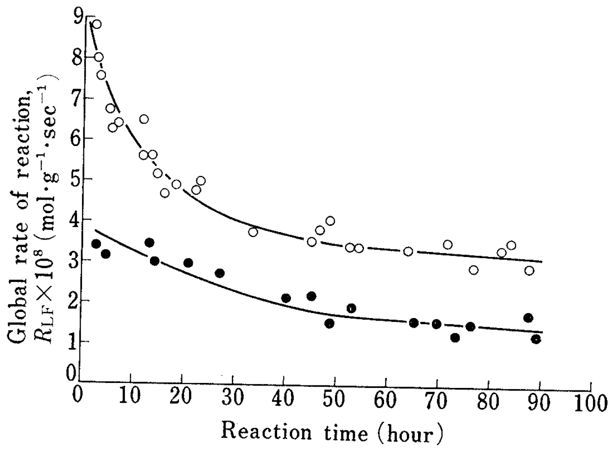

Fig. 2. Deactivation of the Catalyst

u_L=0.10 cm/sec; —○—: d_p=0.110 cm, —●—: d_p=0.242 cm.

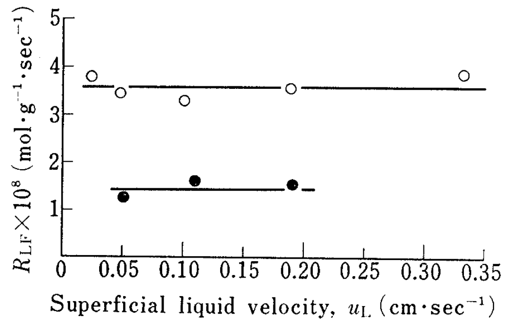

Fig. 3. Effect of Superficial Liquid Velocity on the Global Rate of Reaction in a Liquid-Full Reactor

—○—: d_p=0.110 cm, —●—: d_p=0.242 cm.

5% Pt on carbon catalyst powders. A rapid reaction of glucose to glucosaccharic acid took place initially. Regarding the deactivation of the catalyst it was considered that the glucosaccharic acid occupied the active center for the reaction of glucose to glucosaccharic acid, and that this strong adsorption of the product resulted in a rapid decrease of the reaction. Only under this condition did the other active center for the reaction of glucose to gluconic acid become effective in terms of the consumption of oxygen. In our work, granular catalyst particles were used, so it might take a long time to reach a constant rate. As shown in Fig. 2, the plot is almost linear with a very small gradient. The rate data were taken in the range of this nearly flat region and some corrections, based on the ratio of the individual rate to the mean value, were made to all measurements.

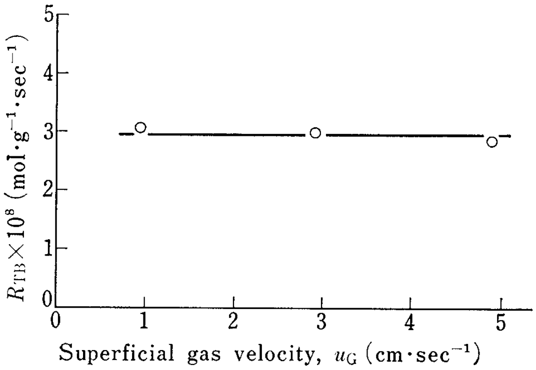

Fig. 4. Effect of Superficial Gas (Oxygen) Velocity on R_{TB}

$d_p=0.110$ cm, $u_L=0.10$ cm/sec.

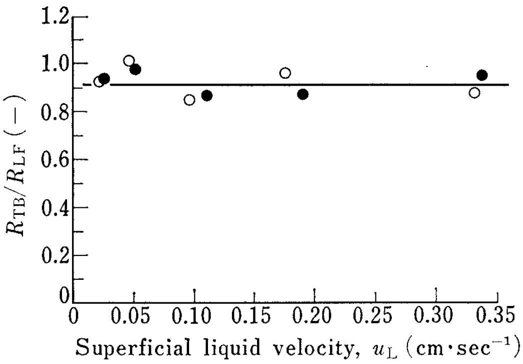

Fig. 5. Effect of Superficial Liquid Velocity on R_{TB}/R_{LF}

—○—: $d_p=0.110$ cm, —●—: $d_p=0.242$ cm.

Fig. 3 shows the effect of superficial liquid velocity, u_L [cm·sec^{-1}], on the global rate of reaction in liquid-full operation. For both particle sizes, the global rates were independent of liquid velocity. That is to say, there was no liquid-solid mass transfer limitation. This result could be confirmed by estimating the concentration, C_s [mol·cm^{-3}], of oxygen in the liquid at the surface of the catalyst particles. By using an available correlation[13] which was recently developed from previous experimental data on liquid-solid mass transfer, C_s was calculated at the smaller particle size ($d_p=0.110$ cm) and the lowest liquid velocity ($u_L=0.0236$ cm/sec); under these conditions the largest mass transfer resistance was expected. C_s was about 80% of the bulk concentration of oxygen in the liquid.

Hirose *et al.*[14] reported that for an identical particle Reynolds number of liquid, the liquid-solid mass transfer coefficient of a trickle-bed reactor in the gas-continuous flow regime was 1.2—2 times larger than that of a liquid-full reactor. This suggests that no liquid-solid mass transfer limitation will be present for a trickle-bed reactor operated with the same liquid velocity, catalyst and temperature as a liquid-full reactor with negligible liquid-solid mass transfer effect.

Next, rate data were taken in the trickle-bed reactor with the same catalyst used in the liquid-full reactor. Fig. 4 shows the effect of superficial gas (oxygen) velocity, u_G [cm·sec^{-1}], on the global rate of reaction at $d_p=0.110$ cm and $u_L=0.10$ cm/sec. In the range of gas velocity used in our work the global rates were nearly constant. In the gas-continuous flow regime there is no significant effect of gas velocity on the liquid-solid mass transfer coefficient.[14] Thus, the results shown in Fig. 4 and Fig. 3 suggest that the liquid-solid contacting efficiency was not influenced by the gas velocity.

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13) P.N. Dwivedi and S.N. Upadhyay, *Ind. Eng. Chem. Process Des. Dev.*, **16**, 157 (1977).
14) T. Hirose, Y. Mori, and Y. Sato, *J. Chem. Eng. Japan*, **9**, 220 (1976).

The effect of superficial liquid velocity on the liquid-solid contacting efficiency was examined at $u_G=2.9$ cm/sec for both $d_p=0.110$ and 0.242 cm. The results are shown in Fig. 5. The ratio of R_{TB} to R_{LF}, that is f, did not change with the liquid velocity. No difference between the particle sizes was detected by statistical analysis. The average value of f was 0.91 and the coefficient of variation was 5.4%.

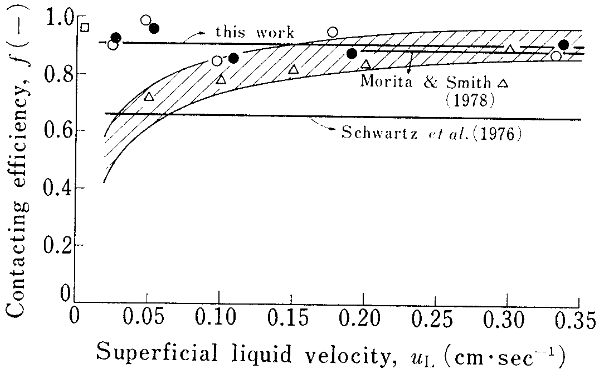

Fig. 6. Contacting Efficiency in a Trickle–Bed Reactor

□: Hartman and Coughlin (1972).
△: Herskowitz *et al.* (1979).
○; $d_p=0.110$ cm} This work.
●: $d_p=0.242$ cm} This work.
▨ Satterfield (1975).

The reported values of liquid-solid contacting efficiency are presented with our experimental results in Fig. 6 as a function of superficial liquid velocity. Satterfield[2] defined the contacting effectiveness as k_{app}/k_v,[15] and he predicted from the results of Bondi[16] that f increases with the liquid velocity. Herskowitz *et al.*[9] investigated the hydrogenation of α-methylstyrene on a Pd–Al_2O_3 catalyst, and reported that the contacting efficiency increased with the liquid velocity. Their results fall within the shaded region (Fig. 6) proposed by Satterfield.[2] Colombo *et al.*[6] presented very similar results, using a tracer technique. In contrast, Hartman *et al.*[5] found that the contacting efficiency was an average of 0.89 over a range of liquid velocity (0.00046—0.0062 cm/sec) for the oxidation of SO_2 with air in a countercurrent flow of gas and water through a bed of activated carbon particles. Sedricks and Kenney[17] reported $f=0.86$ for the hydrogenation of crotonaldehyde in a trickle-bed reactor. Schwartz *et al.*[7] defined the contacting efficiency as a function of total BET area that was wet. The fraction of total pore volume filled with liquid was characterized by a constant average value of 0.78, based on tracer-determined holdup, and 0.66, bassed on volumetrically measured holdup, over a wide range of liquid velocity (0.03—0.50 cm/sec).

In this work, data were taken for a system for which gas phase reaction did not occur and liquid-solid mass transfer resistance was negligible. The liquid-solid contacting efficiency was nearly constant, and the average value was 0.91. That is, the liquid was dispersed quite well over the outer surface of the carbon particles even in the region of low superficial liquid velocity. This implies that the flow pattern of the liquid did not change over the range of liquid velocity tested and the increase of liquid velocity only caused an increase of liquid film thickness.

As described above, there is no consistency in the reported value of liquid-solid contacting efficiency. Satterfield[2] stated that the important quantities are the liquid-solid contact angles and the dispersion properties affected by the surface tension and the combination of liquid and solid materials. Onda *et al.*[18] concluded that the degree of wetting depended on surface energy from measurements of the contact angles between various kinds of packing materials and three kinds of liquids and of the surface tensions of these liquids. Additional studies will be needed, for example, on the relationship between the contacting efficiency and the characteristics of liquid and solid materials. In such studies it would be preferable to choose a reaction system with no gas phase reaction and negligible mass transfer effects.

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15) k_{app}: apparent reaction rate constant in a trickle-bed reactor. k_V: reaction rate constant in an autoclave.
16) A. Bondi, *Chem. Technol.*, 185 (Mar., 1971).
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