JOURNAL OF CATALYSIS 1, 508–520 (1962)

Heat and Mass Transfer in Methanol Synthesis—Optimum Operating Conditions of the Reactors

I. PASQUON AND M. DENTE
From the Istituto di Chimica, Industriale Politecnico, Milano

Received April 10, 1962

Concentration gradients in the pores of the catalyst granules, which contribute to lowering the practical effectiveness of the catalyst itself, are established for industrial reactors for the synthesis of methanol from CO and H_2. For operating conditions on an industrial scale and for a ZnO-Cr_2O_3 catalyst, the effectiveness values are calculated to be about 0.5–0.7. These values are in agreement with experimental data.

The other mass transfer and heat transfer phenomena occurring in the catalytic bed can be neglected. The calculations relative to these last phenomena have been carried out by simplified procedures.

By taking into account the kinetic data and the secondary reactions, the optimum range of working temperature for a reactor operating at about 300 atm corresponds to approximately isothermal conditions (~395°C) for the greater part of the catalytic bed; only toward the end of the reactor would a slight cooling of the reactants be suitable.

These optimum operating conditions are very close to those obtained in various industrial reactors built in Italy.

I. INTRODUCTION

The kinetic study of the synthesis of methanol from CO and H_2 was carried out some years ago with the aid of an experimental reactor of the integral type, which was practically isothermal (*1, 2, 3, 4*). The catalysts examined were based on ZnO-Cr_2O_3 (*1, 2*) and on ZnO-CuO-Cr_2O_3 (*2, 3*). The results obtained permitted the deduction that the reaction rate can be expressed by the following equation:

$$r = \frac{f_{CO}p_{CO}f_{H_2}{}^2p_{H_2}{}^2 - f_{CH_3OH}p_{CH_3OH}/K}{(A + Bf_{CO}p_{CO} + Cf_{H_2}p_{H_2} + Df_{CH_3OH}p_{CH_3OH})^3} \qquad (1)$$

The values of the A,B,C,D factors and of the equilibrium constant K, were reported in previous papers (*1, 2, 3*). The fugacity coefficients, calculated at the total pressure of the system, can be deduced from the known generalized diagrams.

Equation (1) and the numerical values of the factors contained in it had been obtained with granules of catalyst of dimensions ranging from 0.6 to 0.9 mm (*1*). It was observed that the kinetic data obtained by operating under these conditions were practically independent of the physical phenomena of heat and mass transfer, both outside and inside the catalyst granules, whose effectiveness factor was therefore equal to 1. Moreover, the partial pressures in the bulk stream are practically equal to those occurring at the solid surface.

The data reported above, obtained on a laboratory scale, can be directly applied to the calculation and to the study of the behavior of industrial reactors.

In the present work these data have been used to examine the influence of heat- and mass-transfer phenomena on the kinetics of the reaction of synthesis of methanol in an industrial-type reactor.

Moreover the calculations made have allowed pointing out of the optimum operating conditions of the reactor, also considering the secondary reaction.

II. Operative Parameters

The calculations were done for a Fauser-Montecatini-type reactor with almost adiabatic layers, with intermediate cooling between the layers.

The catalyst, consisting of ZnO-Cr_2O_3, is identical (with the exception of the size of the granules) to that used in the experimental reactor, and has the shape of small cylinders. These are the data for which the calculations have been effected:

Diameter of the catalytic bed	700 mm
Pressure	280 atm
Temperature	330–410°C
Feed rate	28,000 Nm^3/hr
Composition of the gases entering the reactor	12% CO, 80% H_2, 8% inert gases
Dimensions of the catalyst granules (in small cylinders)	ϕ 5.5 mm; l 16 mm
Density of packed catalyst in reactor (ρ_B)	830 kg/m^3
Chemical density of the catalyst (ρ_t)	5400 kg/m^3
Density of catalyst granule (ρ_A)	1730 kg/m^3
Void fraction within a single porous granule (θ)	0.68

The choice of some of these values will be justified further on.

For the practically adiabatic layer reactors, the temperature may be considered constant in almost all of the transverse section of the catalytic bed.

Moreover we shall assume that preferential paths do not exist in the catalytic bed, and owing to the high linear velocity of the gases, we shall also neglect the influence of possible back-mixing phenomena.

III. Influence of the Physical Phenomena on the Kinetic Behavior of the Reactor

The most important physical phenomena which may influence the behavior of the reactor or the interpretation of the kinetic data are:

a nonuniform distribution of the transport rate of reactants and products in each section of the reactor;
heat-transfer phenomena (external and within the catalyst granules);
mass-transfer phenomena (external and longitudinal molecular diffusion and in the pores of the catalyst).

In general, the analysis of some of these phenomena is made rather difficult by the complexity of the equation representing the rate of the over-all reaction process. However, we have observed that if the effects due to the above-mentioned phenomena are of little importance, it is possible to deduce, for some of them, simple "criteria" for their evaluation, only considering terms of the first order. If the effects are considerable, and this can be deduced by the previous "criteria," the linearization does not give rise to satisfactory results, and it is necessary to make use of the complete solution. In the present work, it has been observed that among all the physical phenomena, the diffusion of the reactants in the pores of the catalyst granules most influences the reaction rate. This phenomenon decreases the effectiveness of the catalyst.

1. Nonuniform Distribution of the Rates in the Transversal Sections of the Reactor

The presence of the catalytic filler forces the fluid, whether its flow is turbulent or laminar, into a very tortuous route. Particles of fluid which are found at a distance of the order of magnitude of the diameter of the catalyst granules, undergo very different rates; therefore in each section of the reactor, there is a very wide distribution of the residence time and of conversions and therefore of concentrations. This phenomenon tends to provoke a certain type of radial diffusion, which is peculiar to the packing systems. Moreover each fluid element in its trajectory undergoes continuous accelerations and decelerations. In the deceleration phase (in the spaces between the granules), the fluid is mixed and its composition tends to be uniform. Both phenomena tend to reduce the conversions and to influence systematically the data obtained with a certain type of reactor containing granules with a certain shape and dimensions.

These phenomena have been studied very little (*5*). They will not be considered in this paper; however, it was worth mentioning them, because they are typical of the filling reactors. This is why it is interesting to study them more deeply.

2. Heat Transfer

Temperature gradients, which sometimes can assume considerable importance, are established between the catalyst surface, on which the reaction heat is evolved, and the bulk gaseous phase, in which the temperature is measured. These phenomena are well known and the theoretical relationships for the relative calculations have been dealt with by various authors (*6*). We wish to point out that when the effect of this phenomenon on the reaction rate is of little importance, it is more suitable in every respect, to calculate it in the following way:

$$r = r(T_e) - r(T_i) \cong (\partial r/\partial T)_{T_e} \Delta T \qquad (2)$$

ΔT is given by the above-mentioned authors as follows:

$$\Delta T = -\frac{r\Delta H}{a_m C_p G} j_h^{-1}(Re_p) Pr^{2/3} \qquad (3)$$

It is therefore immediately possible to obtain the relative error made when evaluating the reaction rates, referred to the temperatures in the bulk gaseous phase (which are those experimentally known) with respect to the temperatures of the catalyst surface (which are the actual reaction temperatures):

$$\epsilon_{\Delta T} \ (= \Delta r/r) \cong -(\partial r/\partial T)_{T_e} (\Delta H/a_m G C_p) j_h^{-1}(Re_p) Pr^{2/3} \qquad (4)$$

The numerical values of the function $j_h(Re_p)$ are found in the literature (*6*).

The "criterion" to be assumed in order to evaluate the relative importance of this mechanism is that of the second member of Eq. (4); if this "criterion" is lower than a sufficiently small value (for instance 0.05), the influence of the phenomenon considered on the kinetics of the reaction is practically negligible, because it is justified by the measurements errors. If the "criterion" is much higher than the indicated level, the heat transfer process in the solid–gas interface is important and it is no longer practically indifferent to refer to the temperature T_e or T_i. Moreover, in this case, since the terms of higher order in Eq. (2) are not negligible any more, the simple criterion Eq. (4) cannot be adopted, and it is necessary to adopt the usual treatment.

In the case of the synthesis of methanol, for the operating conditions reported in the previous section, $|\epsilon_{\Delta T}|$ does not exceed 2–3%. Analogous calculations carried out for the laboratory conditions give values of the same order.

It must be observed that, in the case of the industrial reactor, these calculations have been made by supposing that the effectiveness of the catalyst is equal to that of the catalyst used in the laboratory. In practice the effectiveness of the industrial catalyst is lower than that of the laboratory catalyst. Therefore, the errors incurred when evaluating the reaction rate of the industrial reactor, by neglecting the temperature gradients in the solid–gas interface, are lower than those calculated above.

Another thermal phenomenon which must be taken into account consists in the variation of the temperature in the granules of catalyst. This phenomenon was studied in the first approximation by Damkohler (*7*). According to this author, the differences in the temperature which occur between the external surface of the catalyst for the methanol synthesis are of the order of the degree or even lower.

More recent studies (*8, 9*) show that in some particular cases, the difference in temperature between the inside and the outside of the catalyst particles may reach values even of some tens of degrees; these studies, however, cannot be directly used for evaluation in our case since they do not furnish any "criteria."

The evaluation of the temperature gradients on the inside of the catalyst granules, in the case studied here, is based on the work developed by Tinkler and Metzner (*10*). By supposing it to be possible to calculate separately the effect of parameter Λ and of the parameter called by the aforesaid authors ϵ (as if the superimposition procedure were valid) on efficiency η, it is possible to evaluate the increase of η due to the nonisothermicity of the catalyst granules. By assuming, for catalyst granules, an actual thermal conductivity in defect of $k_{\text{act}} = 8 \times 10^{-4}$ cal/cm sec* in our case it is possible to deduce that $\epsilon = -0.25$. On the basis of the diagrams reported in the quoted paper (*10*), it can be said that, with such a value of ϵ and under the operating conditions considered here, the temperature gradient at the inside of the catalyst granules makes the average efficiency η of the catalyst vary from 0.60 to 0.64. This increase, evaluated by excess, can be neglected, taking into account other calculation uncertainties. The corresponding difference existing between the highest temperature of the external surface of the granules and of their center is of the order of a few degrees (*7*).

Bearing in mind that, in the case considered by us, the thermal conductivity of the catalyst granules is higher than that assumed to carry out the calculations reported above, it is possible to believe that such differences in the temperature are negligible; we shall assume that for each particle of catalyst the conditions are practically isothermal.

3. Mass Transfer Phenomena

a. External Diffusion in the Solid–Gas Interface

A phenomenon causing the nonuniformity of concentration is the well-known mass transfer in the solid–gas interface of the granules of catalyst. This phenomenon has been widely studied by various authors (*6*). Also in this case it must be observed that, taking into account the effects of the first order, it is possible to realize at once whether the influence of this phenomenon is negligible or not. The relationship which can be used for this purpose is the following one:

$$\Delta r = r_e - r_i \cong \sum_{j=1}^{N} (\partial r/\partial \bar{p}_j)_{\bar{p}_j = \bar{p}_{je}} \Delta \bar{p}_j \quad (5)$$

where the summation is extended to all the reactants and products and where $\Delta \bar{p}_j$ are data obtained from the following relationship (*6*):

$$\Delta \bar{p}_j = -\frac{\nu_j r M_m P_f}{a_m G} j_d^{-1}(Re_p) Sc_j^{2/3} \quad (6)$$

But $Sc_j \cong \text{constant} = Sc$, and therefore:

$$\epsilon_d \left(= \frac{\Delta r}{r} \right)$$
$$\cong -\frac{M_m P_f}{a_m G} j_d^{-1}(Re_p) Sc^{2/3} \sum_{j=1}^{N} \nu_j \left(\frac{\partial r}{\partial \bar{p}_j} \right) \quad (7)$$

The numerical values of the function $j_d(Re_p)$ are reported in the literature (*6*). Our calculations applying Eq. (7) show that for the operating conditions considered here ϵ_d never exceeds about 2%. Values of the same order can be calculated for the most varied experimental conditions with the laboratory reactor. If the values of ϵ_d should have been higher, the terms of order higher than the first one should not be neglected any more in Eq. (5) and the calculation should have been carried out by the usual methods. In such a case, the reaction rate should be partly controlled by the diffusion process under examination.

In the case considered here one can refer alternately, in the case of the kinetic equation, to the fugacity values in the bulk phase (which are experimentally known) or to those in the solid–gas interface.

We must observe that the two mechanisms of heat and mass transfer in the interface area give effects which tend to compensate each other, because they are of an opposite sign.

b. Longitudinal Diffusion

Let us neglect the presence of radial gradients of concentration and the consequent diffusion due to the above-mentioned

---

* This is the value assumed for isolating catalysts (based on $SiO_2—Al_2O_3$) (*9*). In our case the catalyst is a semiconductor; moreover we operate in the presence of an H_2 excess under pressure, which has a high thermal conductivity.

phenomena of nonuniform velocity of the reagents; we can do so because the condition of the radial derivative of the concentration, which is null on the wall, tends to make macroscopically uniform the radial distribution of the concentration.

We shall examine here the phenomenon of longitudinal diffusion of mass, caused by the presence of longitudinal concentration gradients, due, in their turn, to the presence of the reaction. This phenomenon has already been studied by other authors (*6, 11*). Taking into account only the corrected limiting conditions (*12*) exact analytical solutions have been found for kinetic equations of the first order (*12*), or numerical solutions for other types of equations (*14*). In our case we have assumed *a priori* that the importance of such a diffusive phenomenon is small. In this case it is possible to carry out the calculations—even if approximately—without making hypotheses on the order of the reaction (see Appendix).

The "criterion" drawn leads us to deduce that the error made in the calculation of the conversion, by neglecting the phenomenon of the longitudinal diffusion, is:

$$\alpha R[\gamma^\circ(1)] \ln \frac{R(1)}{R[\gamma^\circ(1)]} \tag{8}$$

The "criterion" allowing judgment of the relative importance of the phenomenon being considered is in Eq. (8); also in this case, it is necessary that its value is below the level of the measurement errors, so that the error incurred in the interpretation of the results, which is due to it is truly negligible, or else so that it can be neglected in the industrial design phase. If the criterion exceeds this level, the longitudinal diffusion cannot be neglected and an exact examination is necessary, since the contribution of the terms in α^2 in Eq. (5) of the Appendix is no longer negligible. In the case which we have studied, the calculations made for different operative conditions, showed "criterion" values lower than 2–3% for the laboratory reactor and even lower for the industrial reactor (due to the high specific flow).

We shall observe that the criterion deduced by us, and represented by Eq. (8), is quite similar to that obtained, for instance, by Danckwerts, who studied the case of the irreversible reactions of the first order (*13*).

c. *Internal Diffusion in the Pores. Effectiveness of the Catalyst*

A final phenomenon of mass transfer which must be analyzed is that of the diffusion of the reagents in the pores of the catalyst from and toward the internal surface. This phenomenon tends to reduce the reaction rate on the internal surface of the catalyst, that is to reduce the "effectiveness."

Different theories have been developed for the calculation of the effectiveness factor using both analytical and numerical calculations (*6, 15–18*). [It must be borne in mind that the introduction of the effectiveness factor modifies Eq. (1) of the reaction rate into the following equation:

$$r = \eta \frac{f_{CO}p_{CO}f_{H_2}{}^2p_{H_2}{}^2 - f_{CH_3OH}p_{CH_3OH}/K}{(A + Bf_{CO}p_{CO} + Cf_{H_2}p_{H_2} + Df_{CH_3OH}p_{CH_3OH})^3} \tag{9}$$
]

Without going into details, it is possible to observe that these theories have been well developed for particles of a well-defined geometric shape; however, it was demonstrated (*17*) that, if the V_p/S_p ratio is assumed as characteristic length, the effectiveness factor is almost independent of the shape.

There are three main methods of diffusion in the pores (*19, 20*):

(A) When the mean free path of the molecules is not small with respect to the pore radius, a Knudsen diffusion occurs. This takes place for low pressures (a few atmospheres) and small radius pores. In our case, the high pressures (300 atm) markedly lower the mean free path and this type of diffusion is excluded.

(B) When the total number of molecules in the reaction markedly varies, a difference of pressure is produced in the pores, which induces a Poiseuille diffusion: In our case, the high excess of H_2 excludes this type of diffusion.

(C) Ordinary diffusion: This is the phenomenon which occurs in our case.

In order to carry out the calculation relative to this phenomenon, it is necessary to know the effective diffusivity of gases in pores (D_{eff}). Unfortunately, relationships allowing the calculation of this factor, are not available.* For instance relationships of the following type have been proposed *(19)*:

$$D_{\text{eff}} = \theta D_g/2$$
$$D_{\text{eff}} = \theta D_g/\theta^{1/2}\sqrt{2}$$
$$D_{\text{eff}} = \theta D_g/\theta^{1/3}\sqrt{2}$$

For $\theta = 0.5$, it is possible to assume $D_{\text{eff}} = \theta D_g/2$; for $\theta > 0.5$, we can assume that the last relationship is the most convenient. In our case $\theta = 0.68$, and

$$D_{\text{eff}} = \theta D_g/\theta^{1/3}\sqrt{2} = \theta D_g/0.9\sqrt{2}$$

should be found.

Considering that at the limit, for $\theta \rightarrow 1$, $D_{\text{eff}} \rightarrow D_g$, and since the general relationships for calculating D_g at high pressure and at high temperature often give values in defect, in order to perform our calculations, we assumed the relationship

$$D_{\text{eff}} = \theta D_g\sqrt{2}.$$

We shall see that an error in the evaluation of D_{eff} causes a lower percentage error in the evaluation of η.

We shall observe that the results obtained from our calculations agree well with experimental data.

For the study of the intraparticle diffusion in the case of the laboratory reactor, it is also easy to deduce a "criterion," only taking into account the effects of first order. On the contrary in the case of the catalyst granules used in an industrial reactor, the contributions of the terms of higher order are important, and therefore we have adopted the general nonsimplified relationship.

The hypotheses already used by the above-mentioned authors, made in order to calculate (in a sufficiently approximate way) the values of the Λ parameter and of the corresponding effectiveness η, are the following ones:

isothermous catalyst particles;
the same porous structure in the catalyst granules of different size;
actual constant diffusivity.

Moreover we assume that in the case examined by us, for not higher variations of concentration in the pores, Eq. (1) can be expressed, as a good approximation, in the following way:

$$r\rho_A = k_v C_{\text{CO}} - k'_v \qquad (10)$$

being:

$$k_v = \frac{f_{\text{CO}}\bar{p}_{\text{H}_2}^2 + f_{\text{CH}_3\text{OH}}/K}{(A + B\bar{p}_{\text{H}_2} + C\bar{p}_{\text{CO}} + D\bar{p}_{\text{CH}_3\text{OH}})^3} \cdot \rho_A z_g RT \cong \text{constant}$$

$$k'_v = \frac{(f_{\text{CH}_3\text{OH}} p^\circ_{\text{CO}} \rho_A/K)}{(A + B\bar{p}_{\text{H}_2} + C\bar{p}_{\text{CO}} + D\bar{p}_{\text{CH}_3\text{OH}})^3} \cong \text{constant}$$

This can be assumed because hydrogen in the reaction is in a remarkable excess and therefore $\bar{p}_{\text{H}_2}$ is almost constant; moreover the diffusion constants for CO and CH_3OH are almost equal.

By assuming that the Eq. (11) is valid, it is easy to demonstrate that the effectiveness factor η is given by the relationships reported in the above-mentioned papers, where only first order reactions were considered.

By applying this method of calculation, it has been checked that the effectiveness of the catalyst used under the laboratory-scale conditions, was in any case higher than 0.97–0.98, that is practically unity.

Table 1 shows the values of the effectiveness coefficient for the industrial reactor.

It may be seen that the effectiveness markedly increases with decreasing temperature, and to a lesser extent, with increasing conversion. However, when approaching the equilibrium—that is for reaction rates tending to zero—the effectiveness tends to one, independently of the reaction temperature.

The values reported in Table 1 have been confirmed by us from experimental data. Actually, by analyzing data obtained with an industrial reactor which used the same catalyst as that considered in this paper, operating between 370 and 410°, an av-

---

* D_{eff} can be evaluated fairly accurately only by experimental means.

TABLE 1

EFFECTIVENESS FACTOR η OF THE ZnO-Cr_2O_3 CATALYST IN INDUSTRIAL REACTORS FOR THE SYNTHESIS OF METHANOL[a]

x (% CO conv.)	T (°C)				
	330°	350°	370°	390°	410°
0	0.91	0.83	0.69	0.58	0.52
10	0.93	0.86	0.71	0.60	0.52
20	0.94	0.88	0.73	0.61	0.53
30	0.95	0.90	0.75	0.63	0.54

[a] $\pi = 280$ atm; ϕ reactor, 700 mm; feeding, 12% CO, 80% H_2, 8% inert; catalyst, $\phi \cong 5.5$ mm; $l \cong 16$ mm; $\theta \cong 0.68$; $\rho_A = 1.73$ g/cm³; $\rho_B = 0.83$ g/cm³.

TABLE 2

OPERATING CONDITIONS OF THE INDUSTRIAL REACTORS FOR THE SYNTHESIS OF CH_3OH

Pressure	250–450 atm
Highest temperature	410–420°
Lowest temperature	320–370°
Composition of the concentration gases entering in the reactor	CO: 8–15% H_2: 60–80% Inert + CO_2: 8–30%
Conversion by passage	15–30% of the entering CO
Space velocity	5000-15000 Nm³/m³ catalyst

erage value of $\eta = 0.67$ has been calculated. The data available for this calculation consisted of some values of temperature along the catalytic bed and of the over-all conversion; using the kinetic data obtained in the laboratory (*1, 2*), the temperature curve along the reactor and the over-all conversion calculated are in good agreement with the experimental data, if the value 0.67 is assumed for the η coefficient in Eq. (9).

IV. OPTIMUM OPERATING CONDITIONS OF THE INDUSTRIAL REACTORS

1. Observations on the Operating Conditions of the Industrial Reactors

Before applying the kinetic data to the research on the optimum operating conditions of the reactor, it is suitable to make some remarks on the actual operating conditions in the industrial reactors. The conditions for reactors built in Italy are reported in Table 2.

It can be seen that the reaction temperature is lower than 410–420°. The reason for this limit is above all due to the fact that by operating at the highest temperatures, the purity of the methanol produced decreases (*2*); moreover temperatures higher than 390–400° cause a rapid increase of the production of methane from CO and H_2.

This reaction, which is thermodynamically more favored than the formation of methanol, is particularly tedious, most of all because of its high exothermicity, which can cause undesired rises of temperature; moreover the formation of methane during the synthesis may cause an excess of this gas in the recycle gases. In some industrial plants, even if the purge of the circulating gas is fairly high, the per cent of methane in the circulating gas entering the reactor reaches 25–30%.

Another reason for which the reaction temperature is not too high, is due to the necessity of lessening the aging phenomena of the catalyst (*2*).

From the data reported in Table 2, it can be seen that the lowest temperature of the reacting gases on the catalyst is 320–370°, depending on the reactors. This is due to the fact that the reaction products are progressively cooled along the reactor, for the well-known reasons connected with the physical-chemical behavior of the synthesis reaction of methanol.

The per cent of CO in the feed-gases of the reactor is rather low. Actually, the highest reaction rate is not obtained with a ratio H_2 to CO = 2, corresponding to the stoichiometric ratio, but is obtained with a higher ratio. This can be attributed to the fact that the carbon monoxide is more adsorbable than hydrogen and, in order to obtain the maximum rate on the surface of the catalyst, it is necessary to operate with gases rich in hydrogen (*1, 2*).

Last, we wish to observe that, at most, only 25–30% of the CO entering the reactor reacts per pass. By operating under pressures of 300 atm this percentage hardly exceeds 25%.

2. Rate–Temperature Diagram

First of all, the composition of the gases entering the reactor for which the reaction is the highest has been calculated. The results obtained for $T = 390°$ are reported in Table 3. It can be seen that the reaction rate of the entering gases, containing from 8 to 12% of CO, depends little on the composition of the same gases. For higher CO content, the reaction rate decreases.

TABLE 3
REACTION RATES[a]

x (% CO conv.)	% CO 8	10	12	14
0	12.7×10^{-2}[b]	13.7×10^{-2}	14.4×10^{-2}	14.5×10^{-2}
10	10.6×10^{-2}	11.1×10^{-2}	11.6×10^{-2}	10.9×10^{-2}
20	8.3×10^{-2}	8.6×10^{-2}	9.0×10^{-2}	8.3×10^{-2}
30	6.1×10^{-2}	6.3×10^{-2}	6.5×10^{-2}	5.6×10^{-2}

[a] $\pi = 280$ atm, $T = 390°C$, 8% inert.
[b] Kmole CH_3OH/hr kg catalyst.

The recipe: 12% CO; 80% H_2; 8% inert gases has been chosen. This percentage of CO corresponds to that used practically in the industrial reactors.

The calculations of the rate–temperature diagram, for different concentrations, have been carried out for $p = 280$ atm. It has been supposed, as, however, was demonstrated experimentally (*1, 2*), that the inert gases (N_2 and CH_4) are such in all respects.

The results obtained are reported in Fig. 1, where they are compared with the data calculated without taking into account the diffusion phenomena in the pores of the catalyst granules.

2. Optimum Operating Conditions

On the basis of Fig. 1, in order to obtain the highest reaction rate, the temperature along the catalyst should obviously follow the curve (optimum kinetic curve) passing through the maxima of the various curves. Therefore the entering temperature (for x equal or slightly higher than 0) should be rather high (>400°) and subsequently continuous cooling along the reactor should be effected so as to obtain the following temperature-conversion correspondence

x (% CO conv.)	10	20	30
t (°C)(approx.)	402	397	390

If the effectiveness of the catalyst is assumed equal to one, the temperature values should be higher.

From the values reported above, it has been observed that also for conversions lower than 20% of the entering CO, the temperature should always be higher than about 400°.

It is of interest to observe that, for each conversion value, the highest reaction rate varies little for a fairly wide range of temperature. Bearing in mind the remarks reported in the previous section, for which the synthesis temperature should not exceed 390–400°C, and considering the behavior of the "optimum kinetic curve" (Fig. 1), it must be concluded that, for conversions lower than 20% of the entering CO, the actual optimum curve should be about an isothermal curve between 390–400°.

Only for conversions higher than about 20% of the entering CO, should the temperature decrease progressively down to 390–395°C. This condition is hardly attainable for an industrial reactor, but if one proposes to operate a layer Fauser-type reactor, for conversions lower than about 20% of CO, the curves relative to each layer should as much as possible approach an isotherm (between 390° and 400°) in-

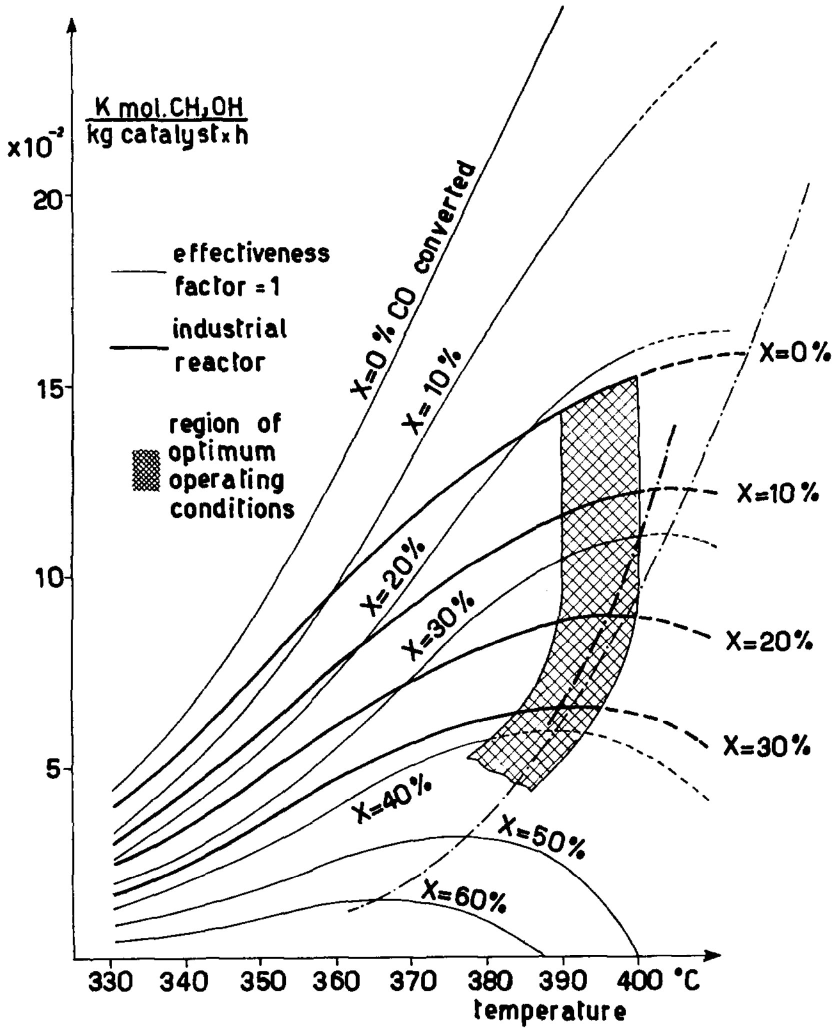

FIG. 1. Rate–temperature diagram of methanol synthesis from CO and H_2 for different conversions: $\pi = 280$ atm; composition of the feed gases: 12% CO, 80% H_2, 8% inert; catalyst, Cr_2O_3-ZnO.

stead of the "optimum kinetic curve" passing through the maxima of the curves reported in Fig. 1.

We have noticed that some Italian industrial reactors operate under conditions which are very similar to those calculated by us.

These remarks point out the difference existing between the synthesis of methanol and the synthesis of ammonia; from the physical-chemical point of view, these two reactions show remarkable analogies, but the absence of secondary reactions in the synthesis of ammonia, allows the calculation for the relative reactors and the carrying out of the reaction taking into account mainly its kinetic parameters.

APPENDIX

If the longitudinal diffusion is taken into account, the differential equation characterizing the longitudinal flow reactor becomes, with regard to the component considered (e.g. CO):

$$\frac{D_{CO,m}\pi^2}{RT(\pi - p_{CO})_{n_t}} \frac{d^2 n_{CO}}{dZ^2} - G\frac{dn_{CO}}{dZ} - r_{CO}\rho_B = 0$$

In the region (I) (which we should suppose to be extended from $Z = -\infty$ to $Z = 0$) preceding the reaction region, the reaction term is absent; analogously in the region (III), subsequent to the catalytic region (which we should suppose to be extended from $Z = L$ to $Z = +\infty$). The reaction region (II) is extended from 0 to L.

It can be also supposed that in the I and III regions, diffusivities have different values from those of region II.

Putting:

$$\alpha = \frac{D_{\mathrm{CO,m}}{}^{\mathrm{II}}\pi^2}{RT(\pi - p_{\mathrm{CO}})_{n_t}LG}$$

$$\beta = \alpha(D_{\mathrm{CO,m}}{}^{\mathrm{I}}/D_{\mathrm{CO,m}}{}^{\mathrm{II}})$$

$$\delta = \alpha(D_{\mathrm{CO,m}}{}^{\mathrm{III}}/D_{\mathrm{CO,m}}{}^{\mathrm{II}})$$

$$R(\gamma) = r_{\mathrm{CO}}\rho_B L/n^\circ{}_{\mathrm{CO}}G$$

$$z = Z/L$$

$$\gamma_{\mathrm{CO}} = n_{\mathrm{CO}}/n^\circ{}_{\mathrm{CO}}$$

and supposing in the first approximation: α,β,δ = constants, we obtain:

In region I $(-\infty < z < 0)$

$$\beta\frac{d^2\gamma}{dz^2} - \frac{d\gamma}{dz} = 0 \qquad (1)$$

In region II $(0 < z < 1)$

$$\alpha\frac{d^2\gamma}{dz^2} - \frac{d\gamma}{dz} - R(\gamma) = 0 \qquad (2)$$

In region III $(1 < z < +\infty)$

$$\delta\frac{d^2\gamma}{dz^2} - \frac{d\gamma}{dz} = 0 \qquad (1')$$

Many authors have studied the limiting conditions intensively. In particular, that used by Hulbert (*11*), that is, $\gamma(z = 0) = 1$, is not consistent with the nature of the problem because it neglects the recall effect diffusion exerted by the reaction present in region II on the molecules flowing in region I*. The limiting conditions adopted by us are spontaneous and in agreement with those reported by other authors in more recent papers (*12, 13, 14*):

In region (I)

for $z = -\infty$ $\gamma_{\mathrm{I}} = 1$,

for $z = 0$

$$\gamma_{\mathrm{I}} = \gamma_{\mathrm{II}} \qquad \beta\left(\frac{d\gamma}{dz}\right)_{\mathrm{I}} = \alpha\left(\frac{d\gamma}{dz}\right)_{\mathrm{II}}$$

In region II

for $z = 0$ $\quad \gamma_{\mathrm{I}} = \gamma_{\mathrm{II}}$

for $z = 1$

$$\gamma_{\mathrm{II}} = \gamma_{\mathrm{III}} \qquad \left(\frac{d\gamma}{dz}\right)_{\mathrm{II}} = 0\dagger$$

In region III

for $z = +\infty$, γ_{III} = finite.

From this condition and from Eq. (1′), it can be deduced immediately:

$$\gamma_{\mathrm{III}} = \text{constant} = \gamma_{\mathrm{II}}(1), \text{ and therefore } (d\gamma/dz)_{\mathrm{III}} = 0$$

We notice that the solution of Eq. (1) is simply:

$$\gamma = 1 - C_1e^{z/\beta}$$

where for $z = -\infty$, $\gamma = 1$; whereas for $z = 0$,

$$\gamma = 1 - C_1$$

and

$$d\gamma/dz = -C_1/\beta$$

In order to solve Eq. (2) we observe that, for our purposes, only solutions for small values of α would be considered. That is why, having considered the unknown function $\gamma(z,\alpha)$ it is possible to write:

$$\gamma(z,\alpha) = \gamma^\circ{}_z + \alpha\Delta(z) + 0[\alpha^2] \qquad (3)$$

and therefore

$$R(\gamma) \cong R(\gamma^\circ) + \alpha\Delta(dR/d\gamma)_{\gamma^\circ} + 0[\alpha^2] \qquad (4)$$

where γ° and Δ are unknown functions; the former represents the distribution of γ in the absence of diffusion processes ($\alpha = 0$); the latter represents the effect (of first order) of the presence of the longitudinal diffusion.

By substituting Eqs. (3) and (4) in Eq. (2), it is possible to obtain the following identity (with regard to the independent parameter)

---

* The criterion obtained by Hulbert corresponds to the term αR appearing in Eq. (13) of the Appendix; therefore, this criterion yields wrong values by excess.

† This condition occurs because for $z = 1$, $(d\gamma/dz_{\mathrm{II}}) = (d\gamma/dz_{\mathrm{III}}) = 0$.

$$\alpha \frac{d^2\gamma^\circ}{dz^2} - \frac{d\gamma^\circ}{dz} - \alpha \frac{d\Delta}{dz} - R(\gamma^\circ) - \alpha\Delta \left(\frac{dR}{d\gamma}\right)_{\gamma^\circ} + 0[\alpha^2] \equiv 0$$

That is

$$-\left[\frac{d\gamma^\circ}{dz} + R(\gamma^\circ)\right] - \alpha\left(\frac{d\Delta}{dz} + \Delta \frac{dR}{d\gamma^\circ} - \frac{d^2\gamma^\circ}{dz^2}\right) + 0[\alpha^2] \equiv 0 \quad (5)$$

The conditions of identity in Eq. (5) make null, for any value of α, the power coefficients of α; therefore:

$$\left.\begin{aligned} &\frac{d\gamma^\circ}{dz} + R(\gamma^\circ) = 0 \\ &\frac{d\Delta}{dz} + \Delta \frac{dR}{d\gamma^\circ} = \frac{d^2\gamma^\circ}{dz^2} \end{aligned}\right\} \quad (6)$$

The first part of Eq. (6) simply states that γ° is the distribution for $\alpha = \beta = 0$ (absence of diffusion). In this case the integral can be expressed in the following implicit way:

$$\gamma^\circ = 1 - \int_0^z R(\gamma^\circ)dz \quad (7)$$

The solution of the second part of Eq. (6) is, on the contrary, the following one, as can be easily checked:

$$\Delta = R(\gamma^\circ)(C_2 - \ln R(\gamma^\circ) \quad (8)$$

This is therefore completely known when γ° is known. C_2 is a constant to be determined.

In the same way it is possible to determine the higher terms of γ. For small α it is enough to consider the linear terms in Eq. 3 and therefore:

$$\gamma_{\text{II}} = 1 - \int_0^z R(\gamma^\circ)dz + \alpha R(\gamma^\circ)[C_2 - \ln R(\gamma^\circ)] + 0[\alpha^2] \quad (9)$$

For $z = 0$, $\gamma^\circ = 1$, therefore

$$R[\gamma^\circ(z = 0)] = R(1)$$

The condition that for $z = 0$ is:

$$\beta \frac{d\gamma_{\text{I}}}{dz} = (-C_1) = \alpha \frac{d\gamma_{\text{II}}}{dz} = \alpha \left(\frac{d\gamma^\circ}{dz}\right)_{z=0} + \alpha^2 \left(\frac{d\Delta}{dz}\right)_{z=0} + 0[\alpha^3] = \left(\frac{d\gamma^\circ}{dz}\right)_{z=0} + 0[\alpha^2]$$

being

$$\left(\frac{d\gamma^\circ}{dz}\right)_{z=0} = -R(1)$$

it gives

$$C_1 = R(1) + 0[\alpha^2] \quad (10)$$

In order to determine C_2, notice that it must be

$$\begin{aligned} \gamma_{\text{I}}(z = 0) &= 1 - C_1 = \gamma_{\text{II}}(z = 0) \\ &= \gamma^\circ(z = 0) + \alpha\Delta(z = 0) + 0[\alpha^2] \\ &= 1 + \alpha R(1)\{C_2 - \ln [R(1)]\} + 0[\alpha^2] \end{aligned}$$

The following has been obtained:

$$C_2 = -1 + \ln [R(1)] \quad (11)$$

Therefore

$$\Delta = -R(\gamma^\circ)\left[1 - \ln \frac{R(1)}{R(\gamma^\circ)}\right] + 0[\alpha^2]$$

$$\gamma = \gamma^\circ - \alpha R(\gamma^\circ)\left[1 - \ln \frac{R(1)}{R(\gamma^\circ)}\right] + 0[\alpha^2]$$

The fraction of CO reacted is given by:

$$\begin{aligned} X &= \left|\alpha \frac{d\gamma}{dz}\right|_{z=0}^{z=1} + \gamma(z = 0) - \gamma(z = 1) \\ &= \alpha \left|\frac{d\gamma}{dz}\right|_{z=0}^{z=1} + \gamma^\circ(z = 0) + \gamma^\circ(z = 1) \\ &\quad + \alpha\Delta(z = 0) - \alpha\Delta(z = 1) + 0[\alpha^2] \\ &= 1 - \gamma^\circ(z = 1) - \alpha R[\gamma^\circ(z = 1)] \cdot \ln \frac{R(1)}{R[\gamma^\circ(z = 1)]} + 0[\alpha^2] \\ &\cong X^c - \alpha R[\gamma^\circ(z = 1)] \ln \frac{R(1)}{R[\gamma^\circ(z = 1)]} \end{aligned} \quad (12)$$

where $X^\circ = 1 - \gamma^\circ(z = 1)$ is the fraction of CO which should react in the absence of diffusion phenomena. The (negative) contribution of the diffusion is:

$$X^\circ - X = \alpha R[\gamma^\circ(z = 1)] \ln \frac{R(1)}{R[\gamma^\circ(z = 1)]} \quad (13)$$

This relationship was applied by us to the calculation of $X^\circ - X$ under the most unfavorable conditions, and precisely to the laboratory reactor in correspondence with the lowest feeding rates [linear rate $v \simeq 0.2$ cm/sec (*1*, *2*)]. For the conditions considered $D_{CO,g} = 0.5–0.6 \times 10^{-2}$ cm²/sec; since $D_{CO,g}$ is lower than $D_{CO,m}$ (*6*), we assumed, for this last value to be used for calculating α, values four times higher than $D_{CO,g}$. With these data, values which are not higher than 2–3% are calculated for $X^\circ - X$.

In the case of the industrial reactor, due to its higher feeding rates with respect to the laboratory reactor, the difference $X^\circ - X$, which depends on $D_{CO,m}G^{-2}$ will be even lower and therefore quite negligible.

NOMENCLATURE

A, B, C, D	Constants of the equation of the reaction rate
a_m	External area of catalyst granules per unit mass (m²/kg)
C_{CO}	Bulk concentration of CO
C_p	Heat capacity of gases (kcal/kg °C)
$D_{CO,m}$	Mean diffusivity of CO (m²/sec)
D_{eff}	Effective diffusivity of gases in pores (m²/sec)
D_g	Diffusivity in gas phase (m²/sec)
$D_p = V_p/S_p$	Characteristic linear dimension of catalyst granules (m)
f_j	Fugacity coefficient of components j
G	Superficial mass velocity (kg/m² sec)
j_h, j_d	Dimensionless function of Reynolds number
k	Thermal conductivity of the gas (kcal/sec m°C)
K	Equilibrium constant for homogeneous reaction of methanol synthesis
L	Depth of catalyst bed in the reactor (m)
M_m	Mean molecular weight of the reaction mixture (kg/kmole)
n_{CO}	CO moles/weight of reaction mixture (kmoles/kg)
n°_{CO}	CO moles/weight of reactants (kmoles/kg) in the feed (kmoles/kg)
n_t	Total moles/weight in the reaction mixture (kmoles/kg)
p_f	Mean logarithmic pressure at catalyst–gas interface (atm)
p_j	Partial pressure of component j in gas phase (atm)
$\bar{p}_j$	Fugacity of component j (atm)
$\bar{p}_{je}$	Fugacity of component j in gas phase (atm)
$Pr = C_p\mu/k$	Prandtl number of the gas
r	Rate of reaction [moles/sec (kg catalyst)]
r_{CO}	Rate of reaction referred to the moles of CO converted [moles/(sec) (kg catalyst)]
r_e	Rate of reaction referred to the fugacities in the bulk phase [moles/(sec)(kg catalyst)]
$Re_p = GD_p/\mu$	Modified Reynolds number
S_p	Total surface area of a single catalyst granule (m²)
$Sc_j = \mu/\rho D_j$	Schmidt number of the component j
T	Temperature (°K)
T_e	Temperature in the bulk phase (°K)
T_i	Temperature at catalyst–gas interface (°K)
V_p	Total volume of a single catalyst granule (m³)
x	% CO converted
y_j	Molar fraction of component j
Z	Abscissa along the reactor (*m*)
z_g	Mean compressibility factor of reaction mixture
ΔH	Enthalpy for the reaction of methanol synthesis (cal/mole)
ϵ	Symbol of error
η	Effectiveness factor for porous catalyst
θ	Void fraction within a single porous granule
Λ	$\sqrt{\frac{k_v}{D_{eff}}}\frac{V_p}{S_p}$
μ	Viscosity of reaction mixture (kg/m sec)
π	Total pressure (atm)
ν_j	Stoichiometric coefficient for component j
ρ	Density of reaction mixture (kg/m³)
ρ_A	Density of catalyst granule (kg/m³)

ρ_B	Density of packed catalyst bed (kg/m^3)
ρ_t	Chemical density of the catalyst (kg/m^3)

References

1. Natta, G., Pino, P., Mazzanti, G., and Pasquon, I. *Chim. e Ind.* (*Milan*) **35,** 705 (1953).
2. Natta, G., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 3, p. 345. Reinhold, New York, 1955.
3. Natta, G., Mazzanti, G., and Pasquon, I. *Chim. e Ind.* (*Milan*) **37,** 1015 (1955).
4. Pasquon, I., *Chim. e Ind.* (*Milan*) **42,** 352 (1960).
5. Beek, J., Jr., and Miller, R. S., *Chem. Eng. Progr.* **55,** *Symp. Series* **25,** 24 (1959).
6. See, for example, Hougen, O. A., and Watson, K. M., "Chemical Process Principles," Vol. 3. John Wiley, New York, 1947; and Smith, J. M., "Chemical Engineering Kinetics." McGraw-Hill, New York, 1956.
7. Damköhler, G., *Z. Phys. Chem.* **A193,** 16 (1943).
8. Schilson, R. E., and Amundson, N. R., *Chem. Eng. Sci.* **13,** 226 (1961).
9. Mingle, J. O., and Smith, J. M., *A.I.Ch.E. Journal* **7,** 243 (1961).
10. Tinkler, J. D., Metzner, A. B., *Ind. Eng. Chem.* **53,** 663 (1961).
11. Hulbert, J. H. M., *Ind. Eng. Chem.* **36,** 1012 (1944); **37,** 1063 (1945).
12. Wehner, J. F., and Wilhelm, R. H., *Chem. Eng. Chem. Sci.* **6,** 89 (1956).
13. Danckwerts, P. V., *Chem. Eng. Sci.* **2,** 10 (1953).
14. Fan, Liang-Tseng, and Bailie, R. C., *Chem. Eng. Sci.* **13,** 63 (1961).
15. Thiele, E. W., *Ind. Eng. Chem.* **31,** 916 (1939).
16. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenoma." John Wiley, New York, 1960.
17. Aris, R., *Chem. Eng. Sci.* **6,** 265 (1957).
18. Schilson, R. E., and Amundson, N. R., *Chem. Eng. Sci.* **14,** 226 (1961).
19. Weeler, A., *Advances in Catalysis* **3,** 249 (1957).
20. Weiss, P. B., Prater, C. D., *Advances in Catalysis* **6,** 143 (1954); **9,** 957 (1957).