JOURNAL OF CATALYSIS 5, 348–355 (1966)

Rate-Determining Steps in Contact Catalytic Hydrogenation in Aqueous Solution

I. Gas Absorption

F. NAGY, Á. PETHŐ, AND D. MÓGER

From the Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest

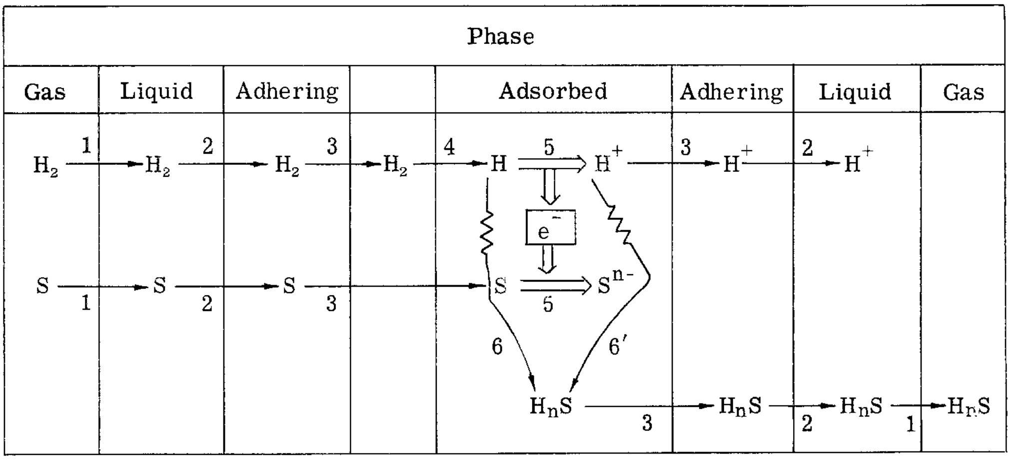
Received July 29, 1964; revised July 12, 1965

Examination of the first step in contact catalytic hydrogenation, the kinetics of H_2 absorption in aqueous solution, in conventional laboratory hydrogenation apparatus, led to the following results:

1. With stirring, H_2 absorption can, under the given conditions, be treated as a first order process.
2. If the dissolved gas enters a reaction, gas concentration cannot be regarded as homogeneous even in the case of stirring. There can be distinguished two liquid spaces: a surface space, in which gas concentration equals the saturation value, and an interior space in which it is less than this value.
3. A method has been devised for the calculation of the true rate constant of a first order reaction from the rate of H_2 sorption, based on the above view on the absorption process.

INTRODUCTION

In hydrogenation, carried out in aqueous solution with gaseous hydrogen on a metal catalyst, the following steps may proceed:



SCHEME 1.

S and H_nS designate the substrate and the product, respectively. The nature of the individual steps is: (1) gas absorption; (2) diffusion through the liquid layer adhering to the catalyst; (3) adsorption; (4) dissociation; (5) electrochemical oxidation or reduction; and (6) surface reaction. (These steps may, of course, be reversible.)

Investigation of the reaction mechanism requires knowledge of the rate-determining step and its kinetic relations. The present paper, the first in a series, deals with the first step, the kinetics and mechanism of gas absorption under conditions of usual laboratory contact catalytic hydrogenation.

It will be demonstrated that under the given conditions the liquid phase may be divided into two parts, an interior and a surface space. Liquid in the surface space can be taken as saturated with the gas under consideration, whereas liquid in the interior space, though homogeneous statistically, is saturated only at the rate of absorption so that further reaction there starts from solution unsaturated with respect to the gas in question. In these conditions the rate of gas absorption can be represented by first order kinetics

$$W_1/v = k_1(x^0 - x)$$

where k_1, the rate constant of the absorption process, is a function of geometry, the intensity of stirring, temperature, etc.; v is the volume of the liquid phase; x^0, the saturation value; and x, the instantaneous value of volume concentration of the gas.

In the investigation of the kinetics and the mechanism of liquid (aqueous) phase contact catalytic hydrogenation on a laboratory scale, reaction rate is generally determined by following the amount of hydrogen taken up by the suspension under atmospheric pressure. As the process is composite, several physical steps have to proceed simultaneously with the chemical reaction proper. Thus there always arises the necessity of identifying the rate-determining step. The amount of gas taken up by the suspension, the kinetics of hydrogen sorption, are in the first place characterized by the rate-determining step. If this is not the surface reaction, the kinetics of sorption does not give any information about the reaction mechanism. This view was first applied to liquid-phase contact catalytic hydrogenation by Elovich and Zhabrova (*1*). They distinguished three domains with respect to the rate-determining step: the diffusional, kinetic, and intermediate domains. The rate-determining steps in these domains are the diffusion of dissolved hydrogen to the catalyst surface, the surface reaction, or both of them, respectively. This treatment, though correct in principle, is incomplete. Subject to criticism are in the first place the criteria that should establish in which of these domains a given experimental set-up is working, as these criteria have not been based on a kinetic analysis of the individual steps.

The possible rate-determining steps have already been treated in our earlier papers (*2*). Scheme 1, which essentially agrees with that of Coenen (*3*) but for the electrochemical steps (always to be kept in mind in aqueous solution) is founded hereupon.

KINETICS OF GAS ABSORPTION

The kinetics of gas absorption have been discussed by Higbie (*4*), mainly with respect to industrial absorbers. His work was extended by Danckwerts (*5*), who developed the theory of gas absorption kinetics, covering the cases of simultaneous chemical reaction. In the present paper it is our purpose to establish an approximate kinetic relation and its experimental verification, which permits the evaluation of the rate of sorption under given conditions in the case of laboratory-scale liquid-phase contact catalytic hydrogenation.

If a gas phase is in contact with a liquid, the components being indifferent towards each other, saturation of the liquid by the gas (or gases) proceeds by the following steps: Gas molecules have to reach the surface, enter the liquid phase and pass into the interior of the liquid. This latter step proceeds by diffusion if there is no convection. If the liquid is stirred, gas molecules are transported from the surface to the interior of the liquid by combined diffusion and convection. There is no direct experimental evidence concerning the rate of the gas molecules entering the liquid phase but it can be estimated on assuming linear sorption kinetics. Let us consider a liquid column of uniform cross section and infinite length with a surface Q in contact with the gas. The coordinate z is perpendicular to the surface and points to the interior of the liquid phase. For a surface element $Q\delta z$ the equation of continuity, based on linear sorption kinetics and Fick's first law is

$$\alpha w^g Q = Q\left[w^f - D\left(\frac{\partial x}{\partial z}\right)_{\delta z} + \delta z\left(\frac{\partial x}{\partial \tau}\right)_{\delta z/2}\right] \tag{1}$$

where w^g is the number of moles of gas striking the surface in unit time; w^f, the number of moles reentering the gas phase in unit time; D and x, the diffusion constant and concentration of the gas, respectively; and α, the accomodation coefficient, giving the ratio of gas molecules entering to those striking the surface.

For $\delta z \to 0$, Eq. (1) goes over into

$$\alpha w^g - w^f = -D(\partial x/\partial z); \qquad z = 0 \qquad (2)$$

According to the kinetic theory of gases we have

$$w^g = (\bar{c}/4RT)p^0; \quad w^f = k^f x; \quad z = 0 \qquad (3)$$

where $\bar{c}$ is the mean velocity of gas molecules; R, the gas constant; T, the temperature in degrees Kelvin; p^0, the (constant) gas pressure; and k^f, the desorption rate constant of the dissolved gas.

In equilibrium, i.e., when the liquid is saturated by the gas, there follows from (2) and (3)

$$\alpha(\bar{c}/4RT)p^0 = k^f x^0 \qquad (4)$$

where x^0 is the saturation concentration of gas in the liquid.

Taking into consideration Henry's law and introducing the absorption coefficient

$$H \equiv x^0/p^0 \qquad (5)$$

we have from (4) and (5)

$$k^f = (\alpha\bar{c}/4RT)\frac{1}{H} \qquad (6)$$

whereby k^f can be calculated from α, $\bar{c}$, R, T, and H.

Using (3) and (4), relation (2) becomes

$$k^f(x^0 - x) = -D(\partial x/\partial z); \qquad z = 0 \qquad (7)$$

Thus the concentration and the quantity of absorbed gas can be calculated from the following system of equations, if the liquid contains no gas at $\tau = 0$:

$$\begin{aligned} \partial x/\partial \tau &= D(\partial^2 x/\partial z^2) \\ k^f(x^0 - x) &= -D(\partial x/\partial z); \qquad z = 0 \qquad (8) \\ x(0, z) &= 0 \\ 0 \leq z &\leq \infty \end{aligned}$$

The solution of these equations is (*6*)

$$\frac{x}{x^0} = \operatorname{erfc}\frac{z}{2\sqrt{D\tau}} - \exp\left(\frac{k^f}{D}z + \frac{(k^f)^2\tau}{D}\right) \operatorname{erfc}\left(\frac{z}{2\sqrt{D\tau}} + \frac{k^f}{\sqrt{D}}\sqrt{\tau}\right) \qquad (9)$$

where

$$\operatorname{erfc} y \equiv 1 - \operatorname{erf} y$$

$$\operatorname{erf} y \equiv \frac{2}{\sqrt{\pi}}\int_0^y e^{-y'^2}dy'$$

From Eq. (9) the change of gas concentration at $z = 0$ as a function of time is

$$\frac{x(\tau, 0)}{x^0} = 1 - \exp\left[\frac{(k^f)^2\tau}{D}\right]\operatorname{erfc}\frac{k^f}{\sqrt{D}}\sqrt{\tau} \approx 1 - \frac{1}{k^f}\left(\frac{D}{\pi\tau}\right)^{1/2} \qquad (10)$$

The order of magnitude of the error of approximation is

$$\frac{1}{2(k^f)^3}\left(\frac{D^3}{\pi\tau^3}\right)^{1/2}$$

According to Eq. (10) the time (τ^*) required for complete saturation of the liquid at $z = 0$ is

$$\frac{x(\tau^*, 0)}{x^0} \equiv 0.999 \approx 1 - \frac{1}{k^f}\left(\frac{D}{\pi\tau^*}\right)^{1/2}$$

or (11)

$$\tau^* \approx \frac{D}{\pi}\frac{10^6}{(k^f)^2}$$

In the calculation of k^f for the case of hydrogen and water the following values (for 20°C) have been used:

$$\begin{aligned} D &= 5 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1} \\ \text{H} &= 8.1 \times 10^{-7}\ \text{mole cm}^{-3}\ \text{atm}^{-1} \\ \bar{c} &= 1.8 \times 10^5\ \text{cm sec}^{-1} \qquad (12) \end{aligned}$$

Inserting these values into Eq. (6)

$$k^f = (2.3 \times 10^6)\alpha\ \text{cm sec}^{-1} \qquad (13)$$

From this value of k^f and Eqs. (11) and (12)

$$\tau^* = 3 \times 10^{-12}\alpha^{-2}\ \text{sec} \qquad (14)$$

As may be seen from (14), taking $\alpha > 10^{-4}$ the concentration of dissolved hydrogen at $z = 0$ reaches the saturation value in a lapse of time $\tau^* < 3 \times 10^{-4}$ sec, which is practically instantaneous as compared with the rate of hydrogenation. As there is no theoretical reason for α being smaller than 10^{-4}, it is justified to treat the kinetics of gas absorption on the assumption that the liquid at $z = 0$ is saturated with respect to the gas under consideration.

As a further check of the validity of the assumption that under the given conditions the liquid surface can be taken as saturated with the gas in question during all of the adsorption process, let us examine the dissolution of H_2 in unstirred, pure water. Among the boundary conditions there figures the assumption mentioned: $x(\tau, 0) = x^0$.

In a cylindrical liquid layer of finite thickness (L) the rate of gas absorption without stirring is—according to the above—governed by the differential equation

$$\partial x/\partial \tau = D(\partial^2 x/\partial z^2)$$

$$x(0, z > 0) = 0; \quad x(\tau, 0) = x^0 \left.\frac{\partial x}{\partial z}\right|_{z=L} = 0$$

$$0 \leq z \leq L \qquad (15)$$

The solution of this equation gives the quantity (N) of hydrogen taken up in time τ

$$\frac{N}{N^0} = 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left[-\left(\frac{2i+1}{2L}\pi\right)^2 D\tau\right] \qquad (16)$$

where N^0 is the equilibrium quantity.

Of the infinite sum in Eq. (16) there has to be considered after a certain time τ_m only the first member. In this case Eq. (16) may be linearized

$$\log\left(1 - \frac{N}{N^0}\right) = \log\frac{8}{\pi^2} - \left(\frac{\pi^2}{4L^2} D \log e\right)\tau; \qquad \tau > \tau_m \qquad (17)$$

Figure 1 shows the experimental results plotted according to transformation (*17*). The experimental points do, for $\tau >$ 3–4 hr, indeed fall on a straight line as required by (17).* Considering Eq. (12) and the fact that $L = 2.45$ cm in our experiments, the expected intercept and slope of Eq. (17) are 0.0993 and 0.891×10^{-5} sec^{-1}, respectively. The values calculated from Fig. 1 are 0.1 and 0.92×10^{-5} sec^{-1}. The good agreement (within 5%) demonstrates the validity of the assumption [$x(\tau, 0) = x^0$] used in deriving Eq. (17).

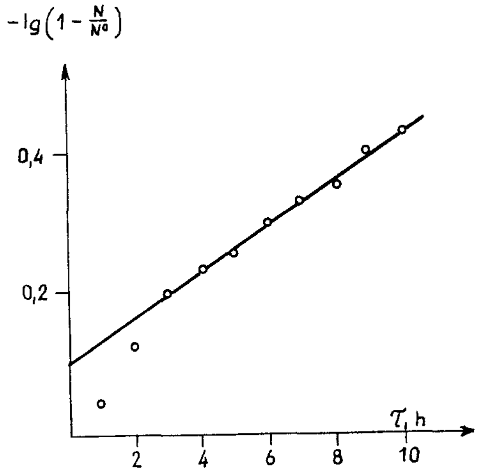


FIG. 1. Rate of absorption of H_2 without stirring.

If the liquid is stirred, dissolved gas molecules are being transported to the interior of the liquid not only by diffusion, but also by convection. For these conditions Danckwerts (*5*) has derived relations covering the stationary state. In the transient state such relations are difficult to handle, especially, if there is simultaneous chemical reaction. We have tried therefore to derive a kinetic equation of gas absorption starting from the simplified absorption mechanism and have verified it in the case of laboratory-scale liquid-phase hydrogenation.

According to Danckwerts' concept, stirring results in a turbulent flow of the liquid, which leads to a renewal of liquid in the surface layer at a given rate. It may be assumed with confidence that, proceeding from the surface towards the interior of the liquid, a concentration gradient exists only up to a certain distance. Beyond this the

---

* The experimental points for times 1 and 2 hr deviate from the straight line more than should be expected on the basis of Eq. (16). The reason for this lies in the experimental technique, which introduces a relatively large error into the determination of small amounts N of gas absorbed.

concentration distribution of the dissolved gas will be statistically homogeneous. For the surface layer in which a concentration gradient can be observed there may be substituted a liquid film saturated with dissolved gas, while the amount of dissolved gas is that of the liquid layer thus substituted. Correspondingly, the liquid can be divided into two spaces, a surface space and an interior space. Exchange of liquid between the two spaces is brought about by the turbulent flow induced by stirring. Liquid in the surface space is saturated with respect to the gas under consideration while gas concentration in the liquid in the interior space is homogeneous, but reaches its saturation or stationary value only as a function of the rate of absorption. The rate of absorption therefore is determined by the amount of gas taken up by the liquid coming to the surface space in unit time, i.e.,

$$dN/d\tau = (\delta v)\nu(x^0 - x) \qquad (18)$$

where δv is the volume of the surface space and ν the frequency of exchange of the liquid contained therein.

If at time $\tau = 0$ the liquid contains no gas the material balance is

$$N = (\delta v)x^0 + (v - \delta v)x \qquad (19)$$

From (18) and (19) we have

$$\frac{dN}{d\tau} = (v - \delta v)\frac{dx}{d\tau} = (\delta v)\nu(x^0 - x) \qquad (20)$$

$$\frac{dx}{d\tau} = \frac{(\delta v)\nu}{v - \delta v}(x^0 - x)$$

and for $x(0) = 0$

$$\frac{x}{x^0} = 1 - \exp\left[-\frac{(\delta v)\nu}{v - \delta v}\tau\right] \qquad (21)$$

$$\frac{N}{N^0} = 1 - \frac{v - \delta v}{v}\exp\left[-\frac{(\delta v)\nu}{v - \delta v}\tau\right] \qquad (22)$$

A linear form of Eq. (22) is

$$\log\left(1 - \frac{N}{N^0}\right) = \log\left(1 - \frac{\delta v}{v}\right) - \left(\frac{\delta v}{v - \delta v}\nu \cdot \log e\right)\tau \qquad (23)$$

Figure 2 presents experimental values of absorption in this linearized form. (The abscissas of the individual plots are shifted by 10 min each.) In our experiments 50 ml of water was placed in a round bottom flask of about 100 ml. The stirrer was a piece of iron wire in a glass envelope, driven by a rotating permanent magnet from outside. The sign n of the figure designates revolutions per minute (*7*).

The experimental points in Fig. 2 fall indeed on a straight line, thus proving the applicability of Eq. (23). The intercept of the curves is zero within the limits of error, i.e., according to Eq. (23)

$$1 - (\delta v/v) \approx 1 \qquad (24)$$

which means that under the given conditions the volume of the surface space is much smaller than that of the interior space.

From relation (24) it follows that the rate of absorption w_1 can, in the given conditions, be expressed by

$$W_1 \equiv dN/d\tau = k_1 v(x^0 - x) \qquad (25)$$

$$k_1 \equiv (\delta v/v)\nu \qquad (26)$$

where k_1 is the rate constant of the absorption process.

Thus the rate constant k_1 for different rates of stirring can be calculated from the curves of Fig. 2 and relations (23) and (26). Figure 3 shows the function calculated in this way. According to this figure k_1 is, under the given conditions, a linear function of the number of revolutions per minute.

THE REDUCTION OF DICHROMATE ION IN AQUEOUS SOLUTION IN THE PRESENCE OF Ag^+ ION CATALYST

As already mentioned, the aim of the investigation of gas absorption is the establishment of the kinetic relations of the first step in liquid-phase contact catalytic hydrogenation. Under the given experimental conditions the absorption mechanism was simplified in such a way that the liquid phase could be regarded as consisting of two parts, the surface space and the interior space. Experiments have shown that the kinetic law derived on these assumptions is valid and that the volume of the surface space is much smaller than that of the interior space. Applicability of a kinetic law, of course,

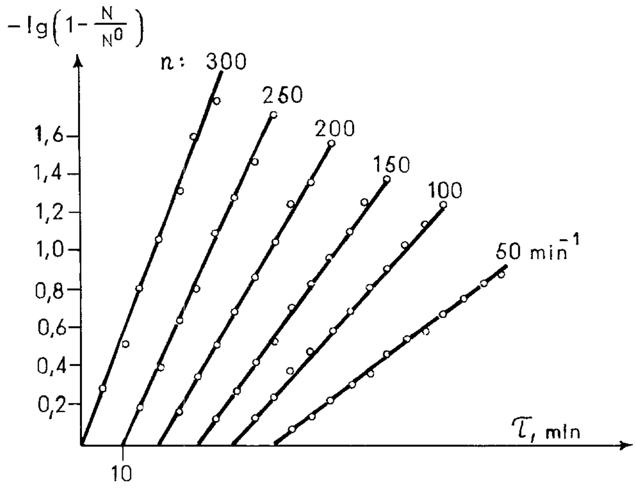


FIG. 2. Rate of absorption of ethylene with stirring.

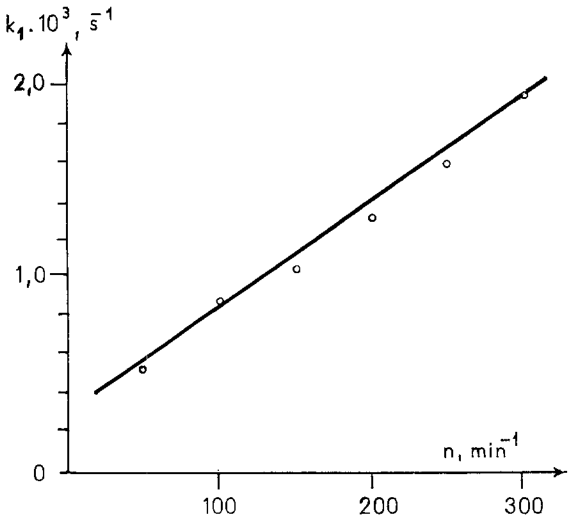


FIG. 3. Dependence of the rate constant of ethylene absorption on intensity of stirring.

is no proof of the assumption underlying it, as different mechanisms can lead to the same rate equation. To prove the justification of our assumptions, therefore, the rate of hydrogen absorption was determined under the same conditions, but with a solution in which there also proceeded a reaction of the first order with respect to hydrogen. As a model reaction the reduction of dichromate ion catalyzed by Ag^+ ions was used, the rate of which can, according to investigations by Webster and Halpern (*8*), be described to a fair approximation by the equation

$$W = k'[Ag^+]^2[H_2] \qquad (27)$$

As the concentration of the Ag^+ ions is constant throughout the reduction of the dichromate, Eq. (27) can be replaced by

$$W = k[x] \quad k \equiv k'[Ag^+]^2 \quad x \equiv [H_2] \qquad (28)$$

Taking into consideration (25) and (28), Eq. (18) is now modified to

$$dN/d\tau = k_1 v(x^0 - x) + (\delta v)kx^0 \qquad (29)$$

For the interior space the material balance

$$dx/d\tau = k_1(x^0 - x) - kx \qquad (30)$$

can be derived from (24) and (29). Solution of Eq. (30) for $x(0) = 0$ gives the concentration of hydrogen in the interior space as a function of time

$$\frac{x}{x^0} = \frac{k_1}{k_1 + k}\{1 - \exp[-(k_1 + k)\tau]\} \tag{31}$$

The quantity of gas absorbed is obtained from Eqs. (29) and (31) with (24)

$$\frac{N}{vx^0} = \left(\frac{k_1}{k_1 + k}\right)^2 \{1 - \exp[-(k_1 + k)\tau]\} + k\frac{k_1}{k_1 + k}\tau \tag{32}$$

From Eq. (32) it follows that after a certain time τ^s absorption becomes stationary (N^s). After attainment of the stationary state Eq. (32) is simplified:

$$N^s = A + B\tau \qquad \tau > \tau^s \tag{33}$$

where

$$A \equiv vx^0[k_1/(k_1 + k)]^2$$
$$B \equiv vx^0[k_1/(k_1 + k)]k \tag{34}$$

Measuring the quantity of absorbed hydrogen at constant pressure and plotting it as a function of time, there should result a curve which goes over into a straight line after a certain time. From the intercept of the extension of this straight part of the curve and its slope, the rate constants of absorption and reaction can be calculated with the aid of relation (34). Executing the measurements at different rates of stirring the calculated rate constant of the reaction should be the same if the assumed mechanism is correct, thus proving the applicability thereof.

Experimental values, obtained in the same way as those of the absorption experiments, are represented in Fig. 4 ($v = 100$ ml; $p_{H_2} = 365$ Torr; $vx^0 = 0.76\,n$ ml; [Ag$^+$] = 0.19 mole/lite; $t = 60$°C). The rate constants calculated from the curves with regard to Eq. (28) are listed in Table 1.

TABLE 1

RATE CONSTANTS FOR DIFFERENT SPEEDS OF STIRRING

n (liter/min)	$k_1 \times 10^3$ (sec^{-1})	$k \times 10^3$ (sec^{-1})	$k' \times 10^3$ (liter^2 mole^{-2} sec^{-1})
50	1.2	0.610	16.85
150	1.8	0.611	16.90
250	3.8	0.605	16.75

As may be seen from the table, the rate constants are, as expected, indeed independent of the speed of stirring. The simplified con-

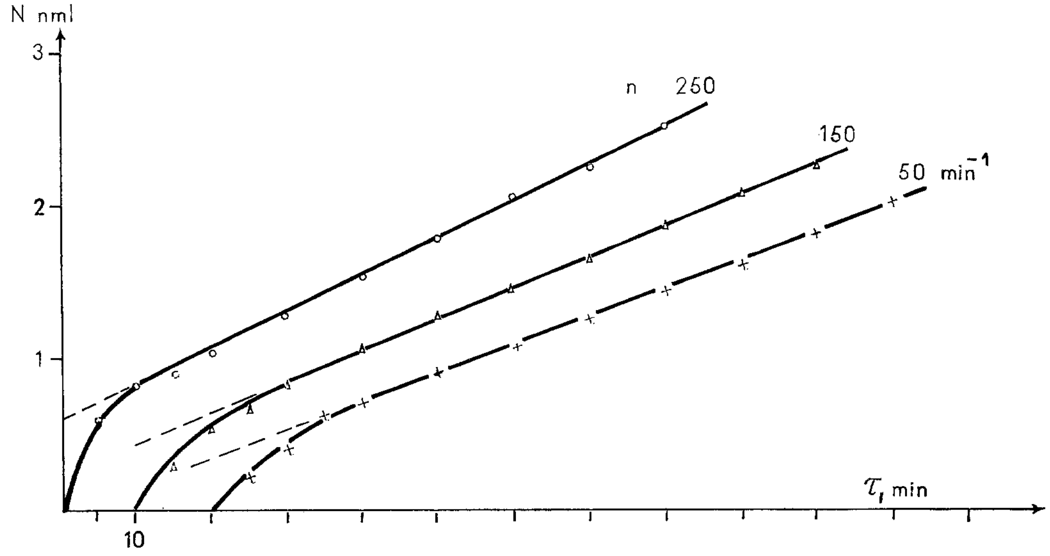


FIG. 4. Rate of absorption of H_2 in solution, containing Ag^+ and $Cr_2O_7^{2-}$ ions at various intensities of stirring.

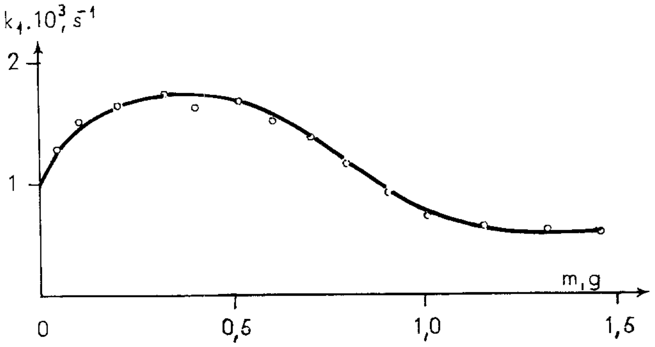


FIG. 5. Dependence of the rate constant of ethylene absorption on the concentration of suspension.

cept of the absorption mechanism, therefore, does not only provide a formally correct rate equation, but is suited to represent the kinetics of a reaction of dissolved gas in the liquid phase correctly.

The rate of gas absorption was also determined under the conditions mentioned in suspensions of different nonadsorbent powders, as contact catalytic hydrogenation is carried out in suspension. The kinetic relations derived for pure water (25) are applicable in this case too. The absorption rate constant k_1 changed with the quantity m of suspended matter in the manner illustrated by Fig. 5 for suspensions of varying nature. (See details in ref. *9*.) According to Fig. 5 the rate of absorption first increases with the concentration of the suspension, then passes a flat maximum and finally decreases. On the basis of the simplified absorption mechanism this can be interpreted as follows. The stirrer sets into motion the particles of the suspension, which through gravity tend to return to the bottom of the flask. This movement of the particles enhances the exchange of liquid in the surface space, raising the frequency of exchange (18) and thus the rate of absorption. In more concentrated suspensions another action of the suspended particles, the increase of viscosity becomes predominant, leading to a decrease of flow velocity and consequently of the rate of exchange of liquid in the surface space and the rate of absorption.

REFERENCES

1. JELOVICH, S. I., AND ZHABROVA, T. M., "Teoreticheskie osnovy gydrirovanye zhirov." Moscow, 1948.

2. NAGY, F., AND TELCS, I., *Acta Chim. Acad. Sci. Hung.* **25**, 193 (1960).

3. COENEN, J. W. E., *Proc. Intern. Congr. Catalyse, 2^e, Paris, 1960* (1961).

4. HIGBIE, R., *Trans. Am. Inst. Chem. Eng.* **31**, 365 (1935).

5. DANCKWERTS, P. V., *Ind. Eng. Chem.* **43**, 1460 (1951); *A. I. Ch. E. J.* **1**, 456 (1955).

6. CARSLAW, H. S., AND JAEGER, J. C., "Conduction of Heat in Solids." Clarendon Press, Oxford, 1959.

7. NAGY, F., AND SCHAY, G., *Acta Chim. Akad. Sci. Hung.* **14**, 421 (1958).

8. WEBSTER, A. H., AND HALPERN, J., *J. Phys. Chem.* **60**, 280 (1956).

9. NAGY, F., MÓGER, D., AND NYITRAY, I., *Acta Chim. Acad. Sci. Hung.* **25**, 99 (1960).