JOURNAL OF CATALYSIS 3, 368–371 (1964)

A Method for Determining the Adsorption Rate Constant of the Nonregenerative Catalyst

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Received March 2, 1964

Reactants in low concentration are carried in an inert fluid stream at constant velocity through a porous solid catalyst bed (or solid reactant) of definite length. The reactants are adsorbed by the catalyst according to the first order rate law, and the reaction products are adsorbed irreversibly by the porous surface of the catalyst bed, whose effective reaction surface area is thus gradually depleted. This paper presents a mathematical solution of both the reactant mass and the adsorbed mass as functions of time and of distance from the entrance of the bed. The utilization of this solution to evaluate the adsorption rate constant in the laboratory is also indicated.

INTRODUCTION

In the laboratory examination of reactions involving heterogeneous catalysts or gas–solid adsorption, an arrangement as shown schematically in Fig. 1 may be employed.

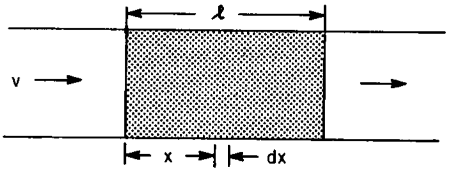

FIG. 1. Catalyst bed.

An inert fluid carrying reactants in low concentration is introduced into the catalyst bed at the left end with a velocity v(cm/sec), which is calculated from Eq. (1),

$$v = u/A\lambda, \qquad (1)$$

where u = volume rate of flow (cc/sec), A = cross-sectional area of the catalyst bed (cm^2), and λ = void fraction of the solid bed. Ordinarily, the catalyst is assumed to be continuously regenerated by desorption of reaction products and, as a result, the catalytic surface available for reaction remains constant with time. Hence, the reaction rate and reactant concentration distributions thoughout the catalyst bed also remain constant with time and the system is considered to be in a steady state. By measuring the concentrations of reactants and products at the exit of the reactor at different flow rates and initial concentrations, the rate parameters of the reaction can be derived and the catalysts' activity and selectivity can be determined. Adequate treatments of the normal situation are available (*1*).

This paper is concerned with a catalyst (or solid-phase reactant) which is not being regenerated because reactants or products are being irreversibly adsorbed so that the surface available for reaction is being depleted. Therefore, the rate of reaction decreases with time, and the rate of escape of unused reactants increases with time. In addition, the reaction product mass is accumulated by the catalyst bed at a decreasing rate. In the following paragraphs, a method of determining the adsorption rate constant from the time-dependent data and the theoretical basis for the method will be described. This method would have important applications in the areas of air purification, removal of CO$_2$ from air by a regeneratable silver oxide bed, poisoning or coking of catalyst beds, and in gas chromatographic and ion exchange columns where kinetic rather than equilibrium factors are controlling and adsorptions are irreversible.

NOTATION

A	Cross-sectional area of the catalyst bed, cm^2.
l	Length of catalyst bed, cm.
λ	Void fraction of catalyst bed.
v	Linear velocity of fluid flow in the catalyst bed, cm/sec.
t	Time, sec.
u	Volume rate of flow, cc/sec.
x	Distance from the entrance section, cm.
γ	Adsorption rate, g/sec cc.*
s	Porous surface density, cm^2/cc.*
c	Mass concentration of reactants in fluid phase, g/cc.*
k	Adsorption rate constant, cc/cm^2 sec.*
m	Mass adsorbed, g/cc.*
s_0	Initial s, cm^2/cc.*
m_∞	Maximum m, g/cc.*
c_0	Initial concentration of reactants in fluid phase, g/cc.*

DERIVATION OF THE DIFFERENTIAL EQUATIONS OF ADSORPTION

For the reaction products adsorbed onto the porous solid catalyst surface, a first order rate law is assumed

$$(\partial m)/(\partial t) = \gamma = kcs \qquad (2)$$

As the mass adsorbed increases, the available surface for reaction decreases proportionately. Hence

$$s = s_0[1 - (m/m_\infty)] \qquad (3)$$

Combining Eqs. (2) and (3), we have

$$(\partial m)/(\partial t) = ks_0[1 - (m/m_\infty)]c \qquad (4)$$

On the other hand, if attention is focused on a small element of volume, Adx, fixed in space (Fig. 1), then the rate of mass disappearance of the reactants must be equal to the rate of accumulation of the mass adsorbed in the solid. Thus

$$-(dc)/(dt) = (\partial m)/(\partial t) \qquad (5)$$

Here c is differentiated totally, rather than partially, with respect to time since c is a quantity in a moving stream, and hence, has a convective part, in addition to the usual nonconvected part, i.e.,

$$(dc)/(dt) = (\partial c)/(\partial t) + v(\partial c)/(\partial x) \qquad (6)$$

Combining Eqs. (5) and (6), we get

$$(\partial m)/(\partial t) + (\partial c)/(\partial t) + v(\partial c)/(\partial x) = 0 \qquad (7)$$

In the above derivation, the pressure and temperature variations throughout the process are assumed small and the volume and structure of the voids are assumed to remain unchanged by the reaction process.

To obtain the boundary and initial conditions, it is noted that Eqs. (4) and (7) are defined in the (x,t) plane only between the lines $x = 0$ and $x = l$, and for $x \leqslant vt$. Moreover, physically downstream adsorption does not affect upstream adsorption. Hence, the proper conditions can only be prescribed on the lines $x = 0$ and $x = vt$. Obviously,

$$m = 0 \text{ on } x = vt \quad \text{and} \quad c = c_0 \text{ on } x = 0 \qquad (8)$$

Therefore, Eq. (4) at $x = 0$ becomes

$$(dm)/(dt) = ks_0c_0[1 - (m/m_\infty)],$$

which has the solution

$$m = m_\infty[1 - \exp(-ks_0c_0t/m_\infty)] \qquad (9)$$

under the condition that $m = 0$ at $t = 0$.

On the other hand, Eq. (7) may be written [using Eq. (4)] as

$$(\partial c)/(\partial t) + v(\partial c)/(\partial x) = -ks_0[1 - (m/m_\infty)]c$$

which on the line $x = vt$ becomes

$$(dc)/(dx) = -(ks_0/v)c \qquad (10)$$

Equation (10) comes about since the convective term in c is zero as we move with the fluid (i.e., on $x = vt$) and that $m = 0$ on $x = vt$. Equation (10) has the solution

$$c = c_0 \exp(-ks_0x/v) \qquad (11)$$

under the condition that $c = c_0$ at $x = 0$.

The boundary and initial conditions for the system of Eqs. (4) and (7) are summarized below:

on $x = 0$:
$m = m_\infty[1 - \exp(-ks_0c_0t/m_\infty)], \quad c = c_0$
on $x = vt$:
$m = 0, \quad c = c_0 \exp(-ks_0x/v)$ (12)

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* In these, cc means "cc of catalyst bed including both voids and solids."

SOLUTION OF THE DIFFERENTIAL EQUATIONS OF ADSORPTION

It can be easily verified by direct substitution that the solution of the system of Eqs. (4), (7), and (12) is

$$m/m_\infty = \frac{z \exp\,(-ks_0x/v)}{1 - z[1 - \exp\,(-ks_0x/v)]}$$

$$c/c_0 = \frac{\exp\,(-ks_0x/v)}{1 - z[1 - \exp\,(-ks_0x/v)]} \qquad (13)$$

where

$$z = 1 - \exp\,[ks_0c_0(x - vt)/(m_\infty v)]$$

DETERMINATION OF THE ADSORPTION RATE CONSTANT, k

In laboratory experiments, it will be necessary to measure the value of c at the exit end of the reactor ($x = l$) as a function of time. In general, the initial increase in c with time will be gradual, starting at a low value (possibly zero), followed by a more rapid increase and finally leveling off as c approaches c_0, when the catalyst bed becomes completely spent. From Eq. (13), $(c/c_0)_{x=l}$ can be plotted versus time with k as a parameter. Thus, the determination of k involves the selection of a theoretical $(c/c_0)_{x=l}$ vs t curve which best fits the experimental one. The rapidly rising portion of the curve may require the most attention since it will be the most sensitive to changes in k. In practice, however, a number of variations from the procedure just described could be developed, depending upon the convenience of application and the objectives in each individual case.

EXAMPLE

Let the catalyst be contained in a tube of 1-cm inside diameter. The catalyst bed has a void fraction of 0.35 and a length of 6 cm. The reactant concentration in the virgin fluid is 3.857×10^{-5} g/cc before entering the catalyst bed. The volume rate of flow is 1650 cc/min. Also $s_0 = 6 \times 10^4$ cm^2/cc, and $m_\infty = 0.45$ g/cc. (see Notation Section).

From Eq. (1),

$$v = 1650/\tfrac{1}{4}\pi \times 0.35 \times 60 = 100 \text{ cm/sec}$$

Also, from the definition of c_0 (see Notation Section),

$$c_0 = 0.35 \times 3.857 \times 10^{-5} = 1.35 \times 10^{-5} \text{ g/cc}$$

after entering the catalyst bed. Hence, all quantities required for Eqs. (13), except k, are now provided.

The results of the computation for several values of k are plotted in Fig. 2. The rapidly

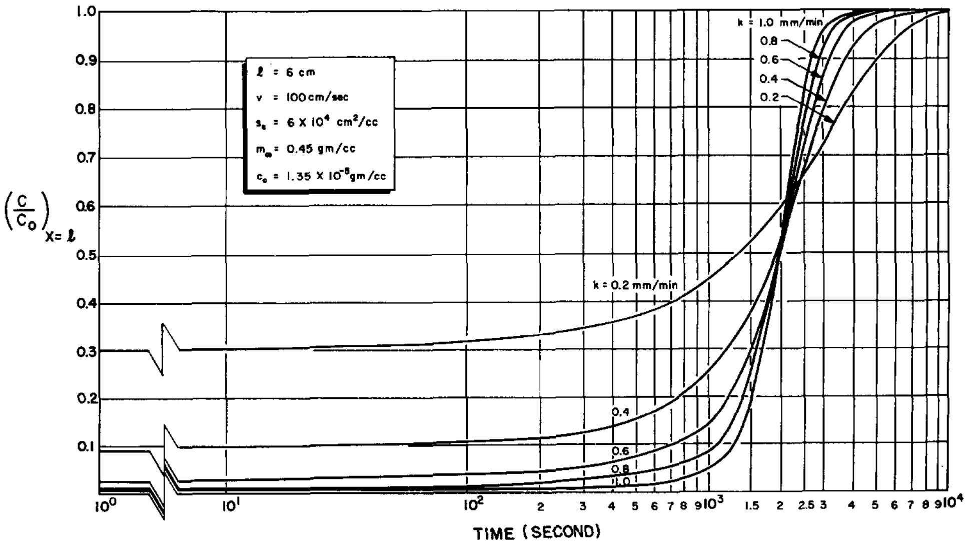

FIG. 2. Example of the calculation of c/c_0 using Eqs. (13).

rising portion of the curves are rather evident. Needless to say, the time scale can be expanded or contracted to suit the individual problem.

ACKNOWLEDGMENTS

Support of this work by the Bureau of Naval Weapons is gratefully acknowledged.

The authors wish to thank Dr. E. R. Cohen, Associate Director of the Science Center, North American Aviation, Inc., for pointing out the analogy of the problem of this paper to the problem of the propagating light pulse in a traveling wave laser (ref. *2*) and hence the mathematical solution.

REFERENCES

1. HOUGEN, O. A., AND WATSON, K. M., "Chemical Process Principles III, Kinetics and Catalysis," Chaps. 18 and 19. Wiley, New York, 1955.

2. BELLMAN, R., BIRNBAUM, G., AND WAGNER, W. G., *J. Appl. Phys.* **54,** 780 (1963).