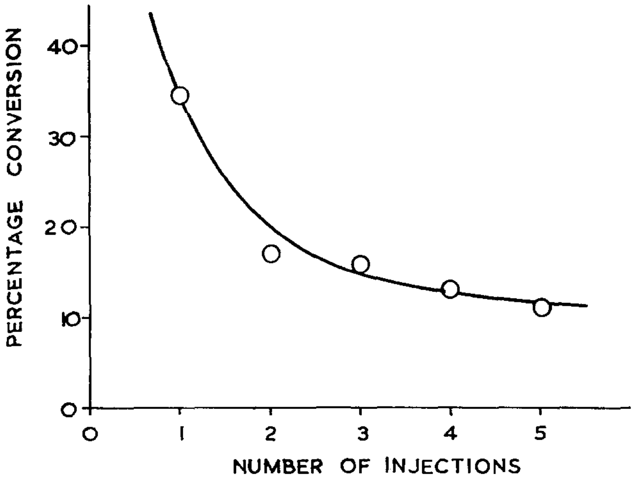

FIG. 2. Decrease in conversion of 1-pentene with increasing number of injections: pulsed-flow reactor at 68°C; 2.5 μl 1-pentene in each injection.

either the solvent or the olefin; further evidence on this will be reported later. It would seem, however, that the results obtained in the continuous-flow reactor may refer to a substantially deactivated catalyst.

Our views on the mechanism of the reaction will be discussed in a later paper.

The application of this method to other possibly more amenable and commercially important systems will readily be conceived.* We have established that many noble metal salts are sufficiently soluble in thermally stable organic compounds of low volatility, such as are commonly used as stationary phases in gas-liquid chromatography, to make their examination seem profitable.

REFERENCES

1. HARROD, J. F., AND CHALK, A. J., *J. Am. Chem. Soc.* 86, 1776 (1964); RINEHART, R. E., AND LASKY, J. S., *ibid.* p. 2516 (1964); CRAMER, R., *ibid.* 87, 4717 (1965); BOND, G. C., DAWSON, J. A., AND HELLIER, M., unpublished work.
2. BOND, G. C., AND HELLIER, M., *J. Catalysis* 4, 1 (1965).

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* Patent protection for this technique has been sought; inquiries for further information will be welcomed.

Lack of Dependence of Conversion on Flow Rate in Catalytic Studies*

In studies of solid catalysts, it is imperative to ascertain the possible influence of temperature and concentration gradients on the rate of reaction. For heat and mass transfer to the external surface of catalytic particles packed in a fixed bed, an easy

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diagnostic test (*1*) consists of checking the effect of flow rate on conversion at constant space velocity (or "contact time"). If no such effect is found, it is concluded that transfer of heat and mass to the particles does not influence the rate of reaction.

The purpose of this note is to bring attention to the fact that this diagnostic test may fail because of its lack of sensitivity under conditions commonly used in the laboratory. An example of such a situation will be presented for a case of theoretical interest.

The difficulty is due to two circumstances. First, the size, d, of the catalyst particles used in experimental work is kept small in order to minimize internal gradients of temperature and concentration. Second, the flow rate is kept at a desirably low value so as to obtain a not too small value of contact time for the small amount of catalyst normally used. The flow rate may be expressed in terms of a linear velocity of flow, v, which is equal to the volumetric flow rate divided by the cross-sectional area of the reactor. As a result of the small value of both v and d, the Reynolds number, $Re = vd/\nu$, where ν is the kinematic viscosity of the reacting fluid, is considerably smaller than in a large-scale operation. This small value of the Reynolds number in typical laboratory work has, in turn, two main consequences. First, the influence of heat and mass transfer may be very serious. Second, the dependence of the coefficients of heat and mass transfer on flow rate may be so weak as to render a test of conversion vs. flow rate quite insensitive. Consequently, it may well happen that at values of Re on the order of 10 the conversion does not appreciably change with flow rate at constant space velocity, even though the influence of heat or mass transfer on the reaction rate may be very severe.

This behavior is clearly seen in the commonly used correlations of heat and mass transfer in packed beds (*2–4*). Thus, from the compilation of data by De Acetis and Thodos (*2*), although the heat transfer coefficient is proportional to $v^{0.55}$ at $Re = 1000$, it becomes proportional to $v^{0.19}$ at $Re = 15$. It is permitted to think that at lower values of Re, the dependence of the heat transfer coefficient on velocity would become weaker still, as the flow in the packed bed becomes completely laminar. This behavior is graphically illustrated in Fig. 1. But data in the range $1 < Re < 50$ are sparse and moreover mass transfer data in this range are subject to corrections due to axial dispersion (back-mixing), as has been noted by Ergun (*5*) and by Bradshaw and Bennett (*6*). Thus for work at low Rey-

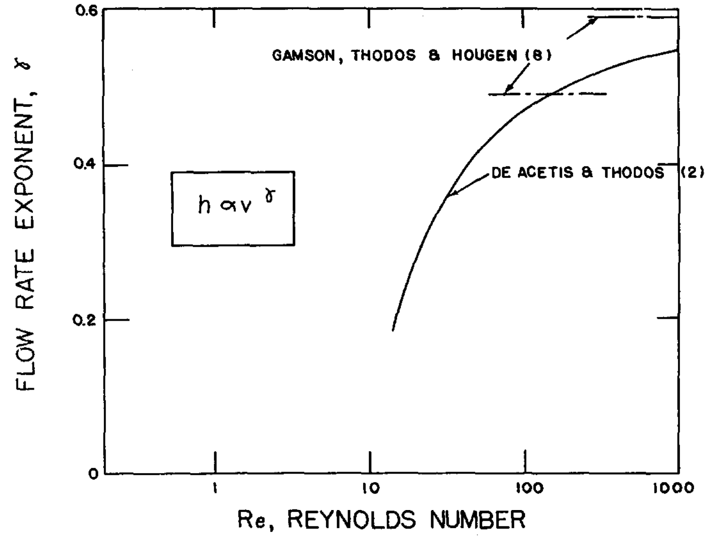

FIG. 1. Effect of flow rate (linear velocity v) on heat transfer coefficient h.

nolds numbers, it is essential to use available correlations in a critical fashion. Moreover, the diagnostic test discussed here will require very precise conversion data or an extended range of flow rates, because, at low values of Re, the transfer coefficient depends only weakly on velocity.

As an example of the difficulties encountered at low values of Re, consider a recent investigation of the dehydrogenation of cyclohexane on a platinum-alumina reforming catalyst by Khoobiar *et al.* (*7*). The authors used a packed bed consisting of alumina pellets which were found to be inert by themselves, mixed with a small amount of catalyst pellets. The purpose of the dilution of the bed was to maintain overall isothermal conditions. Using the heat transfer correlation of Gamson, Thodos, and Hougen (*8*) and Wilke and Hougen (*9*), they calculated the surface temperature of the catalyst pellets. The authors then compared thermodynamic equilibrium conversions at the calculated temperature with observed values and found the observed conversions to be greater than that corresponding to equilibrium. Moreover, the authors applied the diagnostic test discussed in this note and concluded that there was no heat transfer limitation, since conversion was not observed to change as flow rate was decreased by factors of 2 and 3.

These contradictory findings led Khoobiar *et al.* to postulate the migration of hydrogen atoms away from the catalyst pellets into the surrounding medium where, by an unspecified path, these atoms would account for a substantial fraction of the observed conversion. The above difficulties disappear if it is noted that the work was performed at low values of the Reynolds number where, as noted already, it is necessary to use published correlations of heat and mass transfer with caution, and that furthermore, the absence of variation of conversion with flow rate at constant space velocity may not be a sensitive diagnostic test.

Indeed, calculations can be made from the information contained in the publications of Khoobiar *et al.* (*7, 11*). Results of these calculations are shown in Table 1. It is seen that the Reynolds number is low, equal to 8.4. Thus the correlations of Gamson, Thodos, and Hougen (*8*) and of Wilke and Hougen (*9*), which were used by Khoobiar *et al.* should not be used, since they are not valid below $Re = 60$. It is unfortunate that these correlations are presented in ref. (*10*) over an extended range, $10 < Re < 10{,}000$, without mentioning that the data, upon which the correlation was constructed, extended only from $Re = 60$ to $Re = 4000$. If the correlation of De Acetis and Thodos (*2*) is conservatively extended below $Re = 15$ by applying a constant flow rate exponent, γ, of 0.15, the difficulties of interpretation raised by Khoobiar *et al.* disappear, as shown in Table 2 and Fig. 2.

TABLE 1

HEAT TRANSFER CALCULATION FOR RUN 124, REF. (*11*)

Reaction Rate and Operating Conditions	
Reaction rate	0.64 g mole/hr per gram of Pt/Al_2O_3
Conversion	24.8% of the C_6H_{12} dehydrogenated to C_6H_6
Pressure	26.5 atm
Temperature	427°C fluid temperature
Feed composition	6 moles H_2 per mole C_6H_{12}
Fluid Properties	
Flow rate	3.02 g mole/hr of C_6H_{12}
Fluid density	6.0×10^{-3} g/cm^3
Superficial velocity, v	1.2 cm/sec
Kinematic viscosity, ν	0.03 cm^2/sec[a]
Heat capacity	1.04 cal/(g)(°C)
Thermal conductivity	5.8×10^{-4} cal/(sec)(°C)(cm)[b]
Reynolds number, Re	$dv/\nu = 8.4$
Catalyst Properties	
"Effective" particle diameter, d	$= (A/\pi)^{1/2} =$ 2.1 mm
Particle surface area, A	$= 0.14$ cm^2/particle
	$S = 27$ cm^2/g

[a] Reference (*15*).

[b] Reference (*16*).

It is seen in particular that, although the reaction rate is definitely influenced by heat transfer limitations, the change of conversion expected over a threefold variation in

TABLE 2
Results of Heat Transfer Calculations

	Extension of De Acetis & Thodos	Extrapolation of Gamson, Thodos & Hougen
Calculated particle temperature (°C) flow rate = 3 gmole/hr reactant	408	393
Calculated particle temperature (°C) flow rate = 1 gmole/hr reactant	404.5	369
Δ conversion due to drop in flow rate (%)	−2.6	−9
Effect distinguishable from normal scatter of exptl data	No	Yes
Equilibrium conversion[a] at the 3 gmole/hr particle temperature (%)	34	18
Observed conversion (%)	25	25
Conversion conservatively lower than equilibrium?	Yes	No

[a] Reference 14.

flow rate is well within experimental error. In order to calculate this change of conversion from a change in surface temperature, an activation energy $E_1 = 20$ kcal/mole was assumed. This value of activation energy is conservatively high, since Sinfelt (*12*) reports $E_2 = 33$ kcal/mole for the dehydrogenation of methylcyclohexane on a similar platinum catalyst. But since internal diffusional limitations are certainly expected under the conditions used by Khoobiar *et al.*, as indicated by the work of Weaver *et al.* (*13*), a value of E_1 close to $E_2/2$ is reasonable. Khoobiar has suggested an even lower value of E_1, namely 15 kcal/mole. Such a low value of E_1 would reinforce our conclusion that the diagnostic test of variation of flow rate was not sensitive enough for the case at hand.

It is also seen from Table 2 that, if the proper correlation is used, the observed conversion is conservatively lower than the expected equilibrium conversion calculated from data in API Project 44 (*14*). It is therefore concluded that the results of Khoobiar *et al.* do not require any special explanation, but must be considered as straightforward data influenced by heat and mass transfer limitations.

In general, it appears that an application of the diagnostic test of flow rate variation to ascertain the influence of heat or mass transfer limitations, must be accompanied by an investigation of the sensitivity of this test, especially at the low Reynolds numbers frequently encountered in laboratory work. In addition, it is apparent that there

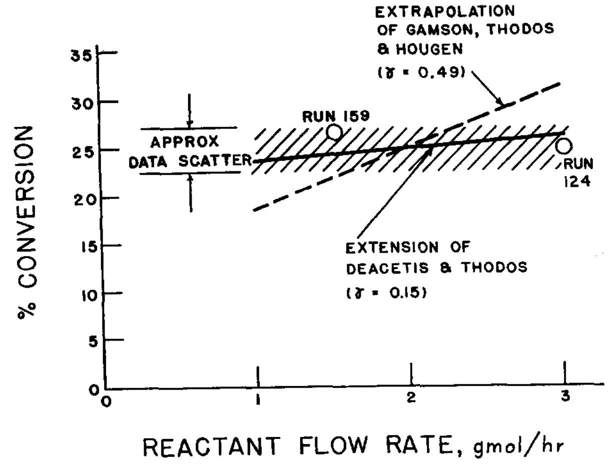

Fig. 2. Lack of dependence of conversion on flow rate in the catalytic studies of Khoobiar *et al.* (*7, 11*).

is a definite need for further study of transfer coefficients at these low Reynolds numbers.

References

1. Levenspiel, O., "Chemical Reaction Engineering," pp. 453–454. Wiley, New York, 1962.
2. De Acetis, J., and Thodos, G., *Ind. Eng. Chem.* **52**, 1003 (1960). This correlation is also contained in Aris, R., "Intro. to the Analysis of Chem. Reactors," pp. 123–125. Prentice-Hall, Englewood Cliffs, New Jersey, 1965; and Satterfield, C. N., and Sherwood, T. K., "The Role of Diffusion in Catalysis," pp. 31–35, Addison-Wesley, Reading, Pennsylvania, 1963.
3. Chu, J. C., Kalil, J., and Wetteroth, W. A., *Chem. Eng. Progr.* **49**, 141 (1953).
4. Sen Gupta, A., and Thodos, G., *Chem. Eng. Progr.* **58**, 58 (1962).
5. Ergun, S. K., *Chem. Eng. Progr.* **48**, 227 (1952).
6. Bradshaw, R. D., and Bennet, C. O., *A.I.Ch.E.J.* **7**, 48 (1961).
7. Khoobiar, S., Peck, R. E., and Reitzer, B. J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 338–352 (North-Holland Publ. Co., Amsterdam, 1965).
8. Gamson, B. W., Thodos, G., and Hougen, O. A., *Trans. Am. Inst. Chem. Engrs.* **39**, 1 (1943).
9. Wilke, C. R., and Hougen, O. A., *Trans. Am. Inst. Chem. Engrs.* **41**, 445 (1945).
10. Hougen, O. A., and Watson, K. M., "Chemical Process Principles—Part 3," pp. 982–987 (Wiley, New York, 1947).
11. Khoobiar, S., "Kinetics of Cyclohexane Dehydrogenation," Ph.D. Dissertation, Illinois Institute of Technology, Chicago, 1960.
12. Sinfelt, J. H., *Advan. Chem. Eng.* **5**, 37 (1964).
13. Barnett, L. G., Weaver, R. E. C., and Gilkeson, M. M., *A.I.Ch.E.J.* **7**, 211 (1961).
14. Am. Petroleum Inst. Res. Proj. 44, "Selected Values of Prop. of Hydrocarbons and Related Compounds." Chem. Thermodynamics Prop. Center, Texas A & M, College Station, Texas, 1963.
15. Bromley, L. A., and Wilke, C. R., *Ind. Eng. Chem.* **43**, 1641 (1951).
16. Lindsay, A. L., and Bromley, L. A., *Ind. Eng. Chem.* **42**, 1508 (1950); Lenoir, J. M., Junk, W. A., and Comings, E. W., *Chem. Eng. Progr.* **49**, 539 (1953).

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The Effect of Alkaline Promoter on Decomposition of Ammonia over the Doubly Promoted Iron Catalyst

Several kinetic expressions have been proposed for ammonia decomposition over the doubly promoted fused iron catalysts whereby an important role of the potassium oxide in the mechanism of decomposition was suggested (*1*, *2*). Recently, the present authors have shown (*3*, *4*) that the rate-determining step of ammonia decomposition over a well-reduced doubly promoted fused synthetic ammonia iron catalyst (4.72% Al_2O_3, 0.31% K_2O, 0.05% SiO_2 as promoters) changes with rising reaction temperature, as deduced from the pressure dependencies of ammonia and hydrogen upon the rate. The rate V was thus found to be expressed as $V = k_1(P_{NH_3}/P_{H_2}{}^{1.5})^{\alpha}$ around 420°C or as $V = k_2(P_{NH_3}/P_{H_2}{}^{0.5})^{\beta}$ above 479°C, where k_1, k_2, α, and β are constants. These results showed that the rate-determining step is the desorption of the adsorbed nitrogen at