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Kinetics of the Hydrogenation of Aniline in the Vapor Phase on a Cobalt-Alumina Catalyst1)

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The kinetics of the catalytic hydrogenation of aniline with a cobalt-alumina catalyst in the temperature range from 160° to 210°C was studied by a differential flow reactor with a fixed bed. (1) The rate of reaction reaches a maximum in the 180—190°C range for the hydrogenation of aniline. From the thermodynamic calculations and the experimental results for a fluidized-bed reactor, the reverse reaction was found to be almost negligible below 200°C under the conditions of the reaction. This phenomenon was explained by the proposed kinetics of the reaction. (2) The initial rate of reaction without cyclohexylamine, and the rate when some cyclohexylamine was added to the reactants, were measured at atmospheric pressure over the following range of conditions of partial pressures; hydrogen 0.3—0.92 atm., aniline 0.05—0.2 atm., cyclohexylamine 0—0.24 atm. It was concluded that a plausible rate-controlling step was the surface reaction, i. e., the reaction between the adsorbed aniline and hydrogen on the surface of the catalyst. The equation for the vapor phase hydrogenation of aniline on a cobalt-alumina catalyst in the temperature range from 150°C to 210°C was determined to be:

$$r = k\frac{K_H{}^3 K_A P_H{}^3 P_A}{(1 + K_H P_H + K_A P_A + K_C P_C)^4}$$

No reports concerning the kinetic study of the catalytic hydrogenation of aniline in the vapor phase are to be found in the literature. We ourselves have, however, previously reported on our kinetic study of the catalytic hydrogenation of aniline on a nickel-diatomaceous earth catalyst.2) In the catalytic hydrogenation experiments, the highest conversion of aniline to cyclohexylamine was obtained in the temperature range from 180°C to 190°C.3) At higher temperatures, the degree of hydrogenation decreased. It is uncertain whether this phenomenon is caused by the nature of the chemical thermodynamic equilibrium or by the reaction kinetics. In order to clear up this point, the experiments reported here were planned.

Experimental

Catalyst Preparation.—The powdered alumina was added to a solution of cobalt nitrate, and the slurry was

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1) Presented at the 5th Symposium of the Chemical Reaction Engineering in Japan, Tokyo, October, 1965.

2) E. Echigoya, H. Hagiwara and K. Morikawa, presented on the 29th Annual Meeting of the Society of Chemical Engineers, Tokyo, March., 1964.

3) H. Hagiwara and E. Echigoya, *Shokubai* (*Catalyst*), **6**, 324 (1964).

stirred for some time; to it was then added, at room temperature, a 1 N ammonium carbonate solution in a slight excess. After it had been kept for one hour at 50°C without stirring, the slurry was filtered, and the filter cake was washed, dried at 100°C, and calcined at 500°C for 2 hr. The cobalt oxide content was about 20%. Before use, the catalyst was reduced at 450°C for 2 hr. with 250 ml./min. of hydrogen inside the same fixed-bed apparatus later used for the hydrogenation reaction. A series of experiments was carried out using powder of the 150—100-mesh range.

Reaction using Fluidized-bed Equipment.—The equipment used for the fluidization experiments consisted of a glass tube 90 cm. long and 5 cm. in diameter. The fluidized-bed runs were made over the temperature range from 150°C to 230°C, using 50—400 g. of 100—150-mesh-size catalysts. The average value of the minimum fluidization velocity used was 2 cm./sec. over the temperature range from 160 to 200°C. A detailed report will be presented in the near future.

Reaction using a Fixed Bed.—The apparatus is shown in Fig. 1. The mixture of reactants entered the catalyst bed, which was maintained at the desired temperature by a solid-particle fluidized thermal bath. The gaseous products leaving the reaction zone were caught in a condenser trap cooled with a mixture of dry ice and methanol, from which condensates were drawn every thirty minutes for gas chromatographic analysis. The aniline and hydrogen concentrations in the reactants were varied by mixing in known amounts of nitrogen gas.

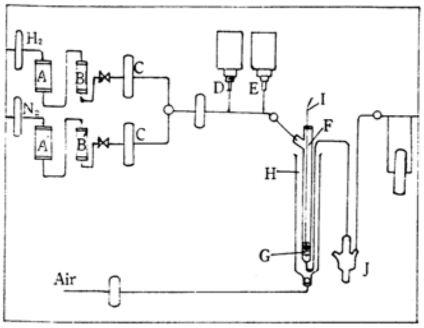

Fig. 1. Flow diagram.

A, A′: Deoxygenizer B, B′: Drying agent
C: Flow meter D: Aniline feeder
E: Cyclohexylamine feeder
F: Reactor G: Catalyst bed
H: Thermal fluidized bath
I: Thermocouple J: Cold trap

Results and Discussion

The Study of the Chemical Reaction Equilibrium for the Aniline Cyclohexylamine System.—Equilibrium constants for the aniline-cyclohexylamine system are little known compared with those of the benzene-cyclohexane system.[4]

Figure 2 shows the thermodynamic chemical equilibrium values calculated using Nernst's equation at a 10 to 1 mol. ratio of hydrogen to aniline. From Fig. 2, the dehydrogenation may be seen to be almost negligible below 200°C under these conditions. From the standpoint of the chemical reaction equilibrium, it is difficult to understand why the conversion obtained using a fixed-bed reactor should pass through a maximum value below 200°C. However, the hydrogenation reaction of aniline is an exothermic one. Thus it is difficult to measure a true reaction temperature in the fixed bed, which produces a large temperature gradient along its axial length. Accordingly, the fluidized bed, which has a large heat-transfer coefficient, was used to get a conversion at a true reaction temperature for this reaction.

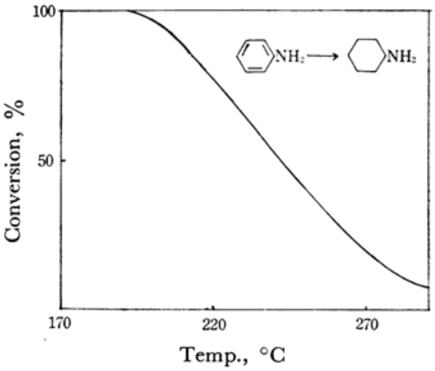

Fig. 2. Relationship between equilibrium conversion and reaction temperature $H_2/C_6H_5NH_2$ mole ratio 10.

The experimental results obtained at a uniform temperature within a fluidized bed are shown in Figs. 3 and 4. From the data, it may be seen that

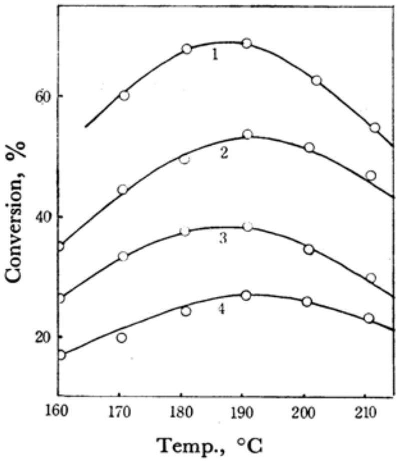

Fig. 3. Experimental data using a fluidized bed.
$H_2/C_6H_5NH_2$ mole ratio 15
Total feed mole 5.893 mol./hr.
Reaction diameter 2 inch.
Catalyst weights 1 266 g. 2 145 g.
3 98 g. 4 49 g.

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[4] G. I. Janz, *J. Chem. Phys.*, **22**, 75 (1954).

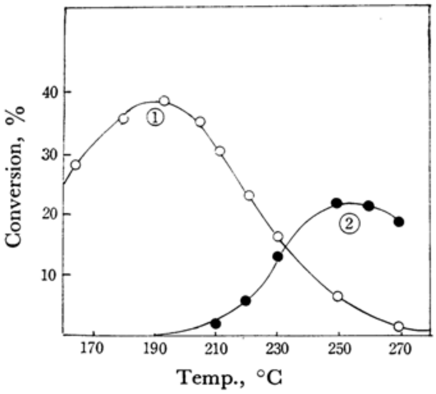
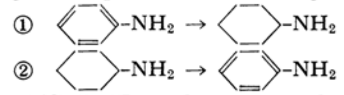


Fig. 4. Experimental data using a fluidized bed.



$H_2/C_6H_5NH_2$ or $C_6H_{11}NH_2$ mole ratio 15
$W/F=33.8$ $u/u_{mf}=2.15$

(1) the points of maximum conversion at the various space velocities were found in the temperature range from 180°C to 195°C, as in the fixed-bed experiments, and (2) the dehydrogenation reaction of cyclohexylamine was comparatively small below 210°C.

From the results obtained above, it may be assumed that the phenomenon of a negative temperature coefficient is caused by the reaction kinetics, not by chemical thermodynamic factors.

The following experiments were designed with this viewpoint in mind.

The Variation in the Catalyst Activity with the Reaction Time.—The changes in the catalyst's activity are shown in Fig. 5. The constant activity of the catalyst was obtained after about an hour and a half and did not change for about 6 hr., but then it gradually decreased. The catalyst was regenerated by passing hydrogen through it at 450°C for 1.5 hr.

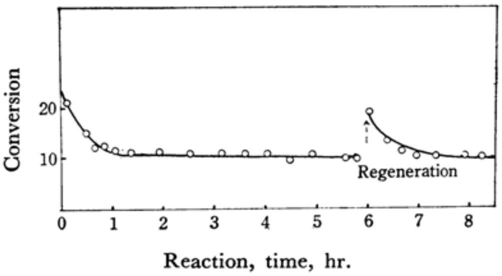


Fig. 5. Variation of catalyst activity with reaction time.
Temp. 180°C $H_2/C_6H_5NH_2$ molar ratio 10
$W/F \simeq 2$

The Dependency of the Fraction of Aniline Converted upon the Gas Space Velocity.—Experiments were first carried out to establish the range of conditions of the linear dependence between the reciprocal of space velocity and the conversion. The space velocity was here given as the volume (ml. at the reaction temperature) of gas coming in contact with 1 cc. of the catalyst per hour.

A series of runs were carried out under identical conditions, using powders of the 100—150-mesh-size range. In Fig. 6, the mole fraction of aniline converted against the reciprocal of space velocity was plotted, where F is a total flow rate [cc./hr]. The results obtained in this range could be treated as those of a differential reactor. A differential rate of reaction could then be calculated by the following approximate equation:

$$r = \Delta x_c/(W/f) \qquad (1)$$

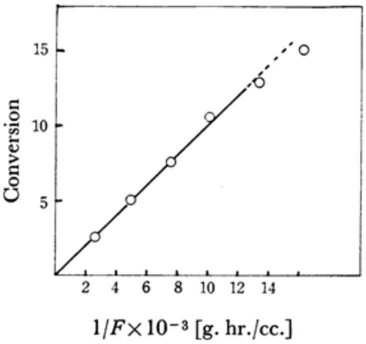


Fig. 6. Relationship between conversion vs. reciprocal of space velocity.
Reaction temp. 180°C
$H_2/C_6H_5NH_2$ mole ratio 10

where r: reaction rate [g.-mol./g. hr.], Δx_c: conversion in the differential reactor, W: catalyst weight [g.], and f: molar flow rate of an aniline-and-cyclohexylamine mixture [g. mol./hr.]. No by-products such as dicyclohexylamine could be found under these reaction conditions.

The Effects of Catalyst-particle Size.—The influence of the mass transfer on the over-all reaction rate was examined by using different sizes of catalyst (i. e., 100—150 mesh, 50—60 mesh, and 10—30 mesh). The results obtained were not at all different, and the effects of the mass transfer were concluded to be negligible.

The Initial Reaction Rate.—*The Dependence of the Initial Reaction Rate on Aniline and on the Hydrogen Partial Pressure.*—The experimental data obtained are summarized in Table I. The initial reaction rate can be expressed as follows:

$$r_0 = kP_A{}^{\alpha}P_H{}^{\beta}$$

where r_0: initial reaction rate, P_A and P_H: partial pressure of aniline and hydrogen, respectively [atm]. The order of the initial reaction as to aniline and to hydrogen partial pressure is given in Table II. From the table, it may be seen that the order

TABLE I. EXPERIMENTAL DATA OF THE INITIAL REACTION RATES

Temp. °C	P_H	P_A	x	r_0 (exp.) $\times 10^{-3}$	r_0 (cal.) by Eq. 2 $\times 10^{-3}$
165	0.91	0.09	7.65	3.6	3.3
	0.636	0.09	3.5	2.55	2.4
	0.454	0.09	1.0	1.80	1.16
	0.30	0.09	0.40	0.80	0.70
	0.80	0.200	11.5	2.90	2.71
	0.80	0.15	5.4	2.95	2.85
	0.80	0.101	3.6	2.93	3.30
	0.80	0.05	2.6	3.0	3.1
180	0.91	0.09	10.2	4.80	4.50
	0.636	0.09	4.0	2.95	2.9
	0.454	0.09	1.15	1.90	1.8
	0.30	0.09	0.46	0.85	0.86
	0.80	0.200	12.8	3.25	3.4
	0.80	0.15	5.9	3.2	3.5
	0.80	0.101	4.0	3.2	3.6
	0.80	0.05	2.5	2.8	3.1
195	0.91	0.09	8.95	4.2	3.9
	0.636	0.09	2.86	2.1	2.2
	0.454	0.09	0.665	1.2	1.2
	0.30	0.09	0.25	0.55	0.5
	0.80	0.20	12.6	3.2	2.85
	0.80	0.15	5.9	3.2	3.0
	0.80	0.101	3.88	3.1	3.02
	0.80	0.05	2.3	2.6	2.5
210	0.91	0.09	8.5	4.0	4.0
	0.636	0.09	3.0	2.2	1.8
	0.454	0.09	0.50	0.9	0.75
	0.30	0.09	0.15	0.30	0.25
	0.80	0.20	10.6	2.7	2.45
	0.80	0.15	4.7	2.55	2.7
	0.80	0.101	3.06	2.45	2.5
	0.80	0.05	1.86	2.1	2.1

TABLE II. THE ORDERS WITH RESPECT TO HYDROGEN PARTIAL PRESSURES AT VARIOUS TEMPERATURES

T °C	α Order with respect to hydrogen partial pressure	β Order with respect to aniline partial pressure
165	when $P_A=0.09$, 1.3	when $P_H=0.8$, ≈ 0
180	when $P_A=0.09$, 1.5	when $P_H=0.8$, ≈ 0.1
195	when $P_A=0.09$, 1.6	when $P_H=0.8$, ≈ 0.15
210	when $P_A=0.09$, 1.7	when $P_H=0.8$, ≈ 0.17

regarding the aniline partial pressure varied between 0 and 0.15 with the temperature, while the order regarding the hydrogen pressure varied between 1.3 and 1.7 with the temperature.

The Determination of the Rate Equation.—According to the Langmuir-Hinshelwood mechanism, the experimental data were discussed on the assumption that the surface reaction was the rate-controlling step. Different mechanisms may be presented for the hydrogenation of aniline, either the following possibilities or a combination of them:

1) Hydrogen is in the molecular state or is dissociated into atoms when adsorbed on the surface of a catalyst.

2) The mode of the addition of hydrogen to aniline is either step-by-step or simultaneous.

3) The adsorption of aniline and hydrogen takes place on the same active sites or on different ones.

4) Hydrogenation takes place between an aniline molecule in the gas phase and a hydrogen molecule adsorbed on the catalyst.

All the mechanisms were checked by comparing the experimental data on the initial rates with the characteristic curves of the modified rate equations. The results indicate that the data obtained can be fairly well correlated by the following rate equation:

$$r_0 = k\frac{K_A K_H{}^3 P_A P_H{}^3}{(1+K_A P_A + K_H P_H)^4} \qquad (2)$$

where k: reaction rate constant [g.-mol./g. hr.],

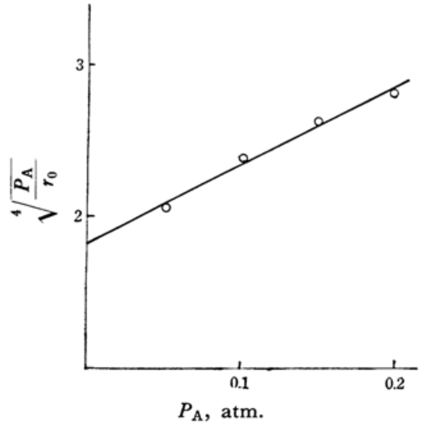


Fig. 7A. Verification of the Langmuir equation. Experiment at $P_H=0.8$ $T=180°C$ P_A variable

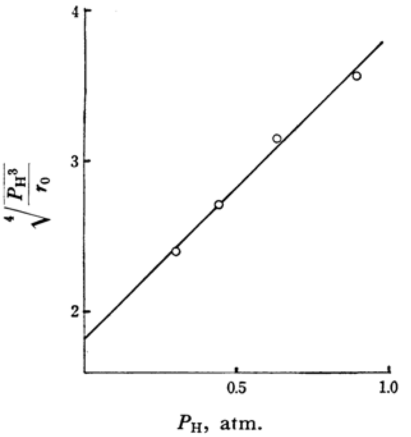


Fig. 7B. Verification of the Langmuir equation. Experiment at $P_A=0.09$ $T=180°C$ P_H variable

K_A and K_H: adsorption equilibrium constant of aniline and hydrogen, respectively [atm^{-1}].

In the above equation, when the hydrogen pressure, P_H, is constant, Eq. 2 can be transformed to the following:

$$\sqrt[4]{\frac{P_A}{r_0}} = \frac{1+K_AP_A+K_HP_H}{\sqrt[4]{kK_AK_H{}^3P_H{}^3}} = \varphi(P_A) \qquad (3)$$

This correlation is shown in Fig. 7A. A linear relationship was obtained between $\sqrt[4]{P_A/r_0}$ and P_A. At the constant aniline partial pressure, P_A, Eq. 2 can also be transformed into Eq. 4:

$$\sqrt[4]{\frac{P_H{}^3}{r_0}} = \frac{1+K_AP_A+K_HP_H}{\sqrt[4]{kK_AK_H{}^3P_A}} = \varphi(P_H) \qquad (4)$$

The correlation is shown in Fig. 7B. A linear relationship was obtained between $\sqrt[4]{P_H{}^3/r_0}$ and P_H. The values of K_H, K_A and k were obtained in the following manner. When P_H is constant, as in Fig. 7A, the gradient gives:

$$A = K_A/\sqrt[4]{kK_AK_H{}^3P_H{}^3}$$

and the point of intersection with the $\sqrt[4]{P_A/r_0}$ axis gives:

$$B = (1+K_HP_H)/\sqrt[4]{kK_AK_H{}^3P_H{}^3}$$

When P_A is constant, as in Fig. 7B, the gradient gives:

$$C = K_H/\sqrt[4]{kK_A{}^3K_H{}^3P_A}$$

and the point of intersection with the $\sqrt[4]{P_H{}^3/r_0}$ axis gives:

$$D = (1+K_AP_A)/\sqrt[4]{kK_AK_H{}^3P_A}$$

From A, B, C and D, the following equation is directly obtained:

$$\frac{B}{A} = \frac{1+K_HP_H}{K_A}, \quad \frac{D}{C} = \frac{1+K_AP_A}{K_H} \qquad (5)$$

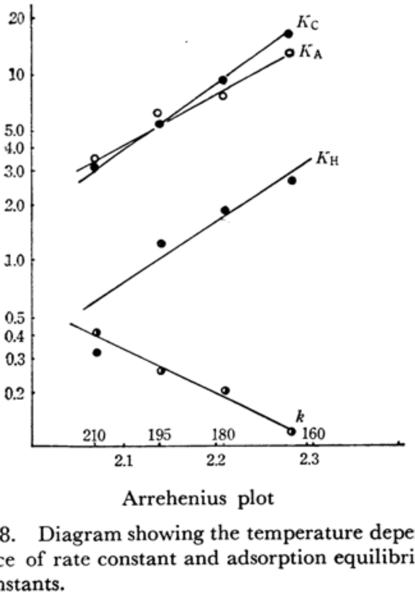


Fig. 8. Diagram showing the temperature dependence of rate constant and adsorption equilibrium constants.

TABLE III. THE VALUES OF THE ADSORPTION EQUILIBRIUM CONSTANTS AND RATE CONSTANT

	165°C	180°C	195°C	210°C	E or Q kcal./mol.
K_H	2.5	1.78	1.20	0.3	13.5
K_A	11.8	7.0	5.8	3.4	12.5
k	0.118	0.20	0.252	0.40	11
K_C	15.5	8.9	6.0	3.1	1.5

Using the above equations, the calculated values of K_A, K_H and k are shown in Table III. These values are reasonable for $K_A > K_H$, and the adsorption coefficient diminishes as the temperature becomes higher. The variation in k with the temperature yields an activation energy of 11.0 kcal./mol. The heats of adsorption of aniline and hydrogen are 12.5 kcal./mol. and 13.5 kcal./mol. respectively (Fig. 8).

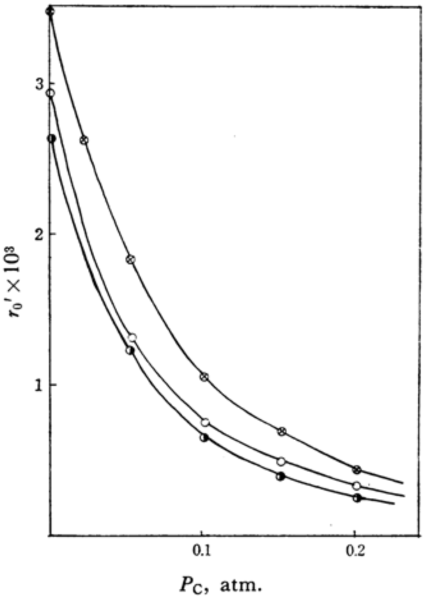


Fig. 9. Inhibition effect of cyclohexylamine. Reaction rate vs. cyclohexylamine partial pressure. $P_H = 0.7$ $P_A = 0.06$ P_C variable
○ 195°C, ⊗ 185°C ◑ 165°C

The Rate Equation with Cyclohexylamine.—The rate of reaction was measured by varying the cyclohexylamine concentration in the stream entering the reactor, while maintaining constant hydrogen and aniline partial pressures. The inhibition effect of cyclohexylamine was very clear throughout the whole range of temperatures (Fig. 9). The logarithmic transformation of this curve, $\log r_0'$ - $\log P_C$, gave curves with negative gradients (Fig. 10). The value of K_C was obtained in the following way. The Langmuir rate equation might be written as follows:

$$r_0' = \frac{kK_AK_H{}^3P_AP_H{}^3}{(1+K_AP_A+K_CP_C+K_HP_H)^4} \qquad (6)$$

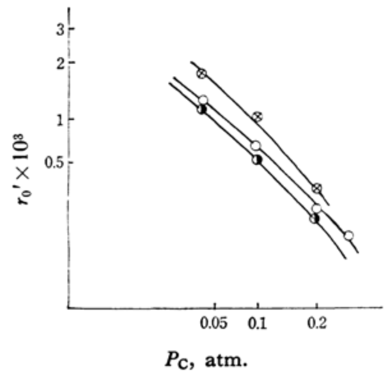


Fig. 10. Orders with respect to cyclohexylamine partial pressure.
○ 195°C ⊗ 180°C ◑ 165°C

where r_0': initial reaction rate with cyclohexylamine, P_C: partial pressure of cyclohexylamine [atm.] and K_C: adsorption equilibrium constant of cyclohexylamine [atm^{-1}]. The modified rate equation was obtained as follows:

$$\left(\frac{kK_H{}^3K_AP_H{}^3P_A}{r_0'}\right)^{1/4} = 1+K_AP_A+K_CP_C+K_HP_H \tag{7}$$

When P_A and P_H were kept constant, the following equation could be obtained:

$$\left(\frac{1}{r_0'}\right)^{1/4} = E+GP_C \tag{8}$$

$$\frac{E}{G} = \frac{1+K_AP_A+K_HP_H}{K_C} \tag{9}$$

The correlation in Eq. 8 was verified at a constant reaction temperature (Fig. 11). Using the values of K_A and K_H found before, the values of K_C were calculated. From the calculated value of K_C, the heat of adsorption of cyclohexylamine was found to be 15 kcal./mol.

As a final result, the following rate equation gives the vapor-phase hydrogenation of aniline to cyclohexylamine on the cobalt-alumina catalyst:

$$r = k\frac{K_AK_H{}^3P_AP_H{}^3}{(1+K_HP_H+K_AP_A+K_CP_C)^4} \tag{10}$$

The average deviation of the proposed equation from the experimental values is about 10%.

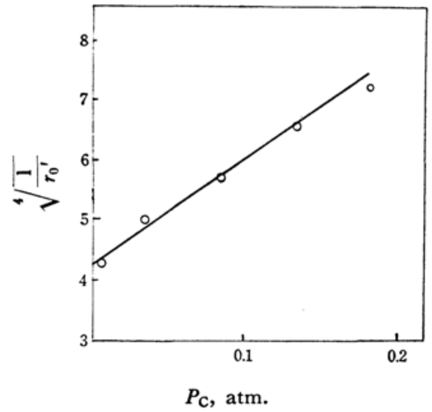


Fig. 11. Verification of the Langmuir equation.
Reaction temp. 180°C

A Test of the Rate Equation Obtained by the Differential-type Flow Reactor.—The conversion as a function of W/F (F: total flow rate [g.-mol./hr.]) was calculated numerically by Eq. 10, and it is plotted in Fig. 12. The data obtained using the integral-type flow reactor are superimposed on the plots in Fig. 12. Qualitatively the data and the plots show an approximate correspondence even though they have been determined by different methods.

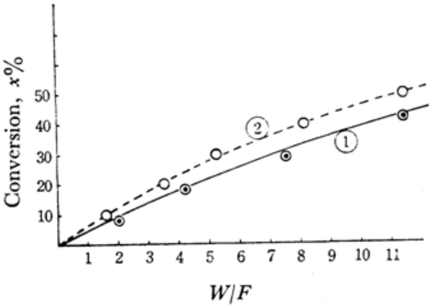


Fig. 12. Comparison of the conversion vs. W/F for the integral method data ① and the calculated values ②.
Reaction temp. 180°C
$H_2/C_6H_5NH_2$ mole ratio 15

Summary

1) The rate of reaction reaches a maximum value at about 180—190°C in the hydrogenation of aniline. According to thermodynamic calculation and experiments using a fluidized bed, the reverse reaction is almost negligible below 200°C under the conditions of the reaction. Therefore, this phenomenon has been assumed to be caused by the reaction kinetics.

2) The kinetics of the catalytic hydrogenation of aniline using a cobalt-alumina catalyst in the temperature range from 160 to 210°C was studied by a differential-type fixed-bed flow reactor. The initial rate of reaction without cyclohexylamine, and the rate when some cyclohexylamine was added to the reactants, were measured at atmospheric pressure over the following range of conditions:

hydrogen	0.3—0.92 atm.
aniline	0.05—0.2 atm.
cyclohexylamine	0—0.24 atm.

As a result of these experiments, it was concluded that the most plausible rate-controlling step was the surface reaction, i. e., the reaction between the aniline and hydrogen adsorbed on the surface of the catalyst. The final equation for the vapor-phase hydrogenation of aniline on a cobalt-alumina catalyst in the temperature range from 150°C to 210°C was as follows:

$$r = k\frac{K_H{}^3K_AP_H{}^3P_A}{(1+K_HP_H+K_AP_A+K_CP_C)^4} \qquad (10)$$

Eq. 10 will be useful if it can be used to predict the rate over a wide range of conditions and, hence, be suitable for use in reactor design. However, it is not possible by kinetic study alone to determine the true mechanism of this reaction.

The authors wish to thank Professor Kiyoshi Morikawa for his useful discussions and guidance.