PRODUCTION OF ANILINE FROM NITROBENZENE

By

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July 31, 1959

Professor Alvin Sloane
Secretary of the Faculty
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Dear Sir:

The thesis entitled "Production of Aniline from Nitrobenzene" is hereby submitted in partial fulfillment of the requirements for the degree Master of Science in Chemical Engineering.

Respectfully submitted,

Carlos Paya-Riera

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ABSTRACT

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Submitted to the Department of Chemical Engineering on August 4, 1959, in partial fulfillment of the requirements for the degree of Master of Science.

This study presents the results obtained in the study of the reaction between nitrobenzene and hydrogen in a fluidized catalytic bed of nickel and copper supported on alumina.

It was found that the nitrobenzene feed rate and the catalyst concentration were the most important variables. Two temperatures were tested, 200°C and 240°C, reaching at both temperatures almost the quantitative conversion. Two catalyst concentrations were studied, 10% and 2% of N_i - Cu.

Using the rate of reaction equations founded was calculated a reactor for the production of 10 ton/day of aniline. This reactor has the following characteristics:

catalyst concentration = 0.5% N_i - Cu
weight of catalyst - 6670 Kg
temperature of catalyst= 240°C
diameter = 2.3 m
height = 2.73 m

Thesis Supervisor:	Edwin R. Gilliland
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I. SUMMARY

This study presents the results obtained in the study of the reaction between nitrobenzene and hydrogen in a fluidized catalytic bed of nickel and copper supported on alumina.

Although the aniline is an important industrial chemical, very few investigations have been done to improve its manufacture. Even today most of the aniline is produced by the old method of reduction of nitrobenzene with iron and hydrochloric acid.

Since the reaction of nitrobenzene with hydrogen is highly exothermic, 235000 cal/mol g. efficient heat removal is essential for proper temperature control.

Recently there have been published some researches and also patents covering the reduction of nitrobenzene with hydrogen in a fixed catalytic bed.

But the poor heat transfer characteristics make it very difficult to maintain the temperature at the desired value.

Fluidized beds, because the solids mix, gives an excellent uniformity of temperature, either in exothermic or endothermic reactions. The peculiarity of this technique seemed to be very attractive for applying to the reaction of nitrobenzene and hydrogen.

The effect of the temperature, feed rate of nitrobenzene, linear velocity of gases and catalyst concentration have been studied, in order to investigate the mechanism of the reaction and obtain kinetics data to calculate the dimension of a commercial reactor.

The reaction was studied in a Pyrex glass reactor 40 mm inside diameter and 25 inches long, heated externally by electric wires. It was found that the nitrobenzene feed rate and the catalyst concentration were the most important variables. Two temperatures were tested, 200°C and 240°C, reaching at both temperatures almost the quantitative conversion. At a nitrobenzene feed rate of 1.2 gr/min and 3.8 gr/min respectively.

Two catalyst concentrations were studied; 10% N_i-Cu and 2% N_i-Cu. The last one prepared by diluting the 10% catalyst with alumina. Was found that the nitrobenzene converted in a given time is proportional to the weight of catalyst.

For a given temperature and catalyst the aniline covversion for different nitrobenzene feed rates presented two different mechanisms. When the nitrobenzene feed rate is low, all the nitrobenzene is converted in aniline and some aniline is over reduced to ammonia and benzene. When the nitrobenzene feed rate increases, the conversion of aniline increases also until it reaches the point of quantitative conversion. If the nitrobenzene feed rate is further increased, then some nitrobenzene goes through the catalyst without reaction and no formation of benzene and ammonia is produced.

It was found that the rate of reaction in these two different zones were:

Aniline decomposition zone 200°C $r = -15.92 \; P_{NH_2}^{1/2}$
240°C $r = -13.7 \; P_{NH_2}^{1/2}$

Partial Conversion of
Nitrobenzene zone 200°C $r = 2.89 \; P_{NO_2}/(1+62.5 \; P_{NO_2})^2$
240°C $r = 0.907 \; P_{NO_2}/(1+8 \; P_{NO_2})^2$

With the rate of reaction equation developed was calculated the size of a commercial reactor for the production of 10 ton/day of aniline, operating with 10% catalyst and 240°C. It was found that the surface of this reactor was not enough for cooling the reaction.

Using the proportionality between nitrobenzene converted and weight of catalyst, it was calculated a reactor for the same production of 10 ton/day and with enough surface for cooling. This reactor has the following characteristics:

Catalyst Conc. = 0.5 %

Weight of Catalyst = 6670 Kg

Temperature of Catalyst = 240°C

Diameter, m. - 2.3

Height, m. - 2.73

In view of the successful characteristics obtained in this study, it has been recommended to study widely all the variables and to operate in pilot plant scale to confirm the influence of the variables and kinetics data for getting definite information to build industrial installations.

II. INTRODUCTION

Aniline is an important industrial organic chemical used in the manufacture of dyes, pharmaceutical compounds and as a solvent.

It is estimated that in 1958 over 150 million pounds of aniline were produced in the United States alone and the demand for it appears to be increasing steadily.

Aniline was first produced (1) in 1826 by the dry distillation of indigo. Today, the principal methods used for the manufacture of aniline are:

1) Reduction of nitrobenzene with iron and hydrochloric acid.

2) Catalytic reduction of nitrobenzene.

3) Amination of chlorobenzene.

4) Amination of phenol.

Of these methods, the first is the oldest and even today most of the aniline produced is manufactured by this method (2). It is a batch process and the aniline produced is mixed with solid residue which requires an additional purification process for removal.

The amination of phenol and chlorobenzene is less important although the last method is used frequently in the U. S. (3).

The development of hydrogenation techniques has made it possible to explore the possibilities of the catalytic reduction of nitrobenzene with hydrogen. During the last few years extensive research work has been carried out on the hydrogenation of nitrobenzene. (4) (5)(6)(7)(8)(9)(10)(11) (12)(13).

The catalytic reduction of nitrobenzene is of industrial importance because all the raw materials are available in large quantities from petrochemical operations, the yields are high and the aniline is obtained continuously and without waste products.

Nitrobenzene can be hydrogenated over a variety of catalysts in both liquid and vapor phases and at both low and high hydrogen pressures. The most important catalysts are:
a) the metals: platinum, palladium, nickel and copper;
b) the sulfides of nickel, cobalt and molybdenum. The metal catalysts are more active than the sulfides. They are however (particularly nickel and copper) readily poisoned by traces of sulphur in the feed. This is not an inconvenience because actually the majority of the benzene used is derived from petroleum and is completely free of sulphur compounds. The major coke-oven producers of benzene which is the other source have recently installed facilities for desulphurization.

The work of Brown and Henke (14) and Gharda and Sliepcevich (15) are probably the most extensive on the catalytic hydrogenation of nitrobenzene.

Brown and Henke used copper oxide prepared by two methods: ignition of the nitrate and by precipitation from the nitrate by hot dilute sodium hydroxide. They studied the effect of changing the conditions for the preparation of the catalyst on the catalyst activity. In addition they determined the effect of reaction temperature and nitrobenzene feed rate on the rate of reduction of nitrobenzene. Since they used a heated tube and measured only the exit temperature of the gases, no great reliance can be placed on these temperature values because their recorded temperatures values must be considerably different from the reaction temperature since the reaction is highly exothermic.

Gharda and Sliepcevich studied the catalytic hydrogenation of nitrobenzene to aniline at atmospheric pressure in the vapor phase over copper catalyst in temperature range of 350-550°F. They investigated both commercial and laboratory prepared copper catalyst. It was found that the catalyst stability and activity was very sensitive to the presence of sulfur compounds and dinitrobenzene in the feed, the ratio of nitrobenzene to hydrogen in the feed, the reaction temperature and the size of the catalyst particles. The rate of reaction over barium-promoted , copper chromite catalyst was determined and it was found that the rate-controlling step was the surface reaction.

A patent was granted to Leon O. Winstrom (11) on the hydrogenation of aromatic nitrocompounds to the corresponding amines. The patent was concerned with an improved process for the catalytic vapor phase hydrogenation of nitrobenzene to aniline. His catalyst was an intimate mixture of nickel sulfide and amorphous alumina. The amount of alumina was about 10% to about 90% of the weight. The catalyst was prepared by sulfiding a mixture of precipitates of insoluble nickel and aluminum compounds selected from the group consisting of nickel and aluminum hydroxides and carbonates produced from water-soluble nickel and aluminum salts by alkaline precipitation. He worked at temperatures ranging from 250°C to 350°C. The patent claims that the best operating conditions were obtained with catalyst particles between 8 and 100 mesh and using a nitrobenzene feed of 300 gr per liter of catalyst.

The reactor used was a Downs type converter. The conversion was almost quantitative and the temperature was 300°C but the author recognized that the peak temperatures in the zones of maximum reaction may be as high as 400 - 450°C. The patent of Paul C. Condit (9) (12) relates to the preparation of amines by the controlled hydrogenation of the corresponding nitrocompounds in the presence of catalyst comprising the sulfides of vanadium, columbium, tantalium, chromium, molybdenum and tungsten supported on activated carbon. The best conditions for obtaining aniline from nitrobenzene was obtained with 10-14 mesh molybdenum sulfide on activated carbon catalyst, using 200% of an excess of the theoretically amount of hydrogen. The nitrobenzene feed rate was about 15 c.c. (liquid) to 20c.c. and the temperature of the bed was about 605°F. The yield was 98% of aniline. The reactor used was a one-half inch diameter stainless steel tube carrying 60 c.c. of catalyst.

The principal difficulty in the continuous fixed catalytic bed process is the removal of the heat of reaction because for each Kgmol of aniline produced, 235,000 Kcal are liberated (16). So it is very difficult to control the temperature and if a high temperature time is produced in the bed, the aniline is destroyed. Besides, one of the most important factors that affect the stability of the highly active catalyst, such as nickel and copper is the temperature. These types of catalyst are stable only in a very narrow temperature range. Hence, the large heat of reaction must be efficiently removed to prevent both the decomposition of aniline and the catalyst deactivation where nickel and copper are used. (15)

Due to the poor heat transfer characteristics of fixed bed catalytic reactors, the temperature is very difficult to maintain at the desired value.

Fluidized beds of solid catalysts have been successful in giving good temperature control in heterogeneous reactions which are very endothermic or exothermic. The excellent uniformity of temperature obtained with these units is due to the rapid internal heat transfer resulting from the solids mixing. While the solid mixing is beneficial in maintaining an essential uniform temperature, it results in bypassing and mixing of the vapor phase which are usually undesirable from the reaction kinetics viewpoint.

In this thesis the reaction between nitrobenzene and hydrogen was studied using a catalyst of nickel and copper supported on alumina in a fluidized bed. The activity of this catalyst at different concentrations of metals will be studied. The mechanism of the reaction will be investigated in order to design an industrial reactor to produce 10 ton/day of aniline.

III. EQUIPMENT

A schematic flow diagram of the equipment constructed for this study is shown in Figure 1.

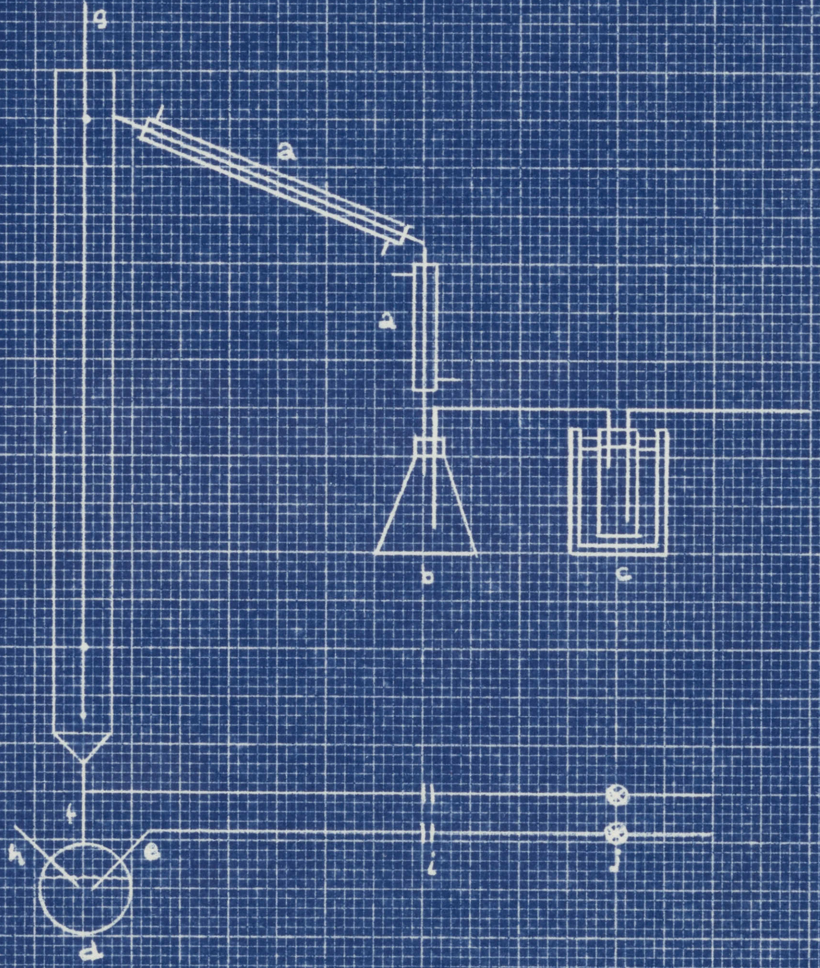
Since the studies were to be conducted at atmospheric pressure and it seems (15) that a steel reactor introduces extraneous catalytic effects, the reactor was made of a Pyrex glass tube. The inside diameter is 40 m.m. and 25 inches high. At the base of the reactor there is a porous plate made also of Pyrex glass to secure good fluidization of the catalytic powder.

The reactor is wound with two independently controlled electric heaters. One heater is used to heat the catalyst bed to reaction temperature at the beginning of a run, and the other one for maintaining the upper part of the reactor above the condensation temperature of the products.

The reactor is covered with insulating materials and a free space is left between the insulation and the pyrex tube for cooling the reactor with air if necessary.

The collection system for the reaction products consist of two water condensers (a) in series in which the majority of aniline is condensed. The aniline condensed in these

Figure 1



Flowsheet of system

water condensers flows by gravity into a glass flask (b). A cold trap (c) cooled with dry ice and acetone is placed after the water condensers to assure that all the aniline from the reactor is condensed.

Connected to the base of the reactor is a heated flask containing nitrobenzene (d). Inside this flask is a glass tube (e) through which a stream of hydrogen is passed. The hydrogen stream passes into the reactor and carries with it the nitrobenzene vaporized in the flask.

At the bottom of the reactor is a connection through which the principal amount of hydrogen is passed (f).

The reactor temperature was measured with three iron-constantan thermocouples (g) inserted axially in the reactor. Two of these were used for controlling the bed temperature and the third one for measuring the temperature of the upper part of the reactor. The e.f.m. measurements of the thermocouples were made with a Leeds and Northrup potentiometer.

The temperature of the nitrobenzene flask was measured with a thermometer inserted in the liquid (h).

The hydrogen flows were metered by capillary flow meters (i). The flow rate was controlled by needle valve (j).

The quantity of nitrobenzene fed was measured by weighing the flask of nitrobenzene before and after the run was made.

Material

The principal materials used in this study were: catalyst, nitrobenzene and hydrogen.

1. Catalyst

In all the runs, nickel and copper catalyst of 10% and 2% concentration in metals were used.

The 10% catalyst was prepared as is detailed later. The 2% catalyst was obtained by diluting a portion of 10% catalyst with alumina .

The raw materials for preparing the catalysts were

a) Nickel (ous) nitrate, crystals, Fisher reagent.

b) Cupric nitrate, crystals, Mallinckrodt reagent.

c) Activated alumina, Alcoa, grade F-1, Mesh 48-100.

2. Gases

Hydrogen was taken directly from commercial cylinders "AIRCO". The purity was about 99.9 percent and the chief impurities were traces of oxygen and water.

3. Nitrobenzene

The nitrobenzene used was reagent grade obtained from Eastman Organic Chemicals.

IV. EXPERIMENTAL PROCEDURE

1. Catalyst Preparation

The activated alumina is first reactivated by heating it for two hours at 400°F. Then the alumina is mixed with a solution of cupric and nickel(ous) nitrate~~d~~s with the required amount of metals present to produce a catalyst of the desired percentage in weight of metals. The mixture is then stirred and heated to dryness. The powder (green colour) is finally heated in a reactor at an uniform temperature of 250°C in fluidized conditions with hydrogen passing through the bed. In this condition the nickel(ous) and cupric nitrate are decomposed to the oxide. The oxides are then reduced to nickel and copper metals supported on the alumina (black colour).

2. The Study of the Reaction Between Nitrobenzene and Hydrogen

The reactor is first packed with the adequate amount of catalyst prepared in the manner described above. Then the upper part of the reactor is heated to 220°C and the catalyst bed to the reaction temperature. Hydrogen is passed through the catalyst bed during the heating process. At the same time, the nitrobenzene in the flask is heated to 200°C by an electric blanket.

Once the required temperature is reached, hydrogen is flown through the nitrobenzene flask. At this stage a run is started.

The duration of each run is such to feed enough nitrobenzene to minimize the error in weighing the nitrobenzene flask.

When the nitrobenzene feed rate is small the reactor temperature is maintained at the desired level by reducing the heat input with a variac. When the feed of nitrobenzene is high it is necessary to eliminate the power from the electric heaters and to cool the reactor with air flowing in the free space between the reactor and the insulation jacket.

The runs with low conversion, the temperature is very difficult to control because a small increase of temperature produces a rapid change in the conversion and therefore a rapid increase in the temperature. These runs were made with a variation in the temperature of ± 5°C.

Once the run is over the hydrogen bubbling through the nitrobenzene flask is stopped and therefore the nitrobenzene feed to the reactor is stopped also. Then the nitrobenzene flask is cooled with air. The reaction temperature is maintained in the bed for a half hour insuring in this way that all of the reaction products passed to the condensers. Then the catalyst temperature is increased to 250°C for an additional half hour. The power is finally shut off and hydrogen is flown through the catalyst a half hour more.

The collector system was very carefully washed first with glacial acetic acid and then with distilled water. The solution is diluted and the aniline titrated with the Reinhardt modified method as is described in detail in the Appendix.

The nitrobenzene flask is weighed before and after the run and the nitrobenzene feed during the run is determined by difference.

In preliminary runs benzene and nitrobenzene were determined for to ascertain that no intermediate reduction products such as azoxybenzene or azobenzene were produced. These analytical methods are also described in the Appendix.

V. EXPERIMENTAL RESULTS

The experimental results obtained in the study of the reduction of nitrobenzene with hydrogen in a fluidized catalytic bed are presented in the Tables I, II, III and IV.

The influence of the feed rate of nitrobenzene was first studied. Figure 2 shows the results obtained at 200°C and Figure 3, the results obtained at 240°C. The other conditions are indicated in each figure and in Tables I and II.

The reactor temperature could not be measured above 240°C because the high exothermic nature of the reaction made it very difficult to control the temperature adequately.

Some runs were made to determine the influence of the superficial gas velocity. These runs are presented in figure 2 and the operating conditions in Table III.

Figure 4 gives data obtained with a catalyst concentration of 2% (N_i-Cu). The other operative conditions are indicated in Table IV.

Resume of operating conditions of the runs about the reaction between hydrogen and nitrobenzene.

TABLE I.

Run	Catalyst Concentration (%N_i-Cu)	Volume of Catalyst c.c.	Nitrobenzene Bath Temp°C	Catalyst Bed Temperature°C	Hydrogen Velocity in Reactor cm/sec	Nitrobenzene Fed to Reactor gr/min	Conversion %
1	10	150	200	200	18.75	0.61	71
2	10	150	200	200	18.75	0.695	92
3	10	150	200	200	18.75	1.280	97
4	10	150	200	200	18.75	1.775	98.7
5	10	150	200	200	18.75	1.84	99.3
6	10	150	200	200	18.75	2.30	95.3
7	10	150	200	200	18.75	2.475	90.3
8	10	150	200	200	18.75	3.25	36.7
9	10	150	200	200	18.75	3.74	27.9
10	10	150	200	200	18.75	3.34	41.6
11	10	150	200	200	18.75	3.67	42.6

TABLE II.

12	10	150	200	240	18.75	1.7	92.4
13	10	150	200	240	18.75	2.0	94.0
14	10	150	200	240	18.75	2.67	95.9
15	10	150	200	240	18.75	2.61	95.7
16	10	150	200	240	18.75	3.87	97.0
17	10	150	200	240	18.75	3.90	96.5
18	10	150	200	240	18.75	0.725	77.8
19	10	150	200	240	18.75	2.61	98.0
20	10	150	200	240	18.75	3.0	97.6
21	10	150	200	240	18.75	3.43	96.4
22	10	150	200	240	18.75	4.27	94.7
23	10	150	200	240	18.75	4.80	93.8
24	10	150	200	240	18.75	5.88	58.9

TABLE III.

Run	Catalyst Concentration (%N_i-Cu)	Volume of Catalyst c.c.	Nitrobenzene Bath Temp°C	Catalyst Bed Temperature°C	Hydrogen Velocity in Reactor cm/sec	Nitrobenzene Fed to Reactor gr/min	Conversion %
25	10	150	200	200	20	1.225	98.4
26	10	150	200	200	25	1.24	96.2
27	10	150	200	200	25	1.23	98.6
29	10	150	200	200	18.75	1.25	97.0
30	10	150	200	200	35	1.59	99

TABLE IV.

31	2	300	197	240	18.75	2.550	22.5
32	2	300	197	240	18.75	0.390	88.3
33	2	300	197	240	18.75	0.990	95.8
34	2	300	197	240	18.75	1.115	96.7
35	2	300	197	240	18.75	1.750	91.9
36	2	300	197	240	18.75	1.590	95.6
37	2	300	197	240	18.75	1.150	93.6

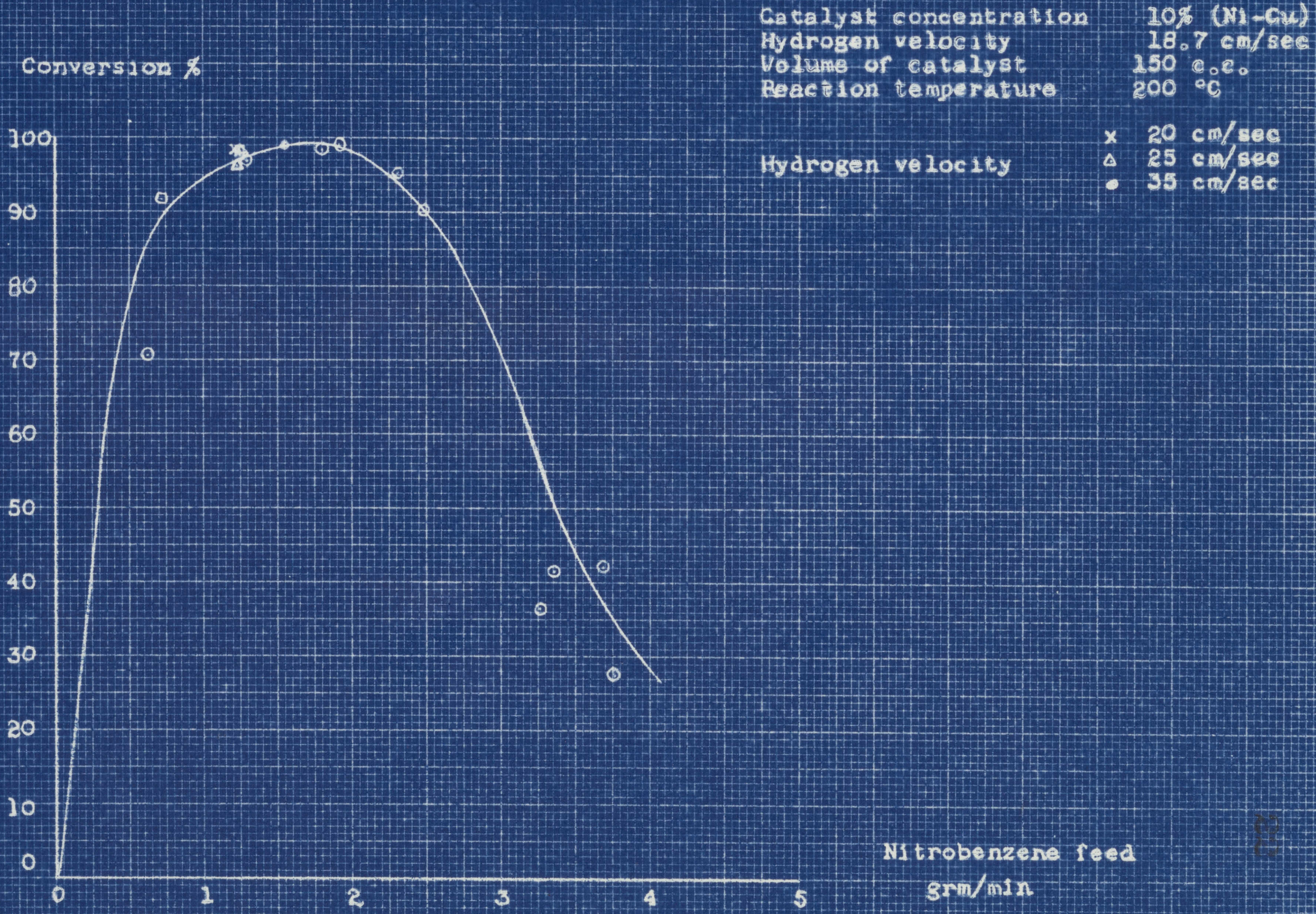
VI. DISCUSSION OF RESULTS

1. A Study of the Effect of Operating Variables on the Reaction of Hydrogen and Nitrobenzene.

a) Nitrobenzene Feed Rate

Preliminary runs indicated that the nitrobenzene feed rate is one of the most important variables affecting the catalytic hydrogenation of nitrobenzene. The data illustrating this are presented in Figure 2. In this Figure the aniline conversion is plotted against the nitrobenzene feed rate, for a temperature of 200° C. The first part of the curve, between zero and 1.7 grm/min. nitrobenzene feed rate, all the nitrobenzene is converted to aniline but some of the aniline produced is decomposed into benzene and ammonia. At a nitrobenzene feed rate of about 1.7 grm/min. almost quantitatively aniline conversion is obtained. As the nitrobenzene feed rate is increased, the conversion of aniline produced from nitrobenzene is decreased. In this zone essentially no aniline is decomposed. As the nitrobenzene feed rate is increased to 3.25 grms/min. it becomes very difficult to control the reactor temperature to within 5°C. Because the hydrogen linear velocity was always constant, the molal ratio hydrogen/nitrobenzene from run to run was changed.

Figure 2



Catalyst concentration 10% (Ni-Cu)
Hydrogen velocity 18.7 cm/sec
Volume of catalyst 150 c.c.
Reaction temperature 200 °C

But always this ratio was enough higher that it did not introduce any influence.

b) Temperature

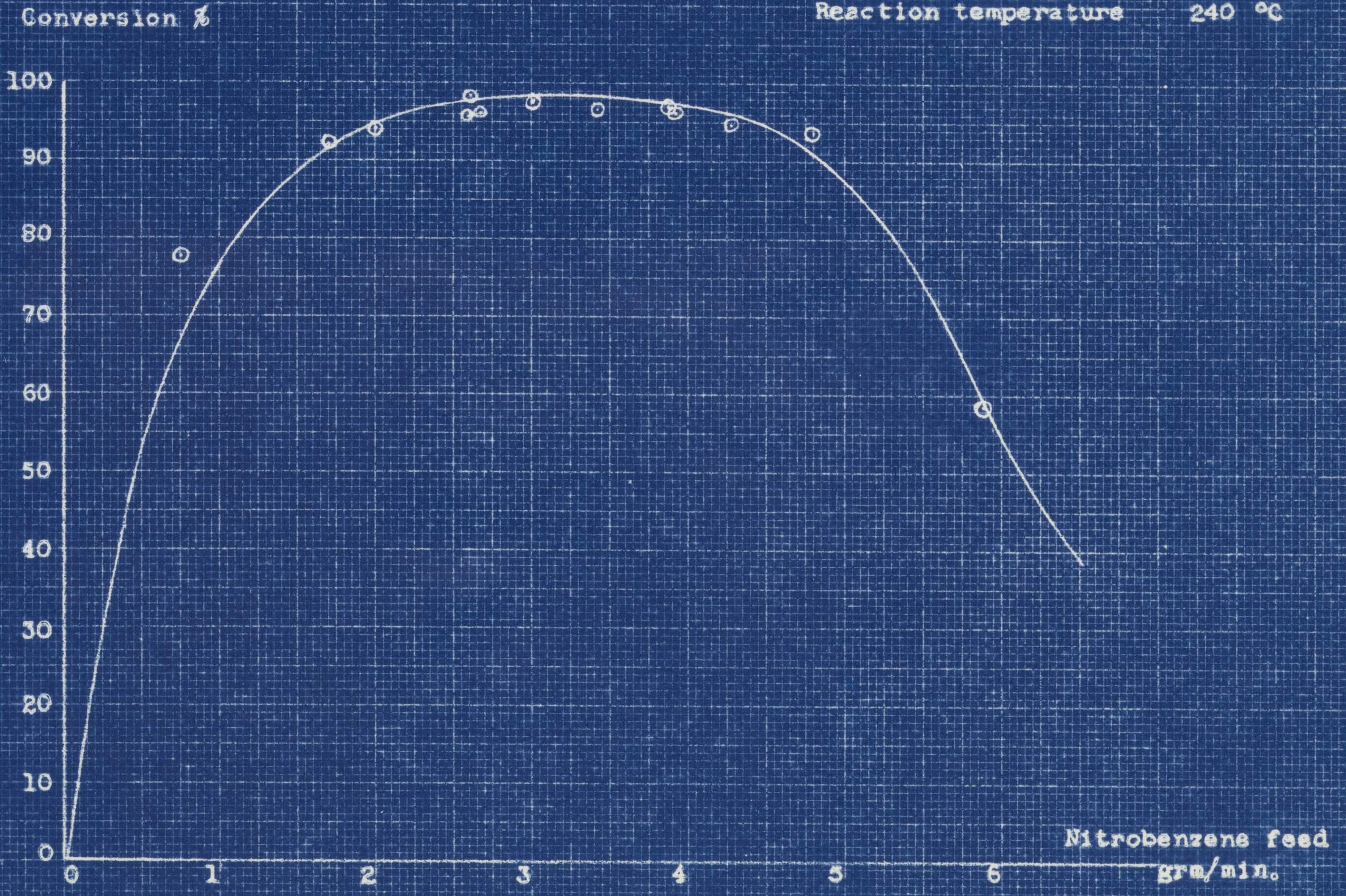
Figure 3 shows the same effect of nitrobenzene feed rate at 240°C. The conversion curve has the same shape as that of Figure 2, but the maximum conversion points extend over a wider range of nitrobenzene feed rates (the curve is flatter).

Figures 2 and 3 show that depending on the nitrobenzene feed rate, it is possible to get about 100% conversion of aniline at higher temperatures. At these higher temperatures, with the other operating conditions the same, the quantitative conversion point is obtained at higher nitrobenzene feed rates than at lower temperatures.

The shape of Figures 2 and 3 can be explained by the hypothesis of strong nitrobenzene adsorption on the catalyst: when the nitrobenzene feed rate is high, such that the number of mols of nitrobenzene are higher than the number of active sites, only a fraction of the nitrobenzene will occupy the active sites replacing the aniline produce. The rest of the nitrobenzene pass through the catalyst without reacts. (Right side of the curves in Figures 2, 3 and 4).

Figure 3

Catalyst concentration 10% (Ni-Cu)
Hydrogen velocity 18.7 cm/sec
Volume of catalyst 150 c.c.
Reaction temperature 240 °C



As the nitrobenzene feed rate decreases, less nitrobenzene goes out without reaction, until the point where the number of mols of nitrobenzene are equal to the number of active sites. Then all the nitrobenzene fed is attracted to the active sites replacing the aniline produced. At this point all the nitrobenzene reacts and the maximum conversion is reached. (Top of the curves in Figures 2, 3 and 4).

If the nitrobenzene feed rate decreases only a fraction of active sites will be occupied by the nitrobenzene replacing only a fraction of the aniline produced. The rest of aniline, still on the catalyst, will react with more hydrogen giving benzene and ammonia. The aniline conversion therefore decreases.

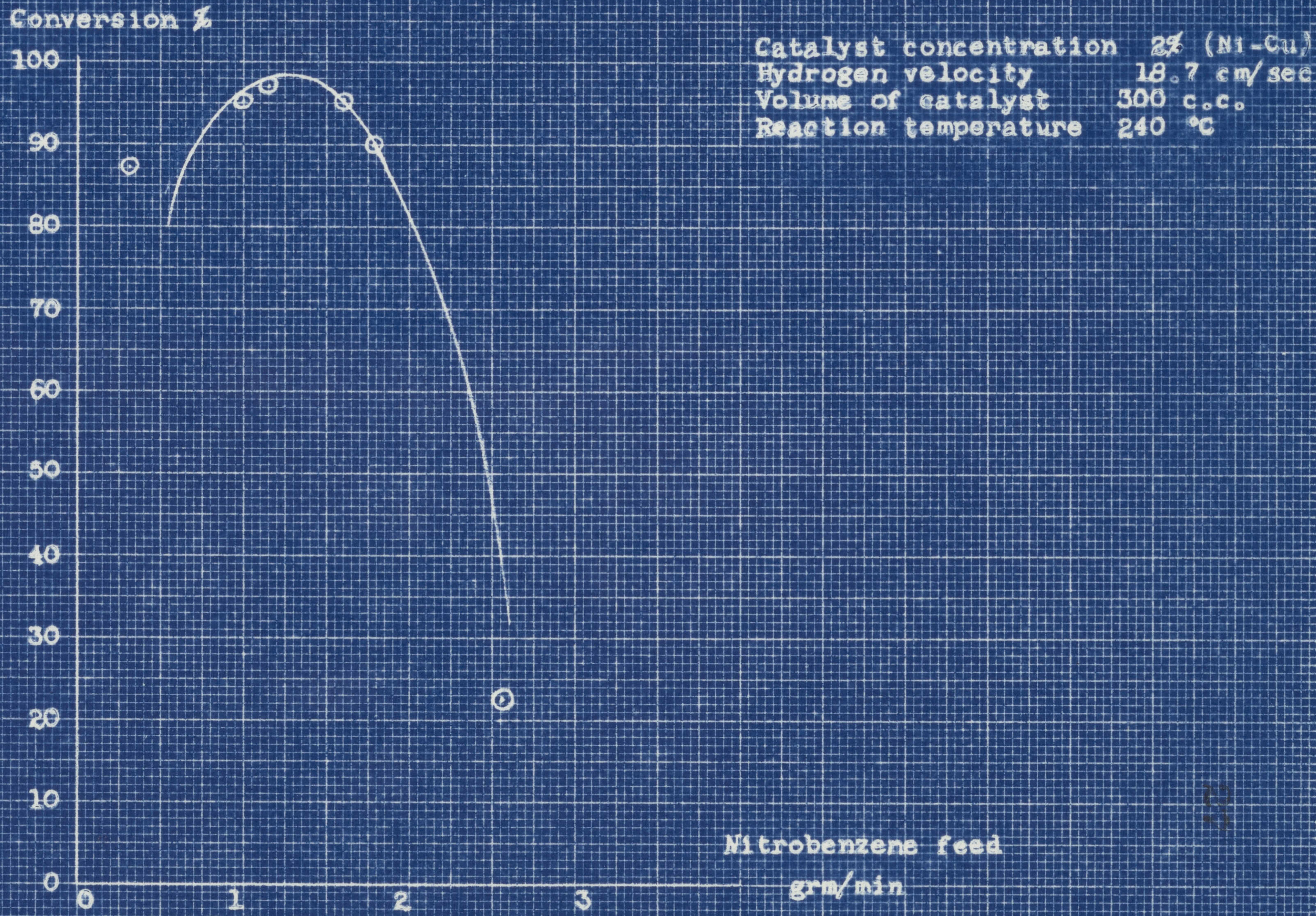
c) Superficial Velocity of Reactors.

Runs 25 to 30 indicate that substantial change in linear velocity of the hydrogen (at constant nitrobenzene feed rate) does not change the aniline production. An increase in linear velocity from 18.7 cm/sec to 25 cm/sec does not increase the conversion of nitrobenzene. The nitrobenzene feed rate was kept constant at about 1.25 gr/min. At 35 cm/sec and with a nitrobenzene feed rate of 1.59 gr/min one run was made with a 97% of conversion. No ammonia was detected in the product stream from the reactor. At the same nitrobenzene feed rate of 1.59 gr/min but at 18 cm/sec of gas linear velocity the yield was 99% but ammonia was detected in the products stream. In other words, at this high velocity some nitrobenzene passes through the reactor without reaction. The almost unchange in conversion of aniline when a hydrogen linear velocity between 18.7 cm/sec and 25 cm/sec was used, can be explained considering the high adsorbtivity of the nitrobenzene on the catalyst, being the vacant active site the most important factor. When the hydrogen linear velocity used was 35 cm/sec, the conversion was lower than when 18.75 cm/sec was used. This indicates a poorer contact between the gases and catalyst and can be explained because in a fluidized bed, when the linear velocity of the gases going through, increase, big bubbles of gases are produced and therefore, the contact between gas and catalyst is poorer.

d) Catalyst Concentration

The effect of catalyst concentration on the conversion of aniline is shown in Figure 4. The results obtained with 10% N_i : Cu on alumina at 240°C is compared with 2% N_i - Cu on alumina. The about 100% conversion point is obtained at a much lower value of nitrobenzene feed rate for the 2% catalyst than for the 10% catalyst. This may be explained by the fact that the number of active sites will be much less for the 2%

Figure 4



Catalyst concentration	2% (Ni-Cu)
Hydrogen velocity	18.7 cm/sec
Volume of catalyst	300 c.c.
Reaction temperature	240 °C

catalyst than the 10% catalyst.

With 2% concentration catalyst, twice the catalyst volume (300 c.c.) was used as compared with 10% catalyst (150 c.c.) The about 100% conversion point with 2% catalyst was obtained at a nitrobenzene feed rate of about 1.25 grm/min. and with 10% catalyst concentration was obtained at a nitrobenzene feed rate of about 3.1 gr/min.

The catalyst activity for the 2% catalyst is:

$$1.25/(300)(0.02) = 0.208 \frac{\text{grm of nitrobenzene}}{(\text{c.c. of catalyst})\frac{(\text{weight of } N_i\text{-Cu})}{\text{weight of catalyst}}}$$

and for 10% catalyst

$$3.1/(150)(0.1) = 0.207 \frac{\text{grm of nitrobenzene}}{(\text{c.c. of catalyst})\frac{(\text{weight of } N_i\text{-Cu})}{\text{weight of catalyst}}}$$

Thus, the catalyst activity is the same in both cases, indicating that with excess of hydrogen, the amount of nitrobenzene that can be converted in a given time is proportional to the amount of catalyst.

e) Ratio of Nitrobenzene to Hydrogen in Feed.

From previous work (15) it is known that if the molar ratio of hydrogen to nitrobenzene is greater than 9, then the hydrogenation of nitrobenzene to aniline is not affected by this ratio. In all the runs made in this study this ratio was kept above this value. The ratio was varied by holding the hydrogen flow rate constant and changing the feed rate of nitrobenzene.

2. Correlation of the Reaction Data

The major variables involved in the present study were nitrobenzene feed rate, bed temperature and catalyst concentration.

A useful means of summarizing the reaction rate results is by preparing graphs of V_R/Fversus conversion, x, where V_R is the catalyst volume and F the feed rate of nitrobenzene. Such plots for representing the experimental data are suggested by the form of the basic design equation for flow reactors.

$$F\,d\,x = r\,d\,V_R \qquad (1)$$

obtained by a material balance for a differential volume of catalyst, and being r the rate of reaction.

The shape of these curves is determined by the nature of the reaction. The curves are therefore useful in predicting qualitatively the reaction mechanism.

a) Reaction Rate of Aniline Destruction

In the first part of the aniline conversion curve, where some of the aniline is reduced to ammonia and benzene, different mechanisms were postulated for the hydrogenation reaction. In each case a rate equation is obtained in accordance with the postulated mechanism. The reaction rate expression is then substituted in the equation (1) in terms of concentration and the equation integrated. The expression obtained was plotted in such a way that a straight line would be obtained if the data fitted the postulated mechanism.

The different mechanisms tested in this were: the reaction rate was assumed to be proportional to

1) the second power of the partial pressure of aniline,
2) the one and half power of the partial pressure of aniline,
3) the one power of the partial pressure of aniline,
4) the half power of the partial pressure of aniline.

The last mechanism fitted very well the experimental data, so

$$r = K\sqrt{P_{⌬ NH_2}} \qquad (2)$$

being

r = rate of reaction

K = specific rate of reaction

$P_{⌬ NH_2}$ = partial pressure of aniline present.

If D = the mol fraction of aniline destroyed then a material balance for a differential volume of catalyst becomes

$$F\,dD = r\,dV_R \qquad (3)$$

Substituting equation (2) in (3) and integrating gives

$$2 - 2\sqrt{1-D} = \frac{K\pi}{\sqrt{A}}\;\frac{V_R}{F} \qquad (4)$$

If $(2-2\sqrt{1-D})$ is plotted as ordinate versus $\left(\frac{V_R}{F}\ \frac{\pi}{\overline{V}_A}\right)$ as abcissa, two straight lines for 200°C and 240°C are obtained and are presented in Figure 5.

The slope of these lines gives the value of the constant K and the equation (2) can be written:

$$\text{at } 200°\text{C } r = -15.92 \left[P_{⌬}\, N\, H_2\right]^{1/2} \qquad (2a)$$

$$\text{at } 240°\text{C } r = -13.7 \left[P_{⌬}\, N\, H_2\right]^{1/2} \qquad (2b)$$

b) <u>Reaction Rate of Aniline Formation</u>

A similar study was done in the second part of the yield curves represented in the Figures 2 and 3. In previous work (<u>15</u>) the reaction rate was found to be proportional to $P_{⌬}\, NO_2$, working with a copper catalyst. This expression does not correlate the experimental data.

The best fit was obtained with a rate expression similar to the Hinselhood Langmuir equation.

From Figure 2, it is clear that because of the scatter in the experimental data at a nitrobenzene feed rate between 3.2 and 3.7 grams per minute due to temperature fluctuations of ± 5°C, the curve in the Figure 6 can be drawn with several different shapes. In this Figure 6 the conversion x is plotted against V_R/F. The solid lines drawn in Figure 6 fit a rate equation of the form:

Figure 5

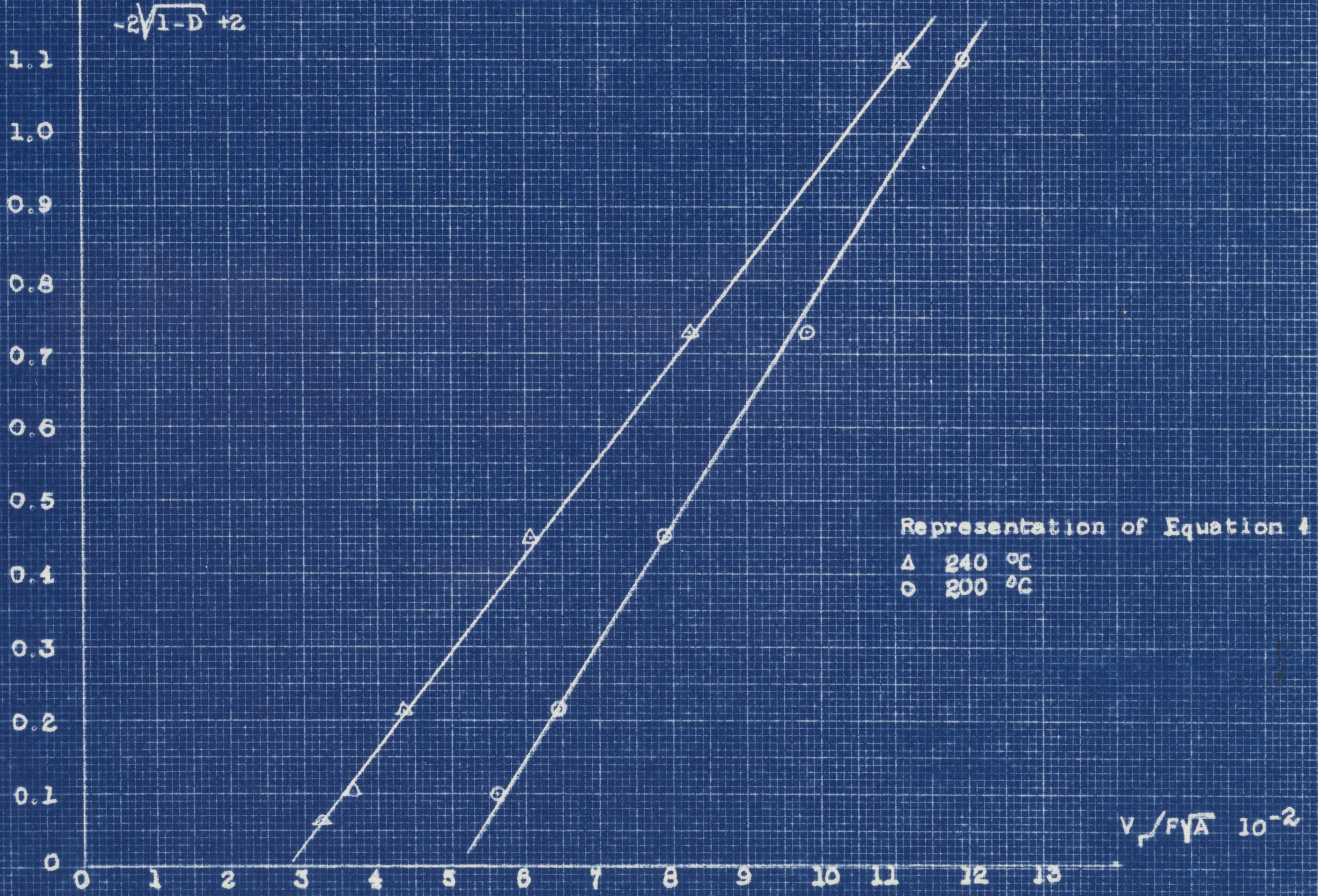
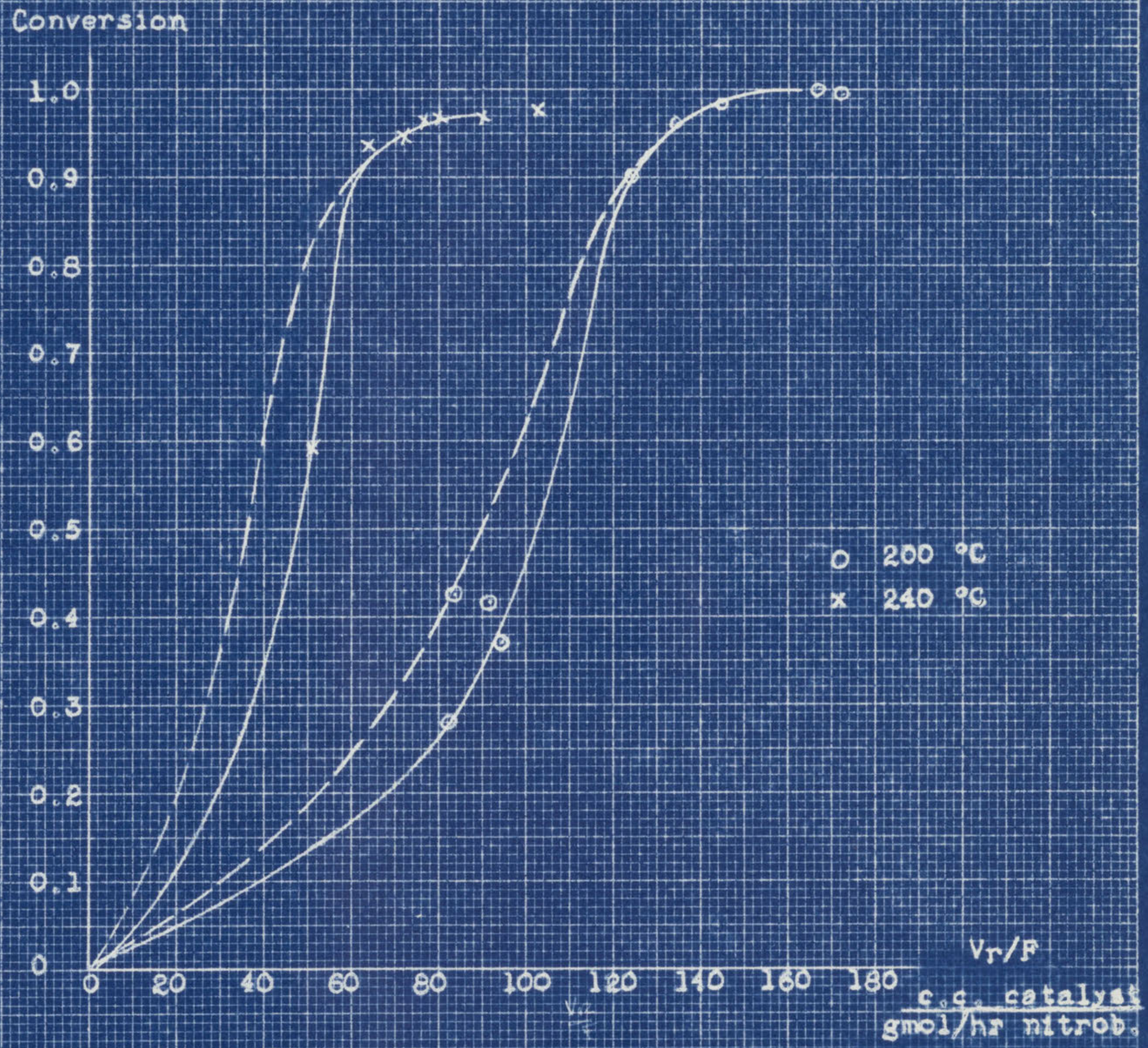

$-2\sqrt{1-D}+2$
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
$V_r/F\sqrt{A}\ 10^{-2}$
Representation of Equation 4
△ 240 °C
○ 200 °C

Figure 6


Conversion
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
120
140
160
180
V_r/F
c.c. catalyst
gmol/hr nitrob.
$\frac{V_r}{F}$
○ 200 °C
x 240 °C

$$r = \frac{K\, b_{\text{⌬}NO_2}\; P^2_{\text{⌬}NO_2}}{(1 + b_{\text{⌬}NO_2}\; P_{\text{⌬}NO_2}{}^2)^2} \qquad (5)$$

In this reaction rate expression there are two unknown constants, K and b. In order to calculate these, it is convenient to measure the reaction rate from the slope of the conversion versus V_R/F curve in Figure 6. Equation (5) can be rearranged to obtain the following expression:

$$P^2_{\text{⌬}NO_2} = \frac{\sqrt{K}}{b_{\text{⌬}NO_2}} \; \frac{P_{\text{⌬}NO_2}}{\sqrt{r}} - \frac{1}{b_{\text{⌬}NO_2}} \qquad (6)$$

If $P^2_{\text{⌬}NO_2}$ is plotted against $P_{\text{⌬}NO_2}/\sqrt{r}$ a straight line is obtained. The result is shown in Figure 7. The slope and intercept of these lines is used to calculate K and b.

The reaction rate equation (5) is obtained by assuming that two molecules of nitrobenzene are attracted towards the same active center and together react with hydrogen. Since this hypothesis does not seem too probable, the following reaction rate expression was used to fit the experimental data:

$$r = \frac{K\; b_{\text{⌬}NO_2}\; P_{\text{⌬}NO_2}}{(1+b_{\text{⌬}NO_2}\; P_{\text{⌬}NO_2})^2} \qquad (7)$$

In the derivation of this expression it was assumed that

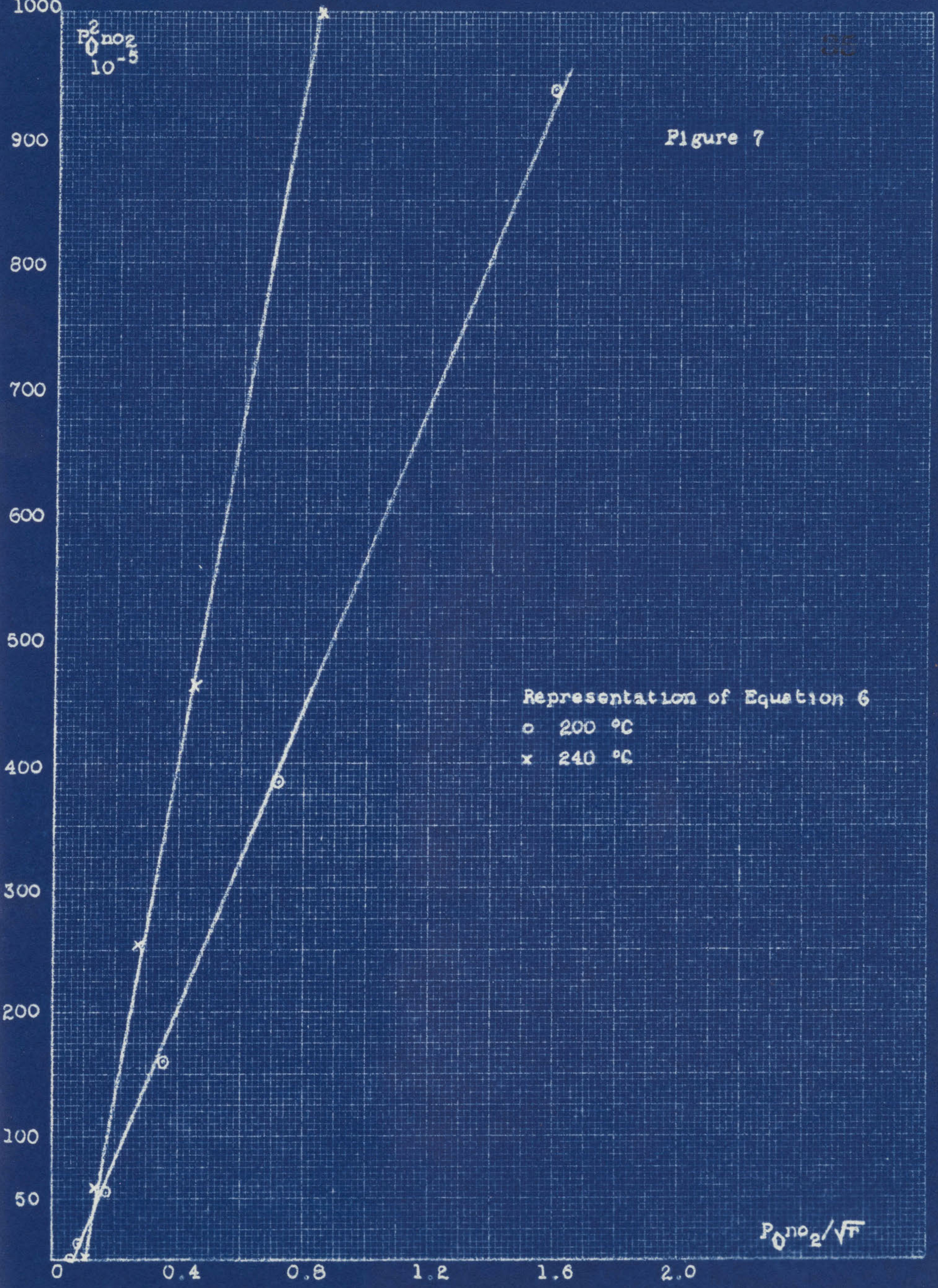


Figure 7

Representation of Equation 6

each molecule of nitrobenzene is attracted towards one active site on the catalyst. As before, the rate of reaction values were taken from the slope of the conversion versus V_R/F curve of Figure 6 and the equation (7) rearranged

$$P_{\text{⌬}NO_2} = \frac{\sqrt{K'}}{b_{\text{⌬}NO_2}} \sqrt{\frac{P_{\text{⌬}NO_2}}{r}} - \frac{1}{b_{\text{⌬}NO_2}} \tag{8}$$

Equation (8) is plotted in Figure 8 giving a straight line. From the slope and intercept were calculated the values of K' and b.

From an economic viewpoint only nitrobenzene conversions above 95% are of interest. Either equation 5 or 7 fit the data above 90% conversions, and therefore both equations can be used in the design equation (1). The mechanism represented by equation (7) seems to be more probable and all the design calculations have been done with this reaction rate expression.

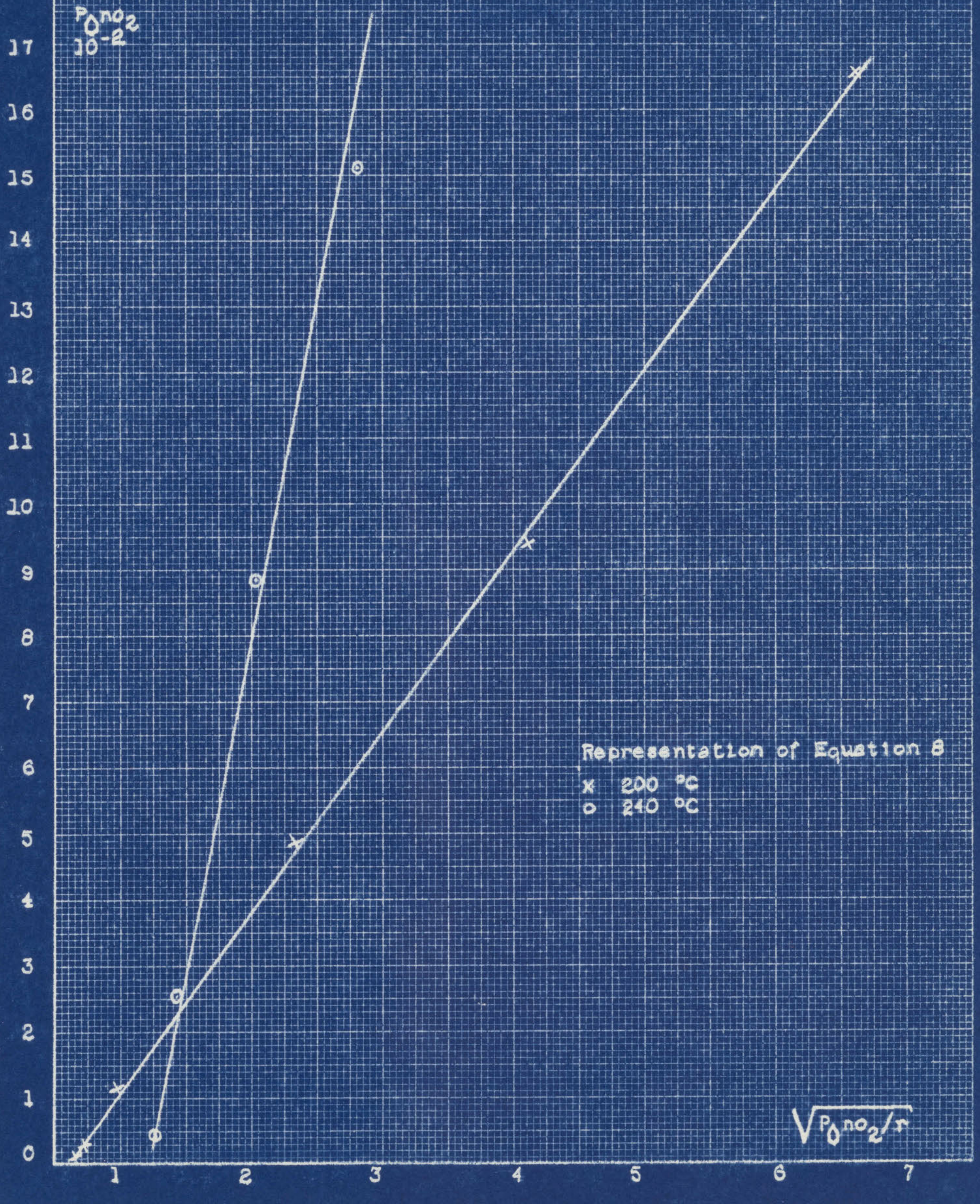
The same calculations were made for 240°C and the plots of equations (6) and (8) are presented in Figure 6 and 7 respectively.

All the calculations are summarized in the Appendix, and the equation (7) can be written:

at 200°C

$$r = \frac{2.89\ P_{\text{⌬}NO_2}}{(1+62.5\ P_{\text{⌬}NO_2})^2} \tag{7a}$$

Figure 8


$\frac{P_0 no_2}{10^{-2}}$
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
$\sqrt{P_0 no_2 / r}$
Representation of Equation 8
x 200 °C
o 240 °C

at 240°C

$$r = \frac{0.907\, P_{\text{⬡}NO_2}}{(1+8\, P_{\text{⬡}NO_2})^2} \qquad (7b)$$

VII. REACTOR DESIGN

On the basis of the results obtained in the laboratory experiences, preliminary calculations have been made for a commercial reactor to produce 10 ton/day of aniline.

These calculations can be done either taking the experimental value for V_R/F or integrating the rate equation.

This last method is followed when no experimental results exist for the desired operating temperature.

In this study the last method will be followed to illustrate the use of the equations developed.

The reaction will be carried out at 240°C. At this temperature, the reaction rate equation is

$$r = \frac{0.907 \; P_{⌬ NO_2}}{(1+8 \, P_{⌬ NO_2})^2} \qquad (7b)$$

or

$$r = \frac{0.907 \; (1-x/15+x)}{\left[1+8 \; (1-x/15+x)\right]^2} \qquad (7c)$$

Substituting 7c in the design equation (1)

$$\frac{V_R}{F} = \int_0^x \frac{\left[1+8 \; (1-x/15+x)\right]^2}{(1-x/15+x)} \, dx$$

and integrating (see Appendix) for a conversion of 98% gives:

$$\frac{V_R}{F} = 79.5$$

In contrast to fixed-bed operations, the mass velocity through the fluidized bed reactor cannot be chosen predominantly on the basis of the kinetic requirements since there is only a narrow range of mass velocities within which stable fluidization is possible.

If a production rate of 9.8 ton/day of aniline corresponding to 13.23 ton/day of nitrobenzene fed is chosen as basis for this study, the diameter of the reactor will be given for the ratio F'/G_f or also V'/v .

The nitrobenzene feed rate is

$13230/(24)(123.12) = 4480$ molgr/hr $\therefore$

$\therefore$ 1216 lb/hr.

Because the ratio hydrogen to nitrobenzene is 15, the molar rate of hydrogen fed to the reactor will be:

$(4480)(15) = 67300$ mol gr/hr ($\therefore$ 298 lb/hr)

The total feed rate will be:

$F' = 1216 + 298 = 1514$ lb/hr.

From the experimental data,

$G_f = G_{H_2} + G_{\text{⬡}NO_2}$

G_{H_2} = 0.15 lit/sec ∴ 4.18 lb/(hr)(ft^2)

$G_{\text{⬡}NO_2}$ = 3.0 grm/min ∴ 29.3 lb/(hr)(ft^2)

so, G_f = 33.48 lb/(hr)(ft^2)

The cross section of the reactor will be

1514/33.48 = 45.2 ft^2

The diameter of the reactor is therefore

D = 7.58 ft or 2.30 m.

The V_R/F expression can be written in the weight basis knowing the apparent density of the fixed bed,

ρ = 140 gr/150 c.c. = 0.934 gr/c.c. ∴ 58.2 lb/ft^3 .

The mass of catalyst w is obtained as follows

$$\frac{w}{F} = (79.5)(0.934)$$

$$w = \frac{(79.5)(0.934)(1514)(454)}{123.12} = 333.5 \text{ Kg} \quad \therefore \quad 735 \text{ lb.}$$

Because the expansion ratio of the bed is 1.6 (see appendix), the volume occupied by the catalyst at operating conditions will be

$$V'_R = \frac{735}{58.2}(1.6) = 20.2 \text{ ft}^3$$

and the height is

$$h = \frac{20.2\ ft^3}{45.2\ ft^2} = 0.445\ ft \therefore 14.6\ cm.$$

The efficiency of the fluidized bed is almost always lower than the fixed bed at the same conditions. This reactor efficiency is an index of the degree to which a given reactor approaches a piston flow reactor, and is a function of all the variables which determine the flow pattern within the reactor.

Because there are no efficiency data for the reaction hydrogen and nitrobenzene it was necessary to compare the present result with the efficiency data for the hydrogenation of ethylene (17).

From a plot of efficiency versus catalyst activity at different linear gas velocities (17), for a value of catalyst activity in the present design of

$$K'' = \frac{836000 \text{ c.c. of gases/sec}}{333500/0.934 \text{ c.c. catalyst}} = 2.35^{1}/\text{sec}$$

and a velocity of 20 cm/sec, the efficiency is 27%. Therefore, the actual volume of catalyst is 20.2/0.27 = 74.8 ft^3 and the height h = 74.8/45.2 = 1.65 ft $\therefore$ 50 cm.

Cooling of the Reactor

It has been pointed out that the principal motive to study the hydrogenation of nitrobenzene in a fluidized bed is because this reaction is highly exothermic (about 235000 cal/molg are released).

In a fixed bed, near the entrance to the bed, the rate of reaction is high and large quantities of heat are released, while near the exit where the rate is low the evolution of heat is relatively small. Because the heat transfer rate from catalyst particle-catalyst particle and between catalyst particle and the gas is small, significant temperature gradients are produced.

The fluidized bed reactor eliminates this problem because the rapid movement of the small catalyst particles eliminates temperature variation within the fluidized bed.

The uniformity of temperature inside the bed simplifies the heat transfer calculations because it is not necessary to consider heat transfer gradients within the bed. In this calculation it is assumed that a finite heat transfer coefficient exists at the reactor wall and that the temperature across the bed is uniform.

The cooling of the reactor will be carried out by water circulating through the jacket around the reactor.

From the heat balance calculation described in detail in the appendix, for the production of 9.8 ton/day of aniline, 846.763 Kcal/hr must be released through the walls of the reactor.

The value of the overall heat transfer coefficient will be assured to be equal to the coefficient between fluidized bed and the reactor walls, because this coefficient is the smallest.

The value for the film coefficient between the fluidized bed and walls has been calculated by two correlations: one is a nomograph obtained by Wen, C. Y. and Fan, Q. T. (18) for dense phase fluidization and the other is a correlation of Mickley, H. S. and Trilling, C. A. (19) corresponding to dilute phase fluidization. To be conservative, the lowest value of the two correlations have been used:

$$h' = U = 49.7 \text{ Btu/hr}^\circ\text{F ft}^2 \therefore 243 \text{ Kcal/hr }^\circ\text{C Om}^2$$

The inlet water temperature is assumed to be 25°C and the water velocity will be enough to provide an outlet water temperature equal to 50°C.

So, the average difference of temperature is

$$\Delta t = 240 - \frac{25 + 50}{2} = 202.5°C$$

Applying the equation

$$Q = UA\ \Delta t_m$$

$$A = \frac{Q}{U\Delta t_m} = \frac{846,763}{(202.5)(243)} = 17.2\ \mathrm{Om}^2$$

So, the heat transfer area necessary to cool the reactor is 17.2 om^2.

It will be necessary to dilute the catalyst in such a way that the available heat transfer area is 17.2 cm^2 since not enough area is available using a 10% catalyst concentration.

This is done by using the approximate correlation

$$10\left(\frac{V_R}{F}\right)_{10\%\ \text{catalyst}} \simeq x\left(\frac{V_R}{F}\right)_{x\%\ \text{catalyst}}$$

It is therefore possible to calculate the catalyst concentration for such a volume that gives the adequate heat transfer area to cool the reactor.

If a catalyst of 0.5% concentration of N_i and Cu on alumina is used, 20 times the catalyst weight necessary for 10% concentration is required. Therefore, if the feed rate F is the same

$$V_R'{}_{0.5\%} = (20)(20.2) = 404\ \mathrm{ft}^3$$

or $h = \frac{404}{45.2} = 8.95$ ft $\therefore$ 2.73 m.

that corresponds to a heat transfer area

$$(\pi)(2.3)(2.73) = 19.6 \text{ m}^2$$

that meet the necessary requirements for cooling.

In the following table are summarized the characteristics of the reactor.

TABLE V

Catalyst Conc. Per cent	Production Ton/day Aniline	Q Kcal/hr Through Wall	Temperature of the bed °C	Diameter m.	Height m.
0.5	9.8	846,763	240	2.3	2.73

VIII. CONCLUSIONS

The following conclusions have been reached:

1) At the two temperatures studied of 200°C and 240°C, practically the quantitative conversion of nitrobenzene in aniline was obtained.

2) The activity of the catalyst is higher than those activities reported in the literature.

3) The catalyst activity increases at higher temperatures.

4) The decomposition rate of aniline is proportional to the half power of the partial pressure of aniline

5) The rate of formation of aniline is proportional to the first power of the partial pressure of nitrobenzene

6) The capacity of conversion of nitrobenzene for an excess of hydrogen is proportional to the weight of the catalyst.

7) The influence of the gas linear velocity on the conversion is small if the fluidized bed characteristics are not changed.

8) Preliminary design for a pilot plant reactor for 10 ton/day of aniline, indicates that this process has very good possibilities for industrial development.

IX. RECOMMENDATIONS

It is recommended to continue the study of all important variables and to confirm the results obtained. To build a pilot plant in order to get more definite information to design an industrial installation.

X. APPENDIX

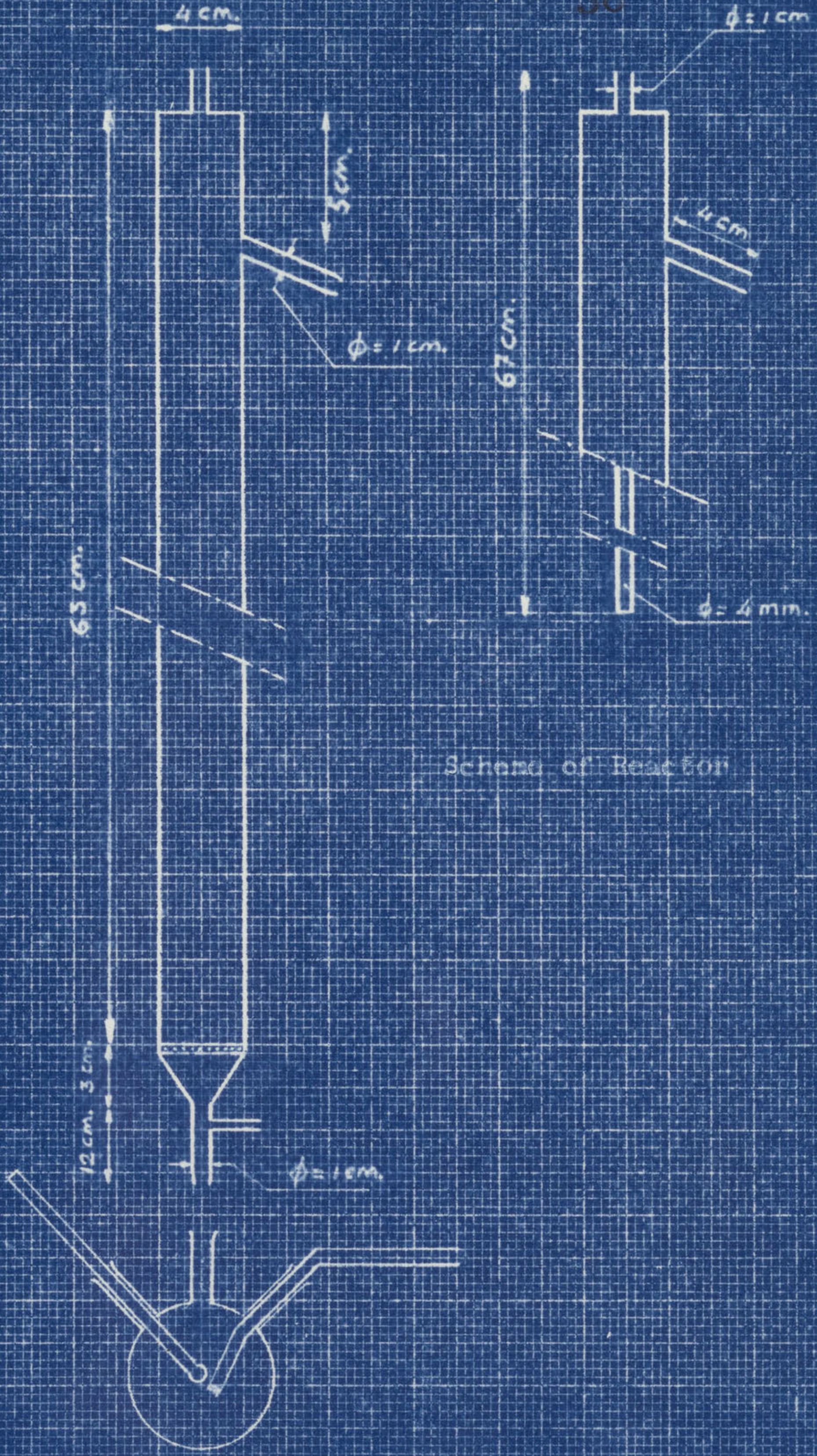
A. Details of Equipment

1. Construction of Reactor

The reactor is a 2" diameter Pyrex tube, 25 in. long. Figure A-1 shows the details of the reactor, dimensions and the place of the different connections. The primary hydrogen is fed through a side connection at the bottom of the reactor. A nitrobenzene flask is connected at the bottom of the reactor. This is a three-neck spherical flask of 500 c.c. of capacity. One of the openings in the flask is used for a thermometer type 0° - 250°C. This thermometer measured the nitrobenzene bath temperature. The other opening is connected to a glass tube of 8 cm. through which the secondary hydrogen is fed. This hydrogen is bubbled through the nitrobenzene bath. The third opening connects the flask with the reactor. The nitrobenzene and hydrogen is fed through this opening to the reactor. The products leave the reactor through a side tube in the upper zone of the reactor.

All the connections in the system were made with ground glass joints.

Figure A-1



Scheme of Reactor

Three thermocouples were installed axially inside the reactor and covered for ceramic insulators. The thermocouples passed through a wood stopper in the top of the reactor and the opening was sealed with epoxi resin.

2. Collection of Products

The aniline that leaves the reactor in the vapor phase is condensed in two water condensers connected in series by a glass elbow of 120° and ground joints 40/24 mm. The first condenser is connected to the reactor with a ground glass joint. The first condenser is a Liebig condenser 60 cm long. The second one is a spiral condenser of 50 cm long.

All the liquid condensed is collected in an erlenmeyer flask of 500 c.c. of capacity. The end of the spiral condenser is connected to this flask by means of a glass tube. A second glass tube connects the flask with a cold trap. This trap is cooled with a mixture of acetone and dry ice. Preliminary tests showed that no losses of aniline occurred in this system.

3. Measurement Dispositive

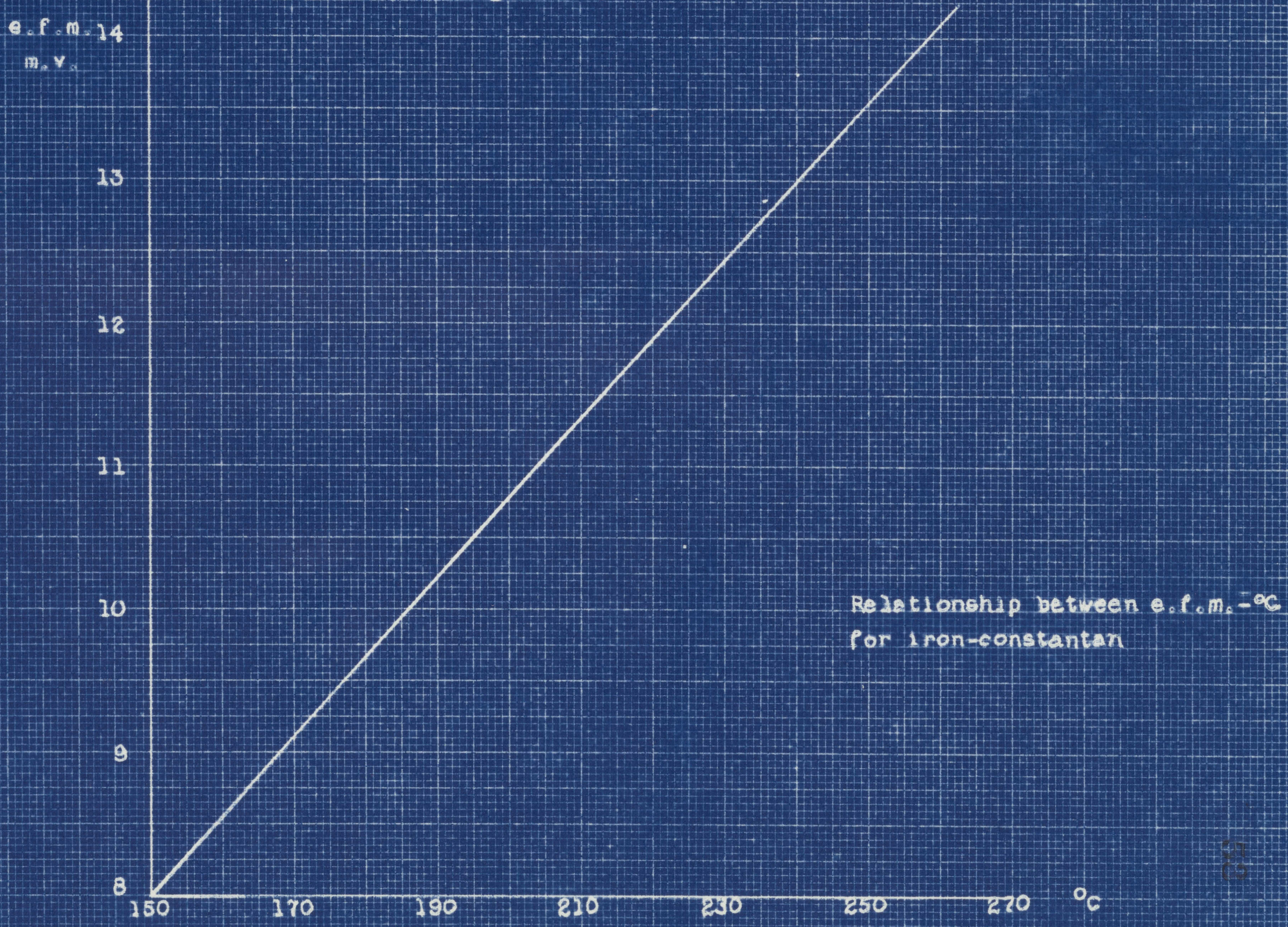
a) Thermocouples

The temperature is controlled with 3iron-constantan thermocouples of 24 gauge. The junctions are made by twisting the 2 wires together and welding the ends with an oxiacetylene flame. The two conductors are covered with insulators made with refractory material of about 5 cm. long and 4 mm diameter. The refractory material have two,four or six holes throughwhich the wires are passed.

The thermocouples are placed axially into the reactor; one junction at about 10 mm. from the reactor's bottom, the second at about 100 mm. from the reactor's bottom, and the third one at the point where the gases leave the reactor. The first two thermocouples are used to determine the catalyst bed temperature. The last mentioned thermocouple is used to ascertain that condensation of the products can occur.

The thermocouples pass through a cork in the top of the reactor. They are welded to copper wires insulated with plastic and connected to a Leeds and Northrup potentiometer. The relationship between the e.m.f. and temperature obtained from the literature for iron-constantan thermocouple is presented in Figure A-2. This relationship was checked at the boiling points of water and sulphur at atmospheric pressure. The values obtained agreed with the relationship presented in Figure A-2. The effect of the welded copper wires on the e. m. f. produced by the thermocouples was also investigated. No significant error was introduced by these wires.

Figure A-2



Relationship between e.f.m.-°C
for iron-constantan

b) Manometers

The pressure of the system was measured at the bottom and top of the reactor and also after the capillary flowmeters. Mercury and oil manometers were used for the pressure measurements.

c) Capillary Flowmeter

Glass capillary flowmeters were used to measure the gas flow rate in all the runs.

The flow meters were calibrated with hydrogen and a wet test meter.

The temperature and static pressure of the gas were measured after the gas passed through the capillary flow meter and the velocity related to the pressure drop.

$$q = C_M \sqrt{\frac{\Delta P}{e}} \qquad e = \frac{PM}{zRT}$$

$$= C_M \sqrt{\frac{\Delta P z R T}{PM}}$$

$$= C_M' \sqrt{\frac{T \Delta P}{PM}}$$

rearranging this equation, gives

$$q \sqrt{\frac{P_{P.O} M}{T_{P.O}}} = C'_M \sqrt{\Delta P}$$

$q_{P.O} \sqrt{\frac{P_{P.O} M}{T_{P.O}}}$ is plotted against ΔP or Δh on a log-log scale.

In this way the flow measurement can be corrected by the changes in temperature and pressure.

$q_{P.O}$ = liters or c.c. per second in post-capillary conditions.

$P_{P.O}$ = absolute pressure post-capillary in inches of mercury.

M = Molecular weight of hydrogen.

$T_{P.O}$ = Absolute temp. post capillary.

The calculation and graphs are presented in the Tables A-1, A-2 and Figures A-3 and A-4.

TABLE A-1

Capillary flow meter calibration for measurements of the primary hydrogen flow.

Δh Inches Oil	$P_{P.O}$ Inches Hg	$T_{P.O}$ °K	$\sqrt{\frac{P_{P.O}M}{T_{P.O}}}$	$q_{P.O}$ lit/sec	$q_{P.O}\sqrt{\frac{P_{P.O}M}{T}}$	Conditions
2.1	29.3	301	0.441	0.0770	0.0339	
5.0	29.35	301	0.441	0.1420	0.0626	Gas: hydrogen
7.0	29.35	301	0.442	0.1755	0.0775	
9.9	29.37	301	0.442	0.2140	0.0946	Patn = 29.3 in.
12.0	29.40	301	0.442	0.2365	0.1045	
15.9	29.40	301	0.442	0.2750	0.1215	
20.1	29.40	301	0.442	0.3060	0.1352	

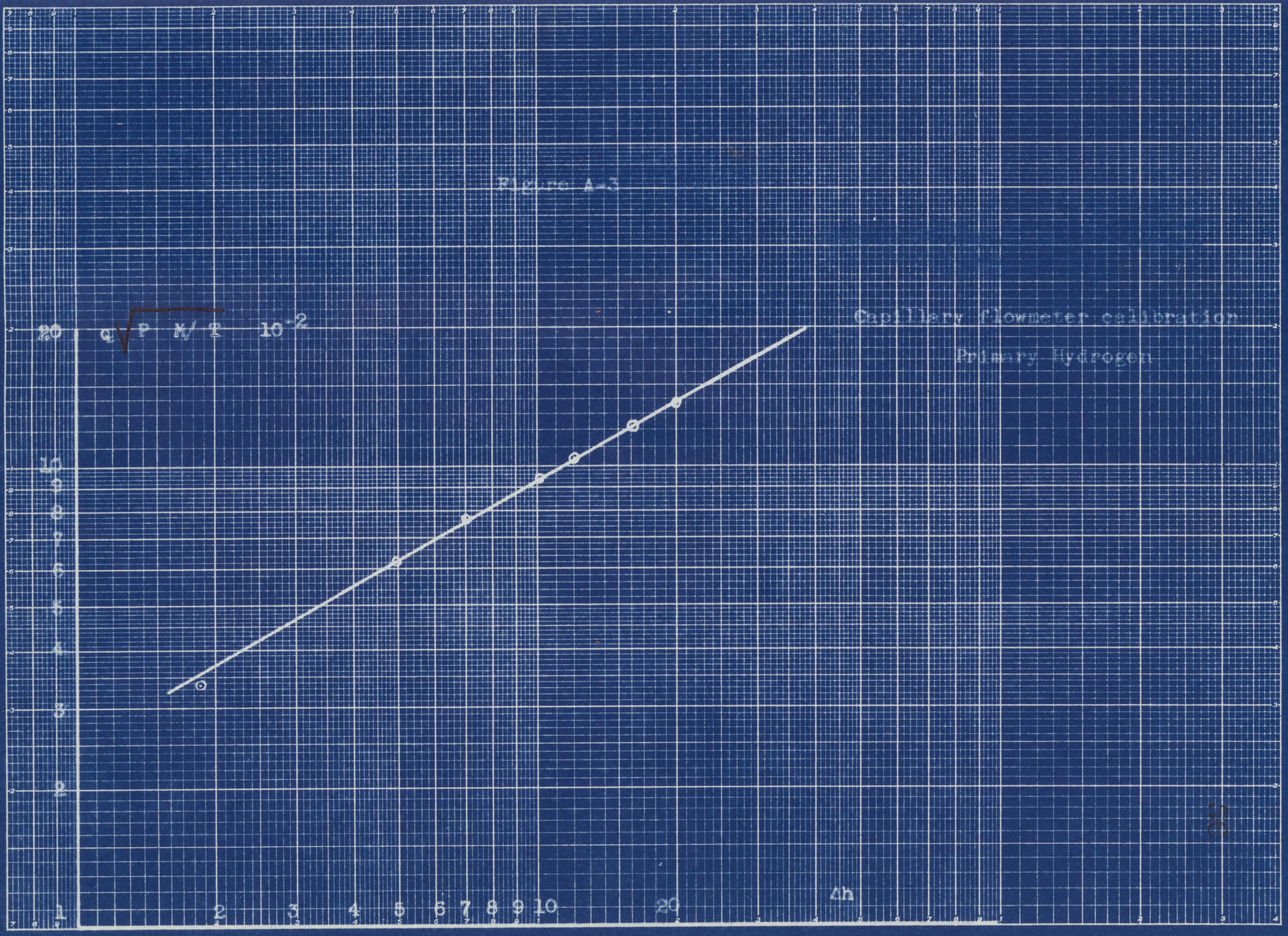
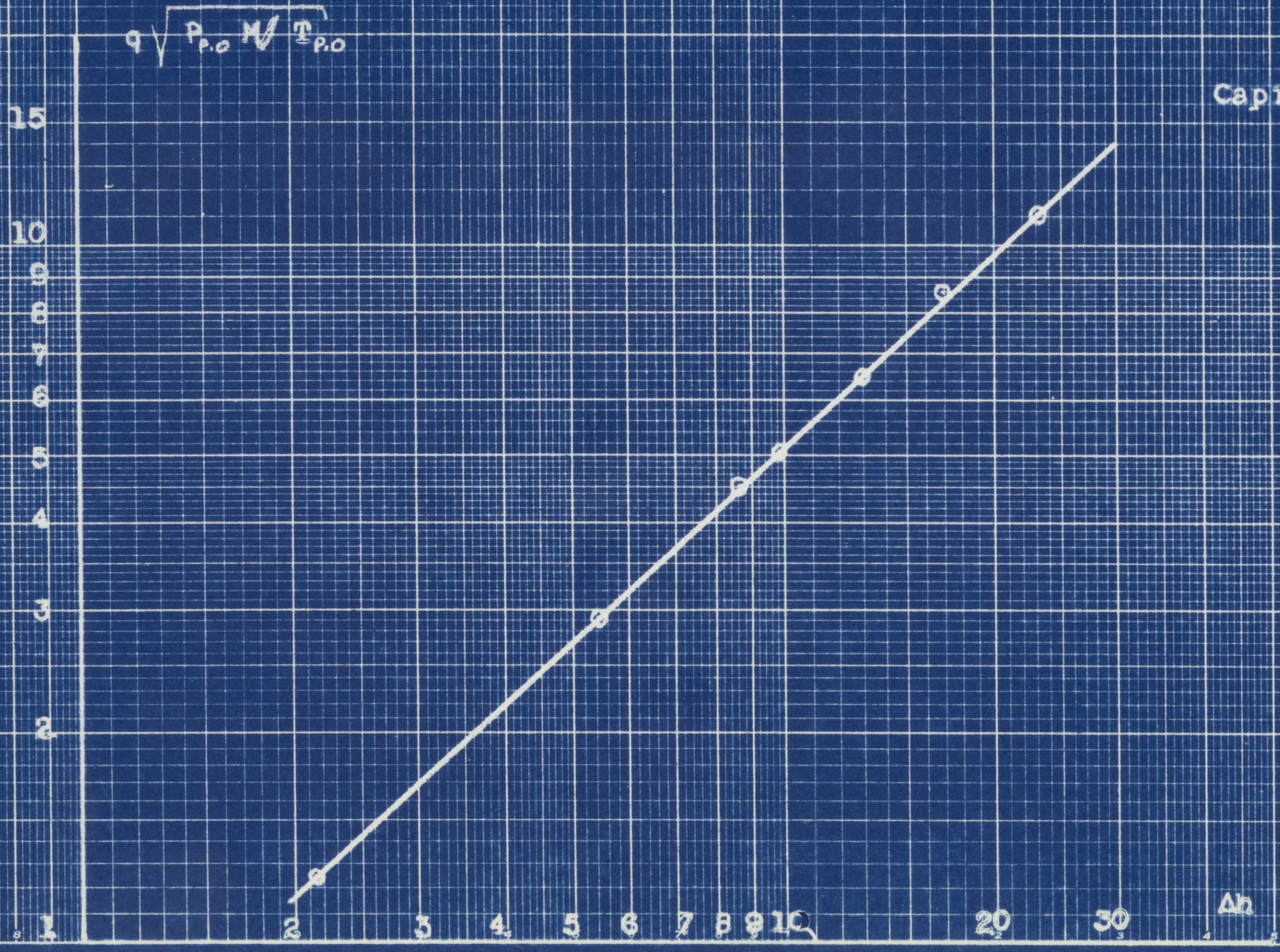


Figure A-3

Capillary flowmeter calibration

Primary Hydrogen

Figure A - 4



Capillary flowmeter calibration
Secondary Hydrogen

TABLE A-II

Capillary flow meter for measurements of the secondary hydrogen flow.

Δh Inches H_2O	$P_{P.O}$ Inches Hg	$T_{P.O}$ °K	$\sqrt{\frac{P_{P.O}M}{T}}$	$q_{P.O}$ c.c./sec.	$q_{P.O}\sqrt{\frac{P_{P.O}M}{T_{P.O}}}$	Conditions
2.15	29.3	301	0.441	2.830	1.25	
5.40	29.3	301	0.441	6.670	2.94	Gas:
8.55	29.3	301	0.441	10.470	4.62	Hydrogen
12.80	29.3	301	0.441	14.700	6.49	
16.55	29.3	301	0.441	19.550	8.62	Patn =
22.90	29.3	301	0.441	25.000	11.00	29.3 in.

4. Fluidization Characteristics

Lewis, Gilliland and Bauer (19) recommended that the best fluidization conditions may be predicted from a plot of the ratio ΔP experimented to ΔP calculated ($\Delta P_{exp.}$ = pressure drop between the top and bottom of the catalytic bed and $\Delta P_{calc.}$ = weight of solid/reactor cross section) versus the modified Reynolds number Re = $D_P V_G \rho_G / \mu_G$: where D_P = particle diameter and $V_G \rho_G \mu_G$ the superficial velocity, density and viscosity of gas respectively.

The best fluidization conditions for a reactor of fixed dimensions and fluidized particle size is that for which the

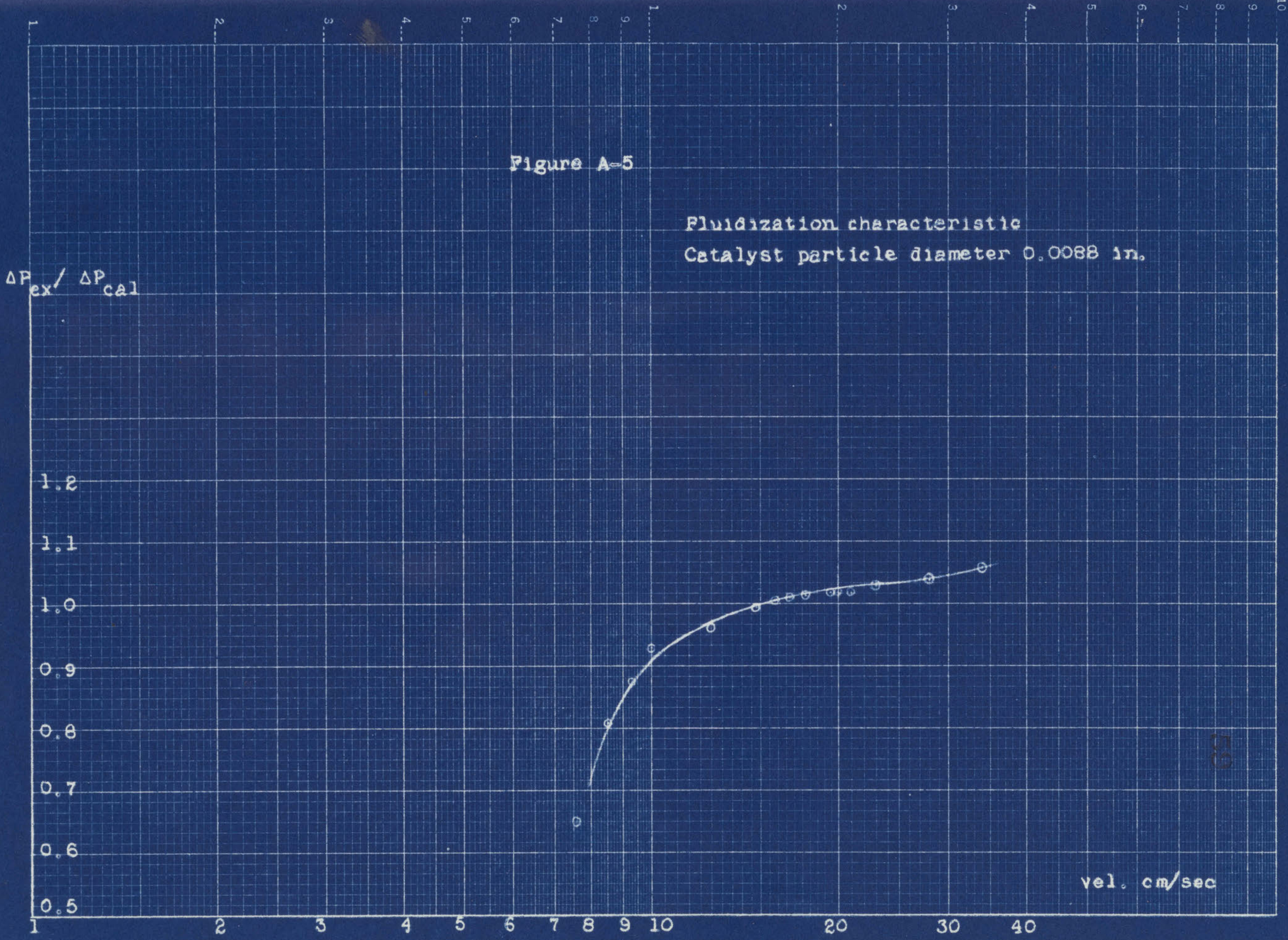


Figure A-5

Fluidization characteristic

Catalyst particle diameter 0.0088 in.

slope of this curve is horizontal. The ratio $\Delta P_{exp}/\Delta P_{calc}$ must be $>$ 1, in other words, the bed must be in suspension.

In this study the average particle size of the catalyst used was 0.0088 inches in diameter.

With this particle size and the operating variables, a curve to linear gas velocity versus $(\Delta P_{exp}/\Delta P_{cal})$ was obtained.

The results are shown in Figure A-4 and Table A-3.

TABLE A-III

Fluidization characteristics of catalyst 10% N_i-Cu on alumina, 48-100 mesh.

Δh Inches Oil	$q_{P.O}\sqrt{\frac{P_{P.O}M}{T_{P.O}}}$	$q_{P.O}$ lit/sec.	V cm/sec.	$\frac{\Delta P_{exp.}}{\Delta P_{calc.}}$	Conditions
2.60	0.043	0.0961	7.65	0.650	catalyst
3.10	0.048	0.1072	8.55	0.808	wt. = 140 gr.
3.60	0.052	0.1162	9.25	0.869	
4.10	0.056	0.1250	9.96	0.930	Reactor
6.10	0.070	0.1565	12.46	0.964	diam.=4 cm.
8.10	0.083	0.1855	14.75	0.994	
9.10	0.088	0.1965	15.65	1.040	Temperature
10.10	0.094	0.2100	16.70	1.086	28°C
12.10	0.100	0.2240	17.80	1.180	
13.10	0.108	0.2410	19.20	1.210	
14.10	0.113	0.2520	20.02	1.227	
18.10	0.130	0.2900	23.10	1.310	
25.00	0.157	0.3510	27.90	1.370	
35.10	0.190	0.4250	33.90	1.500	

From the inspection of Figure A-5 the best range of gas velocity seems to be 18-28 cm/sec.

5. Analytical Methods

a) Analysis of aniline: Reinhardt modified method. The following solutions are required:

1) A solution of 0.1N $KBrO_3$-KBr
2) A solution of 0.1N $Na_2S_2O_3$
3) A solution of HCl concentrate
4) A solution of 10% KI
5) A solution of starch.

Procedure:

To a sample containing the aniline is added 25 c.c. of 0.1N $KBrO_3$-KBr and 20 c.c. of concentrated HCl. A white precipitation of the tribromoaniline is produced. The color of the liquid must be yellow because there is an excess of bromine in the solution. The sample is left for about 10 minutes and 20 c.c. of 10% KI is then added to it. It is necessary to stir the solution one or two minutes. It is then left for 10 minutes and the excess iodine titrated with 0.1N $Na_sS_2O_3$ using starch as indicator.

A blank test is runsimultaneously. The difference in c.c. between the test and blank test multiplied by 1.551 gives the milligrams of pure aniline.

b) Analysis of nitrobenzene in the pressure of aniline and benzene.

1.2 to 1.5 grams of an aniline-benzene-nitrobenzene mixture is weighed and then dissolved in 10 c.c. of glacial acetic acid. A solution of 20 c.c. of HCl (density 1.16) and 50 c.c. of H_2O is then added. This mixture is placed in an ice-H_2O bath until a temperature of 5°C is reached. The mixture is stirred and 3 grm of zinc powder added slowly. The mixture is then stirred for 30 minutes more.

The excess of zinc is separated by filtration. The filtrate is diluted to 1000 c.c. To 10 c.c. of this solution, a solution of sodium hydroxide is added until the solution becomes neutral. A white precipitate appears at this point. The solution is then titrated with 0.1N $Na_2S_2O_3$ as was indicated in the aniline analysis.

The aniline found by titration corresponds to the aniline initially present in the solution plus the nitrobenzene converted to aniline in the course of this analysis. The nitrobenzene is obtained by the difference of this total titration and the direct titration of aniline described in section (a).

c) Analysis of benzene in presence of nitrobenzene and aniline.

50 gr of the mixture and 80 gr of zinc powder is weighed in a flask. The mixture is placed in an ice-water bath until a temperature of 5°C is reached. 320 grm of sulfuric

acid (1:1) is added to the mixture maintaining the temperature at 5°C.[6]

When hydrogen starts to be evolved the flask is connected to a tube packed with active carbon and heated inside an electric furnace. The active carbon adsorbs the benzol produced in the reaction. When the reduction is completed it is heated the furnace to 300°C. The benzol produced was collected in a measuring cylinder. The amount of benzene present in the original sample was then calculated.

B. Sample Calculations

1. Precision of the Data

The data presented were obtained by condensation and analysis of the aniline produced in the hydrogenation of nitrobenzene in a reactor of constant volume and maintaining constant the pressure and temperature during all the runs. Therefore, the precision of the data obtained will depend on the absence of leaks, temperature control, effectivity of condensation system and the precision of titration methods.

Before to begin each run, was checked very carefully the absence of leaks in the apparatus. The reaction temperature was measured frequently and being constant along the runs. The fluidized bed was observed visually during the run because the reactor has along an open window. The fluidization was correct and the pressure drop along the bed was always practically equal to the catalyst weight/cross section of the reactor.

The temperature in the condenser trap cooled with acetone and dry ice was about -30°C. The aniline pressure at this temperature is very low and therefore the losses of aniline by this concept may be considered negligible.

The method of analysis was checked with standard aniline solutions. But because the sample obtained in every run was necessary to dilute, the error introduced was calculated to be about 1%. Besides, the error weighing the nitrobenzene was calculated to be 1%. Therefore the balance of aniline in every run can be assumed to be about 2% in error.

2. Calculations of the conditions in the reactor.

a) Calculation of reactor temperature

Using Figure A- , the temperature is obtained from the e.m.f. read in the potentiometer.

Average reading of the thermocouple = 13 mv

Temperature equivalent from Figure A-2 = 240°C

b) Calculations of pressure

Patmph : 29.7 inches Hg

$P_{\substack{bottom \\ \text{of reactor}}} = 0.6 + 29.7 = 30.3$ in Hg (read from manometer)

$P_{top} = 29.7$ in Hg

$P_{aver} = 29.7 + \frac{0.6}{2} = 30.0$ in Hg

c) Calculation of gas velocity

Experimental data:

$P_{atm} = 29.7$ in Hg

$P_{P.O} = 0.6 + 29.7 = 30.3$ in Hg

$T_{P.O} = 28 + 273 = 301°K$

ΔH manometer = 7.8 inches oil

$D_{Reactor} = 40$ m.m.

From the graph Figure A-2, for $\Delta h = 7.8$, gives

$$q_{P.O}\sqrt{\frac{P_{P.O}M}{T_{P.O}}} = 0.08$$

Therefore,

$$q_{P.O} = \frac{0.08}{\sqrt{\frac{P_{P.O}M}{T_{P.O}}}} = \frac{0.08}{\sqrt{\frac{(30.3)(2.016)}{301}}} = \frac{0.08}{0.451} = 0.177\ \frac{\text{liter}}{\text{sec}}$$

Temperature reactor = 240°C ∴ 513°K

$$q = 0.177 \frac{30.3}{30} \frac{513}{301} = 0.306 \text{ lit/sec}$$

$D_{reactor} = 40$ mm

Cross sectionof of reactor:

$$\frac{(3.14)(4.0)^2}{4} = 12.58 \text{ cm}^2$$

$$v = \frac{q}{s} = \frac{306}{12.58} \frac{\text{cm}^3/\text{sec}}{\text{cm}2} = 24.3 \text{ cm/sec.}$$

3. Calculation of Aniline Produced

The aniline leaves the reactor in the gas phase and is condensed in the condensation system. The different parts of the condensing system are carefully washed with acetic acid and distilled water. The solution is diluted in such a way that 25 c.c. of the final solution has less aniline than the necessary amount to react with 25 c.c. 0.1N $KBrO_3$ (see methods of analysis).

For run n° 33

14.8 c.c. of 0.103N $Na_2S_2O_3$ ≅ 25 c.c. sample

or 15.25 c.c. 0.1N $Na_2S_2O_3$ ≅ 25 c.c. sample.

Water (blank test) = 23.7 c.c.

(23.7)(1.03) = 24.4 c.c.

Net c.c. of $Na_2S_2O_3$ consumed corresponding to aniline

$= (24.4 - 15.25) = 9.15$ c.c. N $Na_2S_2O_3$.

The solution was dilute to a 1000 c.c. and 25 c.c. of this was used.

Total aniline = $(9.15)(40)(40)(1.551) = 23.65$ gr.

Nitrobenzene fed to the reactor = 32.7 gr

Aniline produced at theoretical conversion: 24.7 gr.

Conversion = $(23.65/24.7)\ 100 = 95.8\%$

C. Reaction Rate Calculation

1. Calculation of the Reaction Rate for the Aniline Decomposition Zone.

Equation proposed : $r = -K\sqrt{P_{⬡}\ NH_2} = (2)$

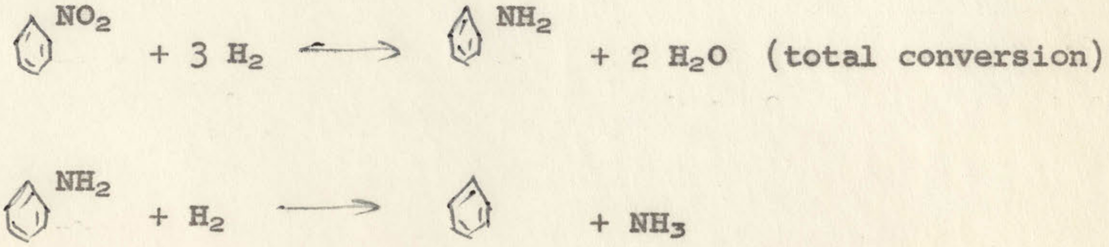
where $P_{⬡}\ NH_2$ is the partial pressure of aniline present.

Let D = the aniline decomposed to benzene and ammonia;

A = the mols of hydrogen fed per mol of nitrobenzene, and

F = the mol/hr of nitrobenzene fed to the reactor.

In this zone all the nitrobenzene is converted to aniline, the total number of mols present is obtained from the equations:



Mols present in the gas stream leaving the reactor:

Hydrogen	A - 3 - D
Benzene	D
Ammonia	D
Water	2
Aniline	1 - D

Total: A

If equation (2) is written in terms of concentration, it takes the following form:

$$r = -K\sqrt{\frac{1-D}{A}\pi} \quad (2a)$$

Substituting equation (2a) in the basic design equation

$F\,dD = r\,dV_R$ and separating variables result in:

$$\int_0^D \frac{dD}{\sqrt{1-D}} = -\frac{K}{F}\,\frac{\pi}{\sqrt{A}}\int_0^{V_R} dV_R$$

integrating gives:

$$-K\frac{V_R}{F}\,\frac{\pi}{\sqrt{A}} = \left(-2\sqrt{1-D}\right)_0^D = -2\sqrt{1-D}+2; \qquad (4)$$

TABLE A-IV

t°c	X=1-D	F	$A=\frac{21.9}{F}$	$\sqrt{A}$	$\sqrt{1-D}$	$-2\sqrt{1-D}+2$	$\frac{V_R}{F\sqrt{A}}$
200	0.2	0.073	300	17.30	0.447	1.106	0.119
	0.4	0.107	205	14.30	0.631	0.737	0.098
	0.6	0.168	130	11.41	0.775	0.450	0.078
	0.8	0.250	87.5	8.85	0.895	0.210	0.064
	0.9	0.345	64.2	8.01	0.949	0.100	0.055
	0.95			6.60	0.970	0.060	0.045

TABLE A-V

t°c	1-D	F	$A = (\frac{21.9}{F})$	$\sqrt{A}$	$\sqrt{1-D}$	$-2\sqrt{1-D}+2$	$V_R/F \sqrt{A}$
240°	0.20	0.083	264	16.23	0.447	1.106	0.1110
	0.40	0.153	142	11.93	0.631	0.737	0.0818
	0.60	0.290	75.5	8.68	0.775	0.450	0.0596
	0.80	0.550	40.0	6.30	0.895	0.210	0.0432
	0.90	0.771	28.4	5.32	0.949	0.100	0.0365
	0.95	1.000	21.9	4.68	0.970	0.060	0.0321

The values of x (1-D) and F are taken from Figure 2 (aniline decomposition zone).

The equation (4) is plotted in Figure 5 giving two straight lines for 200°C and 240°C. This means that the reaction rate expression assumed is correct, and the slope of these lines is the specific reaction rate K. The values of K and b have been calculated by solving the following linear equations.

At 200°C:

$$\left.\begin{array}{l} 1.106 = 0.119\ K - b \\ 0.737 = 0.098\ K - b \\ 0.450 = 0.078\ K - b \end{array}\right\}$$

$$\left.\begin{array}{l} 0.210 = 0.064\ K - b \\ 0.100 = 0.055\ K - b \\ 0.060 = 0.045\ K - b \end{array}\right\}$$

Adding the three first equations and the three last gives:

$$2.293 = 0.295\ K - 3b$$

$$0.370 = 0.164\ K - 3b$$

Solving these two equations $K = 15.92$.

Therefore the reaction rate will be

$$r = -15.92 \left[P_{\text{⌬}\,NH_2} \right]^{1/2} \qquad (2a)$$

At 240°C:

$$\left.\begin{aligned} 1.106 &= 0.11\ K - b \\ 0.737 &= 0.0818\ K - b \\ 0.450 &= 0.0596\ K - b \end{aligned}\right\}$$

$$\left.\begin{aligned} 0.210 &= 0.0432\ K - b \\ 0.100 &= 0.0365\ K - b \\ 0.060 &= 0.0321\ K - b \end{aligned}\right\}$$

These equations are transformed to two equations:

$$2.293 = 0.2524\ K - 3b$$

$$0.370 = 0.1118\ K - 3b$$

From which, $K = 13.7$

and the reaction rate equation will be:

$$r = -13.7 \left[P_{\text{⌬}\,NH_2} \right]^{1/2} \qquad (2b)$$

2. <u>Calculation of the Reaction Rate for the Zone Where No Aniline Decomposition Occurs.</u>

From Figure 6 for 200°C a curve can be drawn through the data with different slopes because of some scatter in the data.

The equation for the reaction rate proposed for the solid line curve is

$$r = \frac{K\ b_{\text{⌬}NO_2}\ P^{2}_{\text{⌬}NO_2}}{(1+b_{\text{⌬}NO_2}\ P^{2}_{\text{⌬}NO_2})^2} \qquad (5)$$

This equation is obtained by assuming that two molecules of nitrobenzene are attracted to one active center and then reacts with hydrogen,

$$A' \,.\, A' + B' \longrightarrow C' + D'$$

The rate of adsorption of two molecules of nitrobenzene (A . A) in the same active center will be:

$$r = K\, P_{NO_2} \sqrt{1-\Sigma\sigma}$$

The rate for desorption is,

$$r' = K' \sqrt{\sigma A \,.\, A}$$

at equilibrium

$$k_A\ P_{NO_2} \sqrt{1-\Sigma\sigma} = k'_A \sqrt{\sigma A' \,.\, A'} \qquad \text{or}$$

$$b_{NO_2} P^{2}_{NO_2} \quad (1-\Sigma\sigma) = \sigma A'A' \qquad (I)$$

For hydrogen $k_B\ P_{B'}(1-\Sigma\sigma) = k'_B\ \sigma_{B'}$ or $(b_{B'} P_{B'}(1-\Sigma\sigma)$

$= \sigma_B$ (II)

Adding (I) and (II) and subtracting from 1

$$1 - (1b_{no_2} P^2_{NO_2} + b_{B'} . P_{B'})(1 - \Sigma\sigma) = 1 - (\sigma_{A'} + \sigma_{B'})$$

$$1 = (1 - \Sigma\sigma)(1 + b_{no_2} P^2_{NO_2} + b_{B'} P_{B'}) \qquad \text{(III)}$$

The rate of reaction is

$$r = k \; \sigma_{A'} \, . \, {}_{A'} \; \sigma_B$$

Substituting $\sigma_{A'}$ and $\sigma_{B'}$ from equations (I) and (II) and combining with (III) gives

$$r = \frac{k \, b_{no_2} P^2_{NO_2} \, b_{B'} P_{B'}}{(1 + b_{no_2} P^2_{NO_2} + b_{B'} P_{B'})^2}$$

Since the hydrogen concentration is very high, it can be included into the constants and therefore the equation will be equal to

$$r = \frac{K \, b_{no_2} P^2_{NO_2}}{(1 + b_{no_2} P^2_{NO_2})^2} \qquad (5)$$

To obtain the value of the constants K and b, it was necessary to rearrange the equation (5)

$$(1 + b_{no_2} P^2_{NO_2})^2 = K \; \frac{P^2_{NO_2}}{r} \; ;$$

$$1 + b_{no_2} P^2_{NO_2} = \sqrt{K'} \; \frac{P_{NO_2}}{\sqrt{r}} \; ;$$

$$P^2_{NO_2} = \frac{\sqrt{K'}}{b_{NO_2}} \, \frac{P_{NO_2}}{\sqrt{r}} - \frac{1}{b_{no_2}} \qquad (6)$$

In this zone the only reaction occurring is the formation of aniline,

If x = the mols of aniline produced per mol of nitrobenzene fed the total mole present in the gases leaving the reactor:

Nitrobenzene	$1 - x$
Hydrogen	$A - 3x$
Aniline	x
Water	$2x$
Total =	$A + 1 - x$

Therefore the value of P_{NO_2} at any moment will be $P_{NO_2} = \frac{x}{A+1-x}\pi$

From Figure 5, the values of the rate of reaction, r, were obtained graphically at different conversions and the corresponding values of V_R / F.

TABLE A-VI

t°c	x	r	F	A	P_{NO_2}	$P^2_{NO_2} \times 10^{-5}$	$P_{NO_2}/\sqrt{r}$
200	0.98	0.0022	1.045	20.95	0.000955	0.09	0.020
	0.95	0.0048	1.128	19.45	0.00256	0.60	0.034
	0.80	0.0225	1.282	17.10	0.01157	13.4	0.077
	0.60	0.0180	1.325	16.55	0.0236	55.7	0.176
	0.40	0.01375	1.565	14.00	0.0412	160	0.350
	0.25	0.0075	1.925	11.37	0.0621	385	0.770
	0.15	0.0037	2.78	7.89	0.0972	940	1.600
240	0.95	0.00294	2.085	10.5	0.00474	2.25	0.0875
	0.80	0.0345	2.68	8.18	0.0249	61.9	0.134
	0.50	0.0235	3.19	6.86	0.0680	463	0.443
	0.35	0.0150	3.83	5.73	0.102	1040	0.850

The equation (6) has been plotted in figure 7 for both temperatures. Straight lines are obtained. From the slope and intercepts, K and b were calculated.

200°C $K = 384$ $b = 0.0327$

240°C $K = 113.8$ $b = 0.00795$.

The proposed equation for the reaction rate for the step line in figure 6 was

$$r = K \frac{b P_{NO_2}}{(L + b P_{NO_2})^2} \qquad (7)$$

This equation was obtained assuming as before the Langmuir-Hensel-wood model but considering that each active center is occupied by one molecule of nitrobenzene rather than two.

As before, the equation is rearranged:

$$b P_{NO_2} = \sqrt{K} \sqrt{\frac{P_{NO_2}}{r}} - 1$$

$$P_{NO_2} = \frac{\sqrt{K}}{b} \sqrt{\frac{P_{NO_2}}{r}} - \frac{1}{b} \qquad (8)$$

TABLE A-VII

t°c	x	r	F	A	P_{NO_2}	P_{NO_2}/r	$\sqrt{P_{NO_2}/r}$
200	0.98	0.0022	1.045	20.95	0.00095	0.43	0.656
	0.95	0.0048	1.128	19.45	0.00256	0.538	0.734
	0.80	0.0135	1.328	16.50	0.0120	0.888	0.942
	0.40	0.00935	1.875	11.65	0.049	5.250	2.290
	0.20	0.0055	2.830	7.75	0.0938	17.00	4.120
	0.10	0.00374	4.84	4.53	0.166	44.30	6.650
240	0.95	0.00294	1.045	20.95	0.00474	1.612	1.270
	0.80	0.0135	3.13	7.00	0.0278	2.060	1.435
	0.50	0.0213	4.21	5.19	0.0880	4.130	2.030
	0.30	0.0185	5.55	3.95	0.1505	8.15	2.850

The equation (8) has been plotted in Figure 8. Two straight lines are obtained. From the slope and intercept the values of K and b_{NO_2} were found:

200°C $K = 2.89$ $b_{NO_2} = 62.5$ (*)

240°C $K = 0.907$ $b_{NO_2} = 8.0$

(*) The fact that K at 200°C is higher than at 240°C is only apparent because these values of K are $K = K\, b_{H_2} b_{NO_2}$

$$\text{Therefore } Kb_{H_2} = \frac{2.89}{62.5} = 0.0463$$

$$Kb_{H_2} = \frac{0.907}{8} = 0.1005$$

The rate equations are

$$200°\text{C} \qquad r = \frac{2.89\; P_{NO_2}}{(1 + 62.5\, P_{NO_2})^2}$$

$$240°\text{C} \qquad r = \frac{0.907\; P_{NO_2}}{(1 + 8\, P_{NO_2})^2}$$

D. Reactor Design Calculation

1. Integration of Reactor Design Equation

$$F\,dx = r\,d\,V_R$$

$$\int_0^{V_R} \frac{dV_R}{F} = \int_0^{x} \frac{dx}{r} \qquad (1)$$

$$r_{240^\circ C} = \frac{0.907\ P_{\text{⬡}NO_2}}{(1 + 8\ P_{\text{⬡}NO_2})^2}$$ and expressed in terms of concentration,

$$r = \frac{0.907\left(\frac{1-x}{15+x}\right)}{\left[1 + 8\left(\frac{1-x}{15+x}\right)\right]^2}$$, substituting into (1)

and integrating

$$\frac{V_R}{F} = \int_0^{x} \frac{\left[1 + 8\left(\frac{1-x}{15+x}\right)\right]^2}{\frac{1-x}{15+x}}\,dx$$

$$= \int_0^{x} \frac{1 + 16\left(\frac{1-x}{15+x}\right) + 64\left(\frac{1-x}{15+x}\right)^2}{\frac{1-x}{15+x}}\,dx$$

$$= \int \frac{15+x}{1-x}\, dx + \int 16\, dx + 64 \int \frac{1-x}{15+x}\, dx$$

$$= -16 \ln (1-x)+(1-x) + 16\, x + 1025 \ln (15+x) - 64(15+x)$$

$$= \Big[1025 \ln (15+x) - 16 \ln (1-x) -49\, x -959\Big]_{o}^{x}$$

$$= 1025 \ln (15 + x) -16 \ln (1-x) -49x - 2770$$

If $x = 0.98$

$$\frac{V_R}{F} = 79.5$$

being V_R = c.c. of catalyst (10% N_i : Cu)

and F = mols gr/hr of nitrobenzene.

2. Calculation of the expansion bed.

The minimum fluidization mass velocity was calculated using the equation

$$G_{Mf} = 688\, D_p^{\;1.82} \frac{\rho_f\, (\rho_s - \rho_f)^{0.94}}{\mu^{0.88}} \qquad (\underline{18})$$

$$D_p^{\;1.82} = 0.0088^{1.82} = 0.000182$$

$$\rho_f\, (\rho_s - \rho_f\,)^{0.94} = 0.00299 \Big[(3.99)(62.3)-0.00299\Big]^{0.94} = 0.746$$

$$\mu^{0.88} = 0.013^{0.88} = 0.022$$

Substituting in the equation gives

$$G_{Mf} = 4.25 \text{ lb/hr ft}$$

The value for G_{Mf} obtained experimentally was 5 lb/hr ft^2

The actual mass velocity for a conversion of 98% was:

$$G_f = G_{NO_2} + G_{H_2}$$

$G_{NO_2} = 3.0$ gr/min $\therefore$ 29.3 lb/hr ft^2

$G_{H_2} = 0.15$ lit/sec $\therefore$ 1390 ft^3/hr ft^2 $\therefore$ 4.18 lb/hr ft^2

so $G_f = 29.3 + 4.18 = 33.48$ lb/hr ft^2

$$\frac{G_f}{G_{Mf}} = 6.7$$

Using a plot expansion bed versus $\dfrac{G_f}{G_{Mf}}$

The R, expansion bed is = 1.6. This is the same as that observed experimentally.

3. Calculation of the Necessary Heat to be Released Through The Walls

Base: 1 hour, and basis temperature of 20°C

Rates
In
Nitrobenzene : 3230 Kg/(24)(123.12)=4480 mol gr ∴.551Kg
Hydrogen : (4480)(15) = 67300 mol gr.
Out
Aniline : 9800/(24)(93.11) = 4395 mol gr.
Hydrogen : 67300-(3)(4480)(0.98) = 54140 mol gr.
Water : (4480)(2)(0.98) 8960 mol gr.

Nitrobenzene

Specific heat liquid = 0.42 cal/gr °C
gas = 39.08 cal/gr mol °K

Heat of vaporization = 79.08 cal/gr.

Boiling point = 210.9 °C

Aniline

Specific heat liquid = 0.57 cal/gr °C
gas = 33.48 cal/gr mol °K

Heat of vaporization = 95.56 cal/gr

Boiling Temperature = 184.4 °C

Hydrogen

Specific heat = 6.95 cal/(mol gr)(°C)

Water

Specific heat vapor = 0.46 cal/gr
liquid = 1 cal/gr

Heat of reaction: 235000 cal/mol gr

Heat input: Heat of reaction + heat of nitrobenzene

Heat of reaction (235000)(4480)(0.98) = 1,032,000,000 cal

Nitrobenzene
+ 551,000 (0.42)(210.9-20) = 44,200,000 cal
+ 551,000 (79.08) = 43,600,000 cal
+ (4480)(39.08)(240-210.9) = 5,100,000 cal

1,124,900,000

Heat output with gases: Aniline + Nitrobenzene + Hydrogen + Water

Aniline
(417,000)(0.98)(0.57)(184.4-20) = 38,140,000
+ (417,000)(0.98)(95.56) = 39,000,000
+ (4395)(33.48)(240-184.4) = 8,170,000

Nitrobenzene
+ (551,000) (0.02)(0.42)(210.9-20) = 880,000
+ (551,000)(0.02)(79.08) = 870,000
+ (85)(39.08)(240-210.9) = 896,500

Hydrogen
+ (54140)(6.95)(240-20) = 82,900,000

Water
+(0.98)(8960)(18)(0.46)(240-100) = 10,150,000
+(8960)(0.98)(18)(540) = 85,300,000
+(8960)(18)(0.98)(100-20) = 12,630,000

Total 278,136,500

Heat net to take out through the reactor walls:

1,124,900,000 - 278,136,500 =

= 846,763,500 cal/hr.

4. Calculation of the Heat Transfer Coefficient Between Fluidized Bed and Walls.

Using a nomograph (x)

$$\frac{G_f}{R} = \frac{(33.48)(0.55)}{(0.013)(1.6)} = 885$$

$c_s = 0.2$ Btu/lb

$\rho_s \; c_s = 11.65$

$\rho_s = 58.2$ lb/ft^3

$K''' = 0.1$ Btu/hr ft $^\circ$F

Using the Mickley and Trilling equation

$$h = 0.0433 \left(\frac{\rho_s^2}{D_p^3}\right)^{0.238}$$

$$= 0.0433 \left(\frac{3380}{4.65} \; 10^{10}\right)^{0.238} = 49.7 \text{ Btu/hr ft}^2 \, {}^\circ\text{F}$$

E. NOMENCLATURE

A = Mols of hydrogen fed, gr mol/hr

A' = 1 mol of nitrobenzene

A'' = Surface of the reactor wall, m^2

B' = 3 mols of hydrogen

b_{NO_2} = constant of the equation 5

c' = 1 mol of aniline

C_M = constant of the equation

C'_M = constant = C_M zR

D = diameter of reactor

D' = mol fraction of aniline destroyed

D'' = 2 mols of water

D_p = particle diameter, inches

F = nitrobenzene feed rate, gr mol/hr

F' = total gas feed rate, gr mol/hr

G_f = total mass velocity lb/(hr)(ft^2)

G_{H_2} = hydrogen mass velocity lb/(hr)(ft^2)

G_{NO_2} = Nitrobenzene mass velocity lb/(hr)(ft^2)

G_{Mf} = Minimum fluidization mass velocity lb/(hr)(ft^2)

h = reactor height

h' = bed-wall heat transfer coefficient

Δh = pressure drop through the capillary meter

K = specific rate of reaction

K' = constant = $K \cdot b_{NO_2}$

K'' = catalyst activity, sec^{-1}

K''' = parameter of the nomograph used in Pbg

M = **molecular weight of hydrogen**

$P_{⬡ NH_2}$ = partial pressure of aniline

$P_{⬡ NO_2}$ = partial pressure of nitrobenzene

$P_{P.O}$ = absolute post-capillary pressure, in. Hg

P_B = partial pressure of hydrogen

ΔP_{exp} = experimental pressure drop through the catalyst fluidized bed

ΔP_{calc} = calculated pressure drop through the catalyst fluidized bed

Q = heat transferred through the reactor wall, Kcal.

$q_{P.O}$ = volumetric gas velocity at post-capillary meter conditions

r = rate of reaction gr mol/(c.c. catalyst)(hr)

$T_{P.O}$ = absolute post-capillary meter temperature, °K

U = total heat transfer coefficient

V_R = volume of the catalyst at fixed bed conditions, c.c.

V'_R = expanded catalyst volume, ft^3

x = conversion of aniline

w = weight of catalyst

Greek Symbols

η = efficiency of fluidized bed

ρ = apparent density of fluidized bed

ρ_f = fluid density lb/ft^3

ρ_s = solid density lb/ft^3

σ = active site in catalyst

$\sigma_{AA'}$ = active site occupied by two mols of nitrobenzene

$\Sigma\sigma$ = total number of active sites

π = total pressure, atm.

F. LITERATURE CITATIONS

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