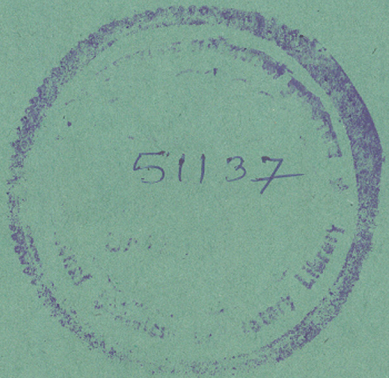


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VAPOUR PHASE CATALYTIC HYDROGENATION OF  
NITROBENZENE TO ANILINE

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A THESIS  
SUBMITTED TO  
THE UNIVERSITY OF BOMBAY  
FOR THE DEGREE OF  
MASTER OF SCIENCE (TECHNOLOGY)

BY  
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National Chemical Laboratory  
Poona 8

  
(D.N. Biseni) <sup>www.</sup> 31/5/63.

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## Chapter I

CHAPTER I  
INTRODUCTION

Aniline is among the most important heavy intermediates in the organic chemical industry. It is generally manufactured by a liquid phase process starting from nitrobenzene or chlorobenzene, or by a vapor phase process starting from nitrobenzene. In addition to these two broad methods of manufacture, there are several other methods by which aniline may be prepared and these are discussed at length in Chapter II.

Vapor phase hydrogenation of nitrobenzene to aniline has several advantages. It is a process which can be made continuous easily, and can be operated at atmospheric pressure. Several patents have been taken on the use of a variety of solid catalysts for this reaction. In general, the catalysts used consist of metals such as copper, chromium, nickel, silver, etc., either by themselves or in mixtures thereof, and sometimes promoted with thorium, tungsten, vanadium, etc. Although several papers have been published on the use of these catalysts,

no investigation embodying a comparative evaluation of these catalysts has been reported. A survey of the literature has also revealed the fact that in most cases no attempt has been made to maintain isothermal conditions before obtaining the conversion data.

One of the principal factors to be evaluated before undertaking the development of a process is the estimation of equilibrium conversions under different conditions. In the case of hydrogenation of nitrobenzene, although this is a reaction that has been industrially used for several years, no thermodynamic study has been reported. The chief difficulty in estimating equilibrium conversions has been the absence of data on the thermodynamic functions of aniline and nitrobenzene. Recently (year 1962) the thermodynamic functions of aniline were calculated by Hutton et. al.<sup>8</sup> from spectroscopic data. But so far there are no published figures on the thermodynamic properties of nitrobenzene.

The principal objective of the study was therefore two-fold: to estimate the necessary

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<sup>8</sup> See reference (3) in Chapter III.

thermodynamic properties of nitrobenzene from generalized procedures; and to evaluate the performance of a variety of catalysts prepared essentially from copper, nickel and chromium, and to make preliminary kinetic studies using the most favourable catalyst. Experimental studies were not involved in estimating thermodynamic conversions. On the other hand, for kinetics studies a special reactor system was developed incorporating a fluidized bath of hot solids to obtain isothermal conditions in the catalyst bed.



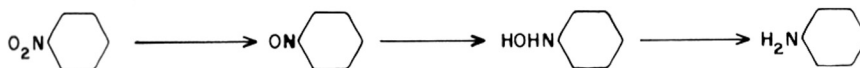
## Chapter II

CHAPTER II  
LITERATURE REVIEW

General

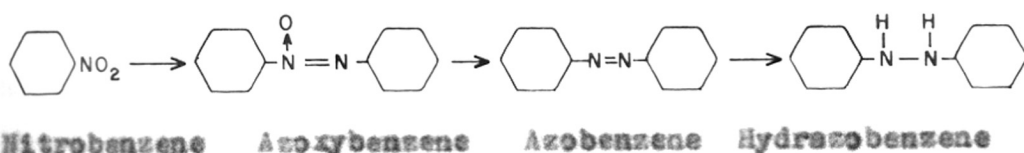
Bechamp's discovery of the reduction of nitro-compounds in the presence of iron and acetic acid and the subsequent application of the reaction by Perkin in 1857 for the preparation of aniline were events of great technical importance in the dyestuff industry; replacement of acetic acid with hydrochloric acid was largely responsible for this technical progress. Later it was found possible to effect the reduction by using a smaller amount of the acid than required theoretically, since the ferrous salt of the acid functioned only catalytically. It has also been demonstrated recently that other salts obtained from strong acids (i.e., AlCl<sub>3</sub>, aniline hydrochloride, etc.) can be successfully employed instead of iron salts.

Sabotier found that nitrobenzene could be reduced by hydrogen in the presence of an active nickel catalyst to aniline, ammonia, benzene, cyclohexane, dicyclohexylamine, cyclohexylamine and diphenylamine. The reduction of nitrobenzene to aniline essentially proceeds according to the following scheme:



Nitrobenzene    Nitrosobenzene    Phenylhydroxylamine    Aniline

The reaction may also proceed in the following manner depending upon the reducing agent and conditions employed:



If the conditions of reduction happen to be too severe the reaction products obtained are chiefly hydrocarbons and ammonia.

The various methods which can be employed for the reduction of nitrobenzene to aniline are summarised below.

- 1) Using a metal salt and an acid, generally iron borings and hydrochloric acid.



Industrially less than 2% of the acid theoretically required by the above reaction is used, because ultimately FeCl<sub>3</sub> acts as an acid in the water solution liberating the necessary hydrogen ions.

- 2) Using sodium bisulfide

Sodium bisulfide acts as a good reducing agent, converting nitrobenzene to aniline by simple boiling, the reaction being:



The resulting sodium thiosulfate is recovered by evaporation and crystallization.

3) Using iron as catalyst at high temperatures and pressures (33)

Aniline can be obtained by the reduction of nitrobenzene with hydrogen or gas mixtures containing hydrogen, in the presence of a catalyst and water at high temperatures and pressures. Thinning of hydrogen with  $\text{CO}_2$  should be resorted to due to the possibility of violent reactions at high temperatures and the explosive nature of the decomposition products.

4) By the interaction of chlorobenzene and ammonia (1)

A mixture containing chlorobenzene and strong aqueous ammonia when heated in an autoclave at  $180^\circ\text{C}$  for 24 hours results in the formation of aniline. The reaction is accelerated by the addition of copper sulphate. Aniline obtained is converted to aniline sulphate by adding sulphuric acid which is filtered, and the free base is obtained by neutralisation and subsequent distillation. A yield of 80% is obtained.

5) Using hydrogen with a nickel catalyst

Nitrobenzene when allowed to react with hydrogen in the presence of a nickel catalyst yields aniline without any intermediate products. However, if such a reaction takes place in the presence of caustic solution, intermediate products such as azoxy, azo and hydrazo derivatives are obtained in succession. These derivatives may all be converted to aniline by

treatment with hydrogen in a neutral solution.

6) Direct ammonolysis of benzene to anilins

Recently a number of patents have been issued involving the direct ammonolysis of benzene to aniline.

7) Electrolytic reduction

Production of amines by electrolytic reduction has been studied extensively and a great deal of work is reported<sup>(31)</sup>. The reduction can be controlled carefully to give high yields with very few by-products.

8) Vapour phase catalytic hydrogenation

This process was taken up for detailed study in this work, and will be briefly described in the following paragraphs.

The procedure involving the vapour phase reduction of nitrobenzene over a solid catalyst has many attractive features, such as (i) continuous operation, (ii) no industrial waste disposal problem (i.e. iron sludge), (iii) saving in power and steam consumption (since the heat in the vapours leaving the catalyst chamber can be made use of), and (iv) operation at atmospheric pressure. However, the method is not without disadvantages which may be: (i) necessity of separating nitrobenzene and aniline if the conversion per pass happens to be low, and (ii) sensitivity of the catalyst surface to poisoning.

The procedure of reduction essentially consists

in passing a mixture of nitrobenzene vapours and hydrogen in excess over a heated catalyst. The reaction being highly exothermic, proper care is needed for maintaining the required temperature. The vapours coming out of the catalyst chamber are condensed and the excess of hydrogen is recycled. The condensed liquid is usually a mixture of aniline and small quantities of nitrobenzene, the two being separated by distillation.

The main factors affecting the reaction are the activity of catalyst, temperature at which the reaction is carried out and purity of hydrogen. It is claimed that oxygen<sup>(24)</sup> if present in hydrogen imparts a brown colour to the product, while CO if present is adsorbed more easily than hydrogen by the catalyst thus diminishing the speed of reduction. The presence of  $H_2S$  acts as an actual catalyst poison, while  $H_2$ ,  $NH_3$  and  $CO_2$  show indirect detrimental effects by decreasing the partial pressure of hydrogen.

#### Review of catalysts used for the vapour phase hydrogenation process

The catalysts employed for this reduction may broadly be divided into two groups: (1) non metallic and (2) metallic.

In the case of non-metallic catalysts, the only ones worth mentioning are silica gel, kieselgur, active charcoal and bleaching earth<sup>(17)</sup>.

A patent to Sendernes<sup>(29)</sup> is probably the first recorded patent having to do with the reduction of organic bodies by hydrogen in the presence of metallic nickel. This patent was for the production of aniline from nitrobenzene, and involved the passing of nitrobenzene in the form of vapours over heated nickel, copper, cobalt, iron or palladium in the presence of hydrogen.

### Copper catalysts

Copper by itself or precipitated on a carrier has been tried extensively in industry. According to Sabatier and Sendernes<sup>(27)</sup>, copper is the best catalyst for hydrogenation of nitrobenzene to aniline, because it does not cause the hydrogenation of the aromatic nucleus.

A U.S. patent<sup>(28)</sup> lists the use of copper salt on pumice in the presence of magnesium oxide.  $MgO$  or  $ZnCO_3$  are claimed to augment the catalytic action of copper. Brown and Henke<sup>(5)</sup> have also studied the reduction using copper catalysts. They produced the catalysts by reducing with hydrogen the oxide obtained by the ignition of copper nitrate, and also from the oxide obtained by the action of caustic soda on copper nitrate. The latter was found to be more efficient.

Irlin<sup>(18)</sup> obtained an optimum yield of 96.5% of aniline by the reduction of nitrobenzene with hydrogen over a mixture of copper and 10% calcium

oxide at 240-250°C. The catalyst was prepared by heating the nitrates at 350°C for 3-4 hours, and by subsequent reduction for 12 hours at 300°C in hydrogen. The catalyst retained its activity for 80 hours, and could be easily regenerated.

Sermeria & Milone<sup>(30)</sup> reduced nitrobenzene to aniline by passing its vapours along with hydrogen over a precipitated copper catalyst on pumice. At 400°C it was found that the reaction



became predominant. Excess of hydrogen was found to give an increased yield, especially at higher temperatures. The catalyst was found to be quite active even after using for several months at the rate of 12 hours/day.

FIAT<sup>(10)</sup> reports describe the catalyst used for the reduction of nitrobenzene at I.G. Farbenindustrie, Ludwigshafen. The catalyst was made by impregnating lumps of pumice stone with a slurry of basic copper carbonate and a 50% solution of sodium silicate. The impregnation was accomplished by spraying this solution on to the pumice stone in a concrete mixer. The catalyst could be regenerated 5-6 times by air oxidation.

Use of cuprammonium nitrate as a catalyst<sup>(19)</sup> is also mentioned. The patent relates to the preparation of the catalyst by impregnation of silica hydrogel with a solution of cuprammonium nitrate. The spent catalyst may be regenerated by passing air over it at 250-350°C,



when the organic deposit is burnt off, and it is probable that some part of the metallic copper is also converted to copper oxide. After regeneration any copper oxide formed is reduced by flushing the system with an inert gas and then reducing with hydrogen at 250°C.

### Nickel catalysts

Finely divided nickel catalyst obtained by the ignition of nickel nitrate and the subsequent reduction of the oxide was tried by Brown & Henke<sup>(3)</sup>. The compounds formed during the catalytic reduction of nitrobenzene depend on the temperature to which the catalyst was previously heated, a low temperature leaving the catalyst too active, and a higher temperature decreasing the speed of reduction to a marked extent. The best temperature for the reduction of nitrobenzene was found to be 260°C.

Thiophene-poisoned nickel catalyst<sup>(22)</sup> loses its capacity to hydrogenate the aromatic nucleus, but not the double bond, nitro group, etc., in the side chain. Thus nitrobenzene is converted quantitatively to aniline at 180°C with such a catalyst. The addition of proper amounts of copper to nickel has the double effect of raising the conversion rate of nitrobenzene and lowering the reduction temperature of the catalyst.

Hydrogenation using a catalyst<sup>(20)</sup> prepared by the reduction of nickel nitrate containing 1.5 to 2%

nickel sulphate gives pure aniline in high space time yield at 180-200°C. Addition of nickel sulphate results in the partial poisoning of the catalyst, which is similar to that caused by a low partial pressure of hydrogen sulphide.

Manufacture of aniline has also been tried on a semi-industrial scale using poisoned nickel catalyst<sup>(23)</sup>. A Japanese patent<sup>(21)</sup> states that ordinary reduced nickel is too active for the reduction of the aromatic nitro compounds. A catalyst containing reduced nickel prepared from nickel nitrate mixed with a compound containing sulphur or chloride is more suitable.

Nickel sulphide<sup>(25)</sup>, prepared by passing  $H_2S$  in a solution of nickel acetate, was found to give a yield of 98.9% of pure aniline from nitrobenzene at 278-300°C, and was found to be a better catalyst than finely divided metallic nickel.

Reduced nickel vanadate<sup>(26)</sup> (75% conversion) was found to be too active for the reduction of nitrobenzene to aniline, as compared with copper vanadate (100% conversion). Lead vanadate was also tried and found to give 99% conversion. The catalysts were prepared by reduction of respective vanadates supported on sufficient asbestos fibre.

Alloys of aluminium<sup>(2)</sup> with nickel and other metals have also been used. Fragments of alloys are

activated with NaOH and are used for reduction at atmospheric pressure. These catalysts are highly active and resist poisoning.

Dinickel phosphide<sup>(32)</sup> prepared by the reduction of nickel orthophosphate in excess of hydrogen yielded 95% of aniline.

A catalyst consisting of nickel sulphide associated with amorphous alumina<sup>(35)</sup> is claimed to have an increased reaction rate, enhanced life, and ease of regeneration.

A modified Urashibara nickel catalyst containing nickel and aluminium<sup>(16)</sup> is reported to give a yield of 65% aniline at 250°C. The catalyst is prepared from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and aluminium containing a small amount of water. Nickel is deposited on aluminium by an exchange reaction.

#### Other catalysts

A silver catalyst prepared from silver carbonate<sup>(4)</sup> has been reported to give a conversion of 98.7%. Silver<sup>(30)</sup> has also been used by precipitation on pumice, and a conversion of 99.5% to pure aniline has been reported.

A cobalt catalyst<sup>(13)</sup> prepared by ignition of the nitrate to oxide at 445°C and subsequent reduction in hydrogen at 400°C was found to be too active for the production of aniline, the reduction being carried to

ammonia and methane. Under the above conditions a Co-Mn catalyst gave between 85 and 100% conversion at 260°C, and a Co-Mo catalyst attained a similar conversion at 300°C. A yield of 99.5% was obtained by using cobalt sulphide<sup>(12)</sup> as a catalyst at 295°C.

A chromium catalyst<sup>(4)</sup> prepared by the precipitation of its hydroxide from a solution of the nitrate by  $\text{NH}_4\text{OH}$  and reduction of the oxide in hydrogen gave a maximum yield of 83% at 320°C. However, copper chromate has been found to give a better yield. The chromate prepared by Brown et. al.<sup>(9)</sup> gave a yield of 99% at 310°C.

$\text{CuCrO}_2$ <sup>(11)</sup> (CuO, 5%;  $\text{Cr}_2\text{O}_3$ , 2%) and silica gel, and Cu-promoted  $\text{CuCrO}_2$  supported on silica gel have also been tried.

Several other metals, either directly or precipitated on a suitable support, have been reported in the literature for this reduction. Among these may be mentioned iron, manganese, tungsten, cerium and uranium<sup>(4)</sup>; tin<sup>(6,34)</sup>; cadmium<sup>(14,15)</sup>; molybdenum<sup>(7)</sup>; and  $\text{Ca(OH)}_2$ <sup>(8)</sup>.

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### Chapter III

CHAPTER III  
THERMODYNAMIC CONSIDERATIONS

Before undertaking investigations on any proposed chemical reaction it is necessary to assess the reaction thermodynamically. For this purpose, the thermodynamic properties of the reactants and products should be known. The reaction under consideration is widely used in industrial practice, but no data are reported on the equilibrium conversions obtainable at different temperatures. In the reaction,



the thermodynamic properties of aniline<sup>(3)</sup>, water<sup>(6)</sup> and hydrogen<sup>(6)</sup> are available, while those of nitrobenzene have not been reported.

In this chapter all the available and estimated thermodynamic properties of the reactants and products have been tabulated, and necessary equations have been developed for extrapolation. Based on these thermodynamic properties, the heat of reaction, free energy of reaction, equilibrium constant, and equilibrium conversion have been calculated as functions of temperature.

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### Thermodynamic properties of nitrobenzene

Due to the non-availability of these data in the literature, use of various generalized procedures had to be made in order to calculate them.

#### Heat capacity

The method of Dobratz<sup>(1)</sup>, which is based on the principle of generalized bond frequencies and their corresponding contributions to the vibrational heat capacity, was used.  $C_p^{\circ}$  values were calculated at different temperatures (300-1,000°K) and the following equation was developed by the method of least squares.

$$C_p^{\circ} = 11.00302 + 4.9698 \times 10^{-2} T + 0.46066 \times 10^{-4} T^2 - 0.04699 \times 10^{-6} T^3 \dots (1)$$

$C_p^{\circ}$  values calculated by this equation, together with the original values (calculated by the method of Dobratz), are plotted in Fig.(1).  $C_p^{\circ}$  data were also computed by group contributions<sup>(4)</sup>. Fig.(2) shows a plot of  $C_p^{\circ}$  as a function of temperature as calculated by both the methods.

#### Heat of formation

No literature value being available, it was calculated from heat of combustion data. Taking 298°K as the reference temperature,

$$\Delta H_c = -739.2^{(2)}$$

$$\Delta H_f C_6H_5NO_2 = 6\Delta H_f CO_2 + 2.5\Delta H_f H_2O - \Delta H_c \quad (1)$$

$$\Delta H_f CO_2 = -94.05 \quad (g)$$

$$\Delta H_f H_2O = -68.32 \quad (1)$$

$$\therefore \Delta H_f C_6H_5NO_2 = 4.22 \quad (1)$$

Now, the latent heat of vaporisation at  $298^\circ K^{(2)}$ ,

$$\Delta H_v = 13.19 \quad (g)$$

$$\therefore \Delta H_f = 13.19 + 4.22 = 17.41 \quad (g)$$

The heat of vaporisation for nitrobenzene is reported by Perry<sup>(5)</sup> as 79.08 cal/gm at  $483^\circ K$ . Using this value,  $\Delta H_v$  at  $298^\circ K$  was calculated from Watson's equation,

$$\frac{\lambda_1}{\lambda_2} = \left[ \frac{1 - T_{r1}}{1 - T_{r2}} \right]^{0.38}$$

where  $\lambda_1$  and  $\lambda_2$  are the heats of vaporisation at reduced temperatures  $T_{r1}$  and  $T_{r2}$

$$\Delta H_v (298^\circ K) = 12.900$$

$$\text{and } \Delta H_f = 4.22 + 12.90 = 17.12 \quad (g)$$

The value of 17.41 was chosen for subsequent calculations.

Free energy of formation

Values of free energy of formation in the range

300 - 1,500°K were calculated by van Krevelen's method<sup>(7)</sup>.

Using a symmetry number of 2, the following two equations were developed for  $\Delta G_f^\circ$  as a function of temperature:

range 300 - 600°K:

$$\Delta G_f^\circ = 10.910 + 8.0627 \times 10^{-2} T \quad \dots (2)$$

Range 600 - 1,500°K:

$$\Delta G_f^\circ = 3.345 + 9.0357 \times 10^{-2} T \quad \dots (3)$$

A plot of  $\Delta G_f^\circ$  vs T in the range 300 - 1,500°K is shown in Fig.(3).

The other thermodynamic properties of nitrobenzene,  $\Delta H_f^\circ$ ,  $H_T^\circ - H_0^\circ$  and  $\frac{G_T^\circ - H_0^\circ}{T}$  at several temperatures have not been estimated, as the necessary data for estimating them were not available.

#### Thermodynamic properties of hydrogen

The thermodynamic properties of hydrogen in the ideal gaseous state are tabulated in Table (1).

#### Thermodynamic properties of aniline

The various thermodynamic functions of aniline have recently been reported<sup>(3)</sup>. These values cover a temperature range of 300 - 1,000°K. In this study it was decided to calculate the equilibrium conversions in the temperature range of 300 - 1,500°K. It was therefore necessary to calculate the thermodynamic properties of aniline by generalized procedures in the range 1,000 - 1,500°K.

### Heat capacity

Values of heat capacity for the ideal gaseous state, together with other thermodynamic properties, are tabulated in Table (2).

The  $C_p^\circ$  values have been plotted in Fig.(4) as a function of temperature. In order to obtain a  $C_p$  equation in the temperature range 300 - 1000°K, the method of least squares was used and the following expression was developed:

$$C_p^\circ = 2.8235 + 7.7834 \times 10^{-2} T + 0.1228 \times 10^{-4} T^2 - 0.03516 \times 10^{-6} T^3 \dots (4)$$

Values calculated by this equation are plotted in Fig.(4) together with the reported data. The average deviation was less than 1%.

$C_p^\circ$  data were also computed by the method of group contributions<sup>(4)</sup> and by Debratz's method<sup>(1)</sup>. These are plotted in Fig.(5). It is apparent that neither of these methods represents the reported spectroscopic data accurately; it was therefore considered advisable to use equation (4).

### Heat of formation

For aniline the reported<sup>(3)</sup> values of  $\Delta H_f^\circ$  at various temperatures have been listed in Table (2), and it was therefore not necessary to estimate them. A plot of  $\Delta H_f^\circ$  as a function of temperature appears in Fig.(6).

### Free energy of formation

Values of free energy of formation up to 1,000°K were available<sup>(3)</sup>. In order to determine the free energy values in the range 1,000 - 1,500°K, it was decided to use van Krevelen's method<sup>(7)</sup>. Using a symmetry number of 2 and values of group contributions reported by van Krevelen, the following two equations were developed for  $\Delta G_f^\circ$ :

range 300 - 600°K:

$$\Delta G_f^\circ = 10.755 + 8.6357 \times 10^{-2} T \quad \dots (5)$$

range 600 - 1,500°K:

$$\Delta G_f^\circ = 22.730 + 7.0727 \times 10^{-2} T \quad \dots (6)$$

Plots of  $\Delta G_f^\circ$  vs T both for the reported values in the range 300 - 1,000°K and for those determined by van Krevelen's method (300-1,500°K) are shown in Fig.(7). It is apparent that van Krevelen values deviate considerably from the reported data. Nevertheless the values of  $\Delta G_f^\circ$  as calculated by this method can be used in the higher temperature range to establish the trend of the equilibrium reaction in that range.

### Thermodynamic properties of water

These properties are tabulated in Table (3).

### Heat of reaction

The heat of reaction as a function of temperature was calculated by using the general equation,

$$\frac{\Delta H_r^\circ}{T} = \Delta a + \frac{\Delta b}{2} T + \frac{\Delta c}{3} T^2 + \frac{\Delta d}{4} T^3 + \frac{I_H}{T} \dots (7)$$

where  $\Delta a$ ,  $\Delta b$ ,  $\Delta c$  and  $\Delta d$  express the differences in the values of  $a, b, c$  and  $d$  between the products and reactants.  $I_H$  is the constant of integration which was determined from the value of  $\Delta H_r^\circ$  at 298°K.  $\Delta H_r^\circ$  at 298°K was calculated from the  $\Delta H_f^\circ$  values of the products and reactants at that temperature:

$$\Delta H_r^\circ (298^\circ\text{K}) = -112.21$$

The final  $\frac{\Delta H_r^\circ}{T}$  equation (298 - 1,000°K) was:

$$\times \left[ \frac{\Delta H_r^\circ}{T} = -380.2126 + 1.5214 \times 10^{-2} T - 0.1059 \times 10^{-4} T^2 + 0.002682 \times 10^{-6} T^3 \dots (8) \right.$$

$\checkmark \left[ \Delta H_r^\circ = -15.04 T + 1.725 \times 10^{-2} T^2 - 0.1127 \times 10^{-4} T^3 + 0.003 \times 10^{-6} T^4 - 108.960 \right]$

Values of  $\Delta H_r^\circ$  in the range of 298 - 1,000°K are tabulated in Table (4), and Fig.(8) shows a plot of  $\Delta H_r^\circ$  vs T.

The magnitude of the values of  $\Delta H_r^\circ$  suggests that the reaction is highly exothermic and the exothermicity increases with temperature.

### Equilibrium constant

The equilibrium constant of any reaction may be calculated from the equation,

$$-\frac{\Delta G_r^\circ}{T} = R \ln K \dots (9)$$

In order to use equation (9) it is necessary that the free energy change accompanying the reaction be known.

In the reaction under consideration,

$$\Delta G_R^\circ = 2 \Delta G_f^\circ(\text{H}_2\text{O}) + \Delta G_f^\circ(\text{C}_6\text{H}_5\text{NH}_2) \\ - 3 \Delta G_f^\circ(\text{H}_2) - \Delta G_f^\circ(\text{C}_6\text{H}_5\text{NO}_2)$$

Values of  $\Delta G_f^\circ$  for nitrobenzene, aniline, water and hydrogen have all been tabulated before. From these,  $\Delta G_R^\circ$  was calculated as a function of temperature, and the resulting values are summarized in Table (5).

The equilibrium constants (K) calculated from equation (9) using the values of  $\Delta G_R^\circ$  at several temperatures are also summarized in the same table. A plot of  $\log K$  vs  $T$  appears in Fig.(9).

#### Equilibrium conversion

The equilibrium conversion of the reaction may be determined from the equation,

$$K = \frac{\left[ \frac{n_R^r \cdot n_S^s}{n_B^b \cdot n_C^c} \right] \left[ \frac{\pi}{n_t} \right]^{\overline{r+s} - \overline{b+c}}}{K_\nu} \quad \dots(10)$$

where  $K_\nu$  is the fugacity coefficient term and is given by

$$K_\nu = \frac{\nu_R^r \cdot \nu_S^s}{\nu_B^b \cdot \nu_C^c} \quad \dots(11)$$

The term  $K_\nu$  is an indication of the deviation from ideality of the reaction and becomes significant at high pressure and low temperature.  $K_\nu$  for this reaction has been calculated from generalized fugacity coefficient

charts, and is shown as a function of temperature and pressure in Fig.(10). It is apparent from the figure that at ordinary pressure,  $K_p$  may be assumed to be unity over the entire temperature range. Assuming  $\gamma$  and  $K_p$  each as being equal to unity, and writing  $x$  as the moles of aniline formed at equilibrium per mole of nitrobenzene, the following equation can be written:

$$K = \frac{4 x^3 (4-x)}{27(1-x)^4} \quad \dots (12)$$

Using the values of  $K$  determined earlier at several temperatures, the conversion was calculated at each of these temperatures by a trial and error procedure. This procedure consisted in solving equation (12) by assuming several values of  $x$ , and then by graphical interpolation determining that value of  $x$  which satisfied the equilibrium constant at that particular temperature.

A plot of  $x$  vs  $T$  as obtained by the trial and error procedure is shown in Fig.(11). The nature of the curve is similar to that for any exothermic reaction. In this particular case it is clear that temperatures above  $900^\circ\text{K}$  should not be employed. In other words even though one may operate at sufficiently low temperatures, hot spots leading to diminished conversion should be avoided.



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## Chapter IV

CHAPTER IV  
EXPERIMENTAL SET-UP

EQUIPMENT

An apparatus incorporating the following essential features was desirable: isothermal conditions in the catalyst tube; constant rate flow of nitrobenzene which could be easily regulated and accurately measured; and constant rate flow of hydrogen which could be regulated independently of nitrobenzene. The set-up used in the experiments is shown in Fig.(12).

Hydrogen feed

A flow meter with carbon tetrachloride as the manometric liquid was used to measure the flow at which hydrogen was passed. Before allowing the hydrogen to pass through the flow meter, it was bubbled through sulphuric acid, and was subsequently passed through towers containing glass wool and caustic soda; in this way sulphuric acid removed the water vapour, glass wool removed the particles of the acid carried over with the gas, and caustic soda neutralized any acid still present in the gas stream. While bubbling hydrogen in sulphuric acid, it was passed through a glass tube drawn to a fine

point just dipping into the acid, as otherwise each bubble of gas tended to cause a deflection in the manometer. The flow meter was calibrated for high rates with a wet gas meter, and for low rates with a cuideometer.

#### Nitrobenzene feed

Nitrobenzene was fed at the top from a constant flow device. A sketch of the device is shown in Fig.(13).

This consisted of a storage vessel (1) which had a ground glass stepped opening at the top. The lower portion of this vessel was connected to a chamber (2) in such a manner that liquid from the vessel would fall at a point somewhere in the middle of this chamber through a tube cut at an angle as shown in the figure. The lower portion of this chamber was connected to a cylindrical tube (3), which ended at the bottom into a drop counting adapter(7). Pressure in chamber (2) and tube (3) was equalized by connecting them at the top. A glass rod (4) with a nichrome wire(6) fused at the bottom was fixed in the cylindrical tube in such a manner that the wire entered into capillary (5) and provided a decreased cross sectional area. This was necessary since the flows involved were very small, and could not be accommodated in the available capillary. Rates of flow could be varied either by changing the wire or by

adjusting its length through the capillary.

The constant flow device worked in the following manner:

Vessel (1) was filled with the liquid to a convenient height. This liquid flowed into chamber (2) up to level (a), and this level was also maintained in cylindrical tube (3). As droplets of liquid fell into the adapter from the cylinder, the level of the liquid in chamber (2) also decreased. But when the level came down to (b) a bubble of air escaped into the storage vessel, and a corresponding amount of liquid entered the chamber to level (a), thus maintaining practically a constant level in the feed system, the limits of error being the variation of liquid head in the range (a) - (b).

This flow device was tested for a variety of liquids, and was found to give constant flow with an average deviation of 2%.

Nitrobenzene from the constant flow device entered a burette which was filled almost to the top in order to provide a sufficient head of liquid. By adjustment of flow of the liquid into the burette from the constant feeding device and the flow out of the burette by means of a pinch cock, it was possible to ensure two important and necessary features: constant flow of nitrobenzene into the reactor, and sufficient

head of flow to take care of pressure fluctuations in the reactor.

Nitrobenzene liquid and hydrogen gas then entered the reactor, in which nitrobenzene was reduced to aniline.

### Reactor

A sketch of the reactor is shown in Fig.(14). The general principle of the reactor was that a fluidized bed of solids was used to heat a U shaped reactor immersed in it. The fluidized bed of solids served such the same purpose as a constant temperature heating bath, with the added advantage that the temperature could be increased to a much higher value.

The reactor system consisted of an outer glass shell with a cone shaped bottom having three inlet tubes for the introduction of compressed air for fluidization. The top section of the shell was fitted to the rest of the shell through a B-60 joint. The reactor, cyclone and thermocouple were fitted to this section of the shell so that they could all be easily removed from the main body of the shell.

The cyclone was used in order to prevent the loss of solids due to fluidization. The shell was filled to half its height with corborandum powder (-100, +120 mesh). This powder rested on a zero number sintered disc and was fluidized by means of compressed

air entering from the bottom inlets. Heating was accomplished by means of nichrome resistance wire wound on the outer surface. The current in the heating circuit (and therefore the heating itself) could be controlled by means of a variac and an ammeter.

A U tube reactor was fused to the top section of the shell as shown in the figure, with provision for the entry of hydrogen and nitrobenzene. The two limbs of the U tube were of different diameters. The limb with the larger diameter was the reaction tube having a zero number sintered disc at the bottom for placing the catalyst and was provided with a thermowell for measuring the longitudinal temperature gradient in the reaction zone. It also had an opening which could be used for charging the catalyst and subsequently for removing the products of reaction. The smaller diameter limb of the U tube acted as a pre-heater for hydrogen and nitrobenzene.

The feed stream consisting of hydrogen and liquid nitrobenzene on entering the reactor, heated by means of the hot fluidized bed of carborendum resulted in the vapourization of liquid nitrobenzene in the unpacked zone of the U tube. The vapours of nitrobenzene and hydrogen entered the reaction tube through the sintered disc, and passed through the catalyst bed where hydrogenation occurred. The vapours consisting of the

products and unconverted reactants were removed from the top.

The vapours coming out of the reactor passed through an air condenser and then through a water condenser. The materials flowing down from the water condenser were collected in a conical receiver. Hydrogen and uncondensed gases were then bubbled through a dilute hydrochloric acid trap, and the excess of hydrogen was measured by passing through a wet gas meter.



## Chapter V

## CHAPTER V

### CATALYSTS USED & THEIR PREPARATION

The various types of catalysts tried and their general methods of preparation will now be briefly described. Broadly the catalysts tried could be classified under two categories: (1) catalysts prepared by impregnating a carrier with metals like copper, nickel and chromium, either promoted or unpromoted, and (2) miscellaneous catalysts. The several catalysts tried in these two categories are listed below.

(1) Copper, chromium, nickel (or mixtures thereof) supported on inert carriers like asbestos, or pumice, etc.

- (i) Copper on asbestos in various concentrations.
- (ii) Copper on pumice in various concentrations.
- (iii) Nickel on asbestos in various concentrations.
- (iv) Mixtures of copper and nickel on asbestos in various ratios and concentrations.
- (v) Various percentages of cadmium as promoter with copper and nickel, on asbestos as carrier.
- (vi) Chromium on asbestos in various concentrations.
- (vii) Mixtures of copper and chromium on asbestos in various ratios and concentrations.

- (viii) Various percentages of cadmium as promoter with copper and chromium on asbestos as carrier.
- (ix) Thorium as promoter with copper and chromium on asbestos as carrier.

(2) Miscellaneous catalysts

- (i) Activated coconut shell charcoal.
- (ii) Activated coconut shell charcoal impregnated with various metallic chlorides, e.g. cadmium chloride, copper chloride, etc.
- (iii) Activated bauxite.
- (iv) Silver on activated bauxite.
- (v) Copper from copper nitrate by ignition.
- (vi) Copper metal powder as such.
- (vii) Copper chromite.
- (viii) Cuprammonium nitrate on asbestos.

Materials

A brief description of the raw materials used in the preparation of the catalysts and their analyses is given below.

(1) Asbestos

B. D. H. laboratory grade powder was used directly without any purification.

(2) Copper nitrate

Commercial grade copper nitrate was used. The copper content of the nitrate solution was estimated by the method of Charlot et al.<sup>(1)</sup>.

(3) Nickel nitrate

Nickel nitrate used was of commercial grade, and was analysed by the method of Cuming and Key<sup>(2)</sup>.

(4) Chromium nitrate

This material was of laboratory grade, and was analysed by Vogel's method<sup>(4)</sup>.

(5) Silver nitrate

It was of A.R. grade and was analysed by the usual method, using standard sodium chloride solution with potassium chromate as an indicator.

(6) Cadmium nitrate and thorium nitrate

These were of A.R. grade, and were used as such without any analyses.

(7) Bauxite

Sheveroy "A" bauxite activated at 450°C for 4 hours was used.

(8) Cocconut shell charcoal

Activated cocconut shell charcoal as received was used.

Preparation of catalysts

(1) Copper, nickel, chromium (and mixtures thereof) impregnated on inert carriers

Catalysts of this type were prepared by soaking an appropriate quantity of the carrier (pumice or asbestos) in a solution of the metallic nitrates. Depending upon the required ultimate concentration of the metal, the appropriate concentration of the corresponding metal nitrate was used.

If a mixture of metals was required, then the corresponding mixture of nitrates was used as the starting material.

After soaking the carrier in the metallic nitrate solution, it was stirred vigorously. To this was added slowly and with constant and rapid agitation a solution of sodium hydroxide till it was alkaline to phenolphthalein. This was then allowed to stand overnight and filtered through a buchner funnel. After washing the precipitate thoroughly with distilled water to remove any alkalinity, the catalyst was dried in an oven at 80°C. This was then ignited in a muffle furnace, the temperature of ignition varying from catalyst to catalyst. The ignition temperatures used and results obtained are discussed in a separate chapter. The resulting oxide was reduced to the metal in situ in the reactor before carrying out the reaction.

*for Cu catalyst, 375°C for Cu and 275°C for Cu-Ni*

## (2) Miscellaneous

Catalysts such as activated bauxite, activated coconut shell charcoal and copper metal powder were used directly without any pre-treatment. The preparation of the other catalysts used in this category is briefly described below.

### (1) Copper from copper nitrate by ignition

Copper nitrate was ignited in a muffle furnace at the required temperature, and the copper oxide was reduced to copper in situ in the reactor.

(ii) Activated coconut shell charcoal impregnated with metallic salts

The required quantity of charcoal was soaked in a 20% solution of the selected metallic salt containing the necessary amount of metal over a period of 2 days. It was then filtered and dried in an oven at 80°C.

(iii) Bauxite impregnated with silver

Activated bauxite was soaked in a 20% solution of silver nitrate overnight, filtered, dried and ignited at the required temperature in a muffle furnace. This gave silver oxide which was reduced to silver in situ in the reactor.

(iv) Copper chromite

The method followed was the one used by Brown et.al.<sup>(3)</sup>. 100 gm of potassium dichromate were dissolved in about 3 litres of distilled water. Enough potassium hydroxide was added to convert the salt to potassium chromate. 150 gm of copper nitrate trihydrate were dissolved in 1.5 litres of water. This solution was added to potassium chromate solution while stirring rapidly. The precipitate was washed three times by decantation and then washed well on a buchner funnel. It was dried in an oven for about 2 days at 80°C.

(v) Cuprammonium nitrate on asbestos

The process consisted in first preparing cuprammonium nitrate by the addition of excess of ammonia to a saturated solution of copper nitrate when cuprammonium nitrate precipitated out. This was filtered and dried at 60°C. in an oven. A saturated solution of cuprammonium nitrate was then prepared, and asbestos powder soaked overnight in it. This was filtered, dried at 60°C, and heated to the required activation temperature in situ before being used.

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## Chapter VI

## CHAPTER VI

### OPERATION AND PRODUCT ANALYSIS

#### Raw materials

##### Hydrogen

Commercial electrolytic hydrogen was used.

##### Nitrobenzene

Commercial nitrobenzene was purified by shaking it with sodium carbonate solution and then distilling first under atmospheric pressure and later under vacuum.

#### Operation

The reactor was first packed with the catalyst. To maintain isothermal conditions it was found necessary to dilute the catalyst with an inert material, since the temperature at the inlet of the feed tended to increase in spite of fluidized bed heating; temperature variations of the order of 50°C were observed. Various diluents, i.e. asbestos powder, kieselghur, porcelain beads, steel balls, copper powder, etc., were tried, and by far the best results were obtained with copper as a diluent.

The catalyst and the diluent were charged into the reaction tube in such a manner that at the bottom portion ( $\frac{1}{2}$ " height) the ratio of the catalyst to diluent

was 1:5. The proportion of catalyst was progressively increased as the distance from the reactor bottom increased, so that only the catalyst was present at the top. The above method of packing the reaction tube, together with the fluidized heating technique adopted, gave an isothermal zone with a temperature variation of less than  $\pm 3^{\circ}\text{C}$ .

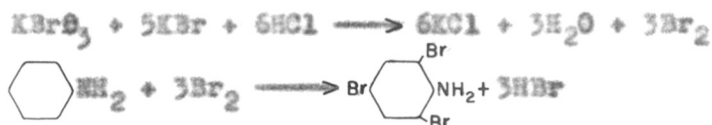
After the catalyst was charged, the flow of hydrogen was started and the inlet for nitrobenzene closed by means of a pinch cock attached to the rubber tubing. The reactor heater was adjusted to the desired pre-treatment temperature. In general the reaction temperature was less than the pre-treatment temperature.

Following the pre-treatment for the necessary time, the temperature of the reactor was brought to about  $20^{\circ}\text{C}$  lower than the required reaction temperature by cutting down the heating. Nitrobenzene flow was then started by opening the pinch cock, with the result that there was a slight increase in the temperature of the reaction tube (due to the high exothermicity of the reaction) as compared to the outside fluidized heating bed. Gradually the temperature in the reaction tube came down nearly to that of the fluidized bed in about 15 minutes. The reactor heater was then adjusted to bring up the temperature to the required value. The products were then sampled periodically for analysis.

### Analysis

The condensate flowing down from the water condenser consisted of aniline, unconverted nitrobenzene, water and hydrogen, which was collected in a receiver containing 50 ml of 1N hydrochloric acid. Aniline was thus fixed as aniline hydrochloride which is soluble in water. Nitrobenzene formed a separate layer which settled at the bottom. Excess hydrogen was bubbled through a dilute hydrochloric acid trap (to remove any aniline still carried over) before it was measured by means of a wet gas meter. The contents of the receiver and the acid trap were mixed together, and any nitrobenzene left unconverted was separated by a separating funnel and its amount noted. The solution was then made up to a known volume - usually 1 litre.

10 ml of the above solution were pipetted in a conical flask. 50 ml of brominating solution (containing 2.783 gm  $\text{KBrO}_3$  and 9.917 gm  $\text{KBr}$  per litre), 50 ml of distilled water and 15 ml of concentrated hydrochloric acid were added to it. The flask was stoppered immediately, shaken for 5 minutes and allowed to stand for  $\frac{1}{2}$  hour.  $\text{KBrO}_3$  reacted with  $\text{KBr}$  in the presence of hydrochloric acid liberating bromine which brominated the aniline present to tribromoanilines:



After the requisite time of  $\frac{1}{2}$  hour, excess bromine was displaced by iodine by the addition of 50 ml of 10% KI, and the liberated iodine was titrated against standard sodium thiosulphate of known normality.



A blank analysis was carried out without using the aniline hydrochloride solution. The difference in the amount of thiosulphate consumed between the blank and sample titrations gave the amount of thiosulphate required by the aniline present. Keeping in view the fact that 6000 ml of 1N thiosulphate = 93 gm of aniline, the amount of aniline present in the total volume was calculated.

#### Sample analysis

Nitrobenzene fed = 4.8 ml  
 = 5.745 gm  
 = 0.4671 gm moles

The contents of the receiver and the trap were mixed, no nitrobenzene was observed. The volume was made up to 1 litre in a measuring flask.

The volume of sodium thiosulphate (0.104 N) required for 10 ml of aniline hydrochloride solution and

50 ml of brominating solution

$$= \begin{array}{l} (i) 29.60 \text{ ml} \\ (ii) 29.40 \text{ ml} \\ (iii) 29.45 \text{ ml} \\ (iv) 29.45 \text{ ml} \end{array} \left. \vphantom{\begin{array}{l} (i) 29.60 \text{ ml} \\ (ii) 29.40 \text{ ml} \\ (iii) 29.45 \text{ ml} \\ (iv) 29.45 \text{ ml} \end{array}} \right\} \text{average} = 29.45 \text{ ml}$$

The volume of thiosulphate required for 50 ml of brominating solution

$$= \begin{array}{l} (i) 54.80 \text{ ml} \\ (ii) 54.80 \text{ ml} \end{array} \left. \vphantom{\begin{array}{l} (i) 54.80 \text{ ml} \\ (ii) 54.80 \text{ ml} \end{array}} \right\} \text{average} = 54.8 \text{ ml}$$

Amount of 0.104 N thiosulphate required for 10 ml of aniline hydrochloride =  $54.8 - 29.45 = 25.35 \text{ ml}$ .

Amount of 0.104 N thiosulphate required for 1 litre of aniline hydrochloride = 2535 ml.

$$\begin{aligned} \text{Now, 6000 ml of 1N thiosulphate} &= 93 \text{ gm of aniline} \\ 2535 \text{ ml of 0.104 N thiosulphate} &= \frac{93 \times 2535 \times .1040}{6000} \\ &= 4.086 \text{ gm of aniline} \end{aligned}$$

Aniline formed in  $\frac{1}{2}$  hour = 4.086 gm or

$$= \frac{4.086}{93} = .04393 \text{ gm moles}$$

$$\begin{aligned} \text{Conversion} &= \frac{0.04393}{0.04671} \times 100 \\ &= 94.08\% \end{aligned}$$

## Chapter VII

## CHAPTER VII

### RESULTS & DISCUSSION

#### a) Homogenous reaction

Before carrying out the studies on catalyst evaluation and the kinetics of the reaction with the selected catalyst, it was necessary to determine if any reaction occurred in the void spaces of the catalyst. The reaction occurring on the catalyst surface would then be the difference between the total reaction and that taking place in the void spaces.

It was thus necessary to evaluate the homogenous reaction rate, if such a reaction indeed occurred. Experiments were therefore carried out at 310°C, using a sufficiently low feed rate without any catalyst in the reactor. Several runs were carried out under these conditions, and it was observed that there was no conversion to aniline. In fact nitrobenzene did not react to give any product, and was recovered as such in the receiver. It may therefore be concluded that conversions obtained by using a catalyst are due entirely to the catalytic activity of the material used. These data may therefore be directly used for the correlation of catalytic reaction rates.



### b) Preliminary catalyst screening

Catalyst screening runs were carried out with the object of evaluating the performance of the several catalysts listed in Chapter V. The normal reaction temperatures employed for these runs varied from 300-350°C, although in some cases the temperatures were increased to 400°C. W/F and nitrobenzene to hydrogen ratio were kept practically constant at 34.54 and 1:4.5 respectively. Whenever the catalysts were found to be promising, two levels of temperature and W/F were normally investigated.

The results obtained with copper, chromium and nickel on asbestos as carrier were by far the most promising, and will be discussed at length. It is interesting first to observe the results obtained with the various miscellaneous catalysts that were used. These results are summarized in Table (6). Activated coconut shell charcoal gave practically no conversion to aniline. Impregnated coconut shell charcoal gave a conversion of 44% at 400°C, but in three hours the conversion fell to 30%. Activated bauxite was not active in this reaction, while 6% silver on bauxite gave about 30% conversion at 300°C; here again the conversion fell to 19% in 3 hours. Copper chromite gave a conversion of 90.7% at about 300°C, but the conversion fell to

60% in 3 hours. The other catalysts tried, i.e. cuprammonium nitrate on asbestos, copper metal powder, copper from ignition of copper nitrate, were not promising. The last named catalyst showed an extremely high initial activity, giving a conversion of almost 100%, but it fell to almost nil in the space of a few minutes. It may therefore be concluded that none of the miscellaneous catalysts listed in Table (6) are satisfactory.

#### Copper, chromium and nickel catalysts

In this section the results obtained with supported copper, supported chromium and supported nickel will be discussed.

The data are tabulated in Table (7). 20% copper on pumice gave a conversion of 44% at 300°C which fell to 36% in 6 hours, while 20% copper on asbestos at the same temperature yielded a conversion of 85%; this conversion fell to 80% in 7 hours. It appears therefore that the use of asbestos as carrier instead of pumice results in an improved conversion.

Several concentrations of copper on asbestos were then tried. The principal objective of the study was not to determine the life of the catalysts, but to observe the conversions that could be obtained. However, in all these cases conversion data were taken over periods ranging from three to eight hours. The

conversions obtained with 10, 15 and 20% copper on asbestos at about 300°C are plotted in Fig.(15) as a function of process time. It may be observed that initially the conversion is low, but it rises to a stable value after about one and a half hours in all the cases. Subsequently the life apparently varies from catalyst to catalyst.

It is interesting to observe that with 10% of copper on asbestos, when the temperature was raised from 302 to 400°C, the conversion fell from 65% to 68%. This is probably due to the fact that at the higher temperature the catalytic activity of copper was so high that nitrobenzene was converted to undesired products, thus reducing the selectivity of the catalyst for the required reduction.

Experiments were also carried out with 20% nickel on asbestos. While in the case of copper an activation temperature of 350°C was chosen from several reported values, in the case of nickel it was considered desirable to try two activation temperatures, and then to carry out the reduction at the same temperature. It was found that with a lower activation temperature the catalyst was so active that most of the nitrobenzene was converted to undesirable products giving a conversion of only 55% to anilins; considerable

quantities of ammonia were observed to be formed. At the higher activation temperature of 325°C, a conversion of 85% was obtained which fell to 84% in 6 hours.

One run was also carried out with 20% chromium on asbestos. In this case a conversion 86.7% was obtained, and there was no diminution in conversion over a period of 4 hours.

From the foregoing results it appears that copper and chromium in certain concentrations can be used as catalysts for this reaction. But the performance of both these catalysts, it was thought, could be improved by using mixtures of copper and chromium or copper and nickel. Several runs were therefore carried out with these mixtures.

Mixtures of copper-nickel and copper-chromium on asbestos as carrier (Promoted and unpromoted)

(i) Copper-nickel catalysts

From the results discussed in the previous section, it is apparent that nickel is extremely active as a catalyst in this reaction, while copper is slightly less active. In order to improve the catalytic activity of copper, without at the same time resorting to more than the minimum requirement of the expensive nickel, experiments were carried out with several ratios of copper and nickel giving a total concentration of 20% (copper and nickel combined). The results are

summarised in Table (8) and plotted in Fig.(16).

It is apparent from Fig.(16) that a ratio of 1:1 gives the most favourable results. Before deciding to accept this ratio, it was considered worthwhile to make preliminary life tests for all these ratios. These are summarised in Table (8) and plotted in Fig.(17). It may be seen from Fig.(17) that as usual the conversion increases in all the cases to a maximum stable value after nearly  $1\frac{1}{2}$  hours of operation. Subsequently all the catalysts were run for  $4\frac{1}{2}$  hours, and it was found that none of them showed any diminution in activity. Although this time was too short to assess the suitability of a catalyst with respect to life, it nevertheless helped in deciding the optimum ratio of copper to nickel (1:1) to be employed.

The next factor investigated was the total concentration of copper and nickel that would give optimum results. In order to determine this value, the total concentration of copper plus nickel was varied from  $\frac{1}{2}$  to 25% using a ratio of 1:1 (Cu to Ni) in all the cases. These results are plotted in Fig.(18). It may be observed that while a concentration of 15% would be adequate, it is desirable to employ a concentration of 20%. A conversion of 90% can be obtained

with this concentration.

(ii) Copper-chromium catalyst

Chromium is known to add stability and life to a copper catalyst. Experiments were therefore carried out with several ratios of copper to chromium, giving a total concentration of 20% (copper plus chromium). The results are summarized in Table (8) and plotted in Fig.(19). As in the case of copper and nickel, here too the most favourable results are obtained with a ratio of 1:1 (copper to chromium).

Using a ratio of 1:1, the effect of total concentration of copper plus chromium was then investigated. The results are summarized in Table (8) and plotted in Fig.(20). It may be seen that here also a concentration of 20% gave the most favourable results, a conversion of about 89% being obtainable with this concentration and a ratio of 1:1 (copper:chromium).

(iii) Copper-nickel and copper-chromium promoted with cadmium or thorium

From the results discussed in the foregoing section, it is clear that a 20% concentration of copper and nickel in the ratio of 1:1 gave a conversion of 90% only. While the conversion could probably be improved at higher values of  $W/F$ , it was considered desirable to determine if at the same  $W/F$  and temperature, the

conversion could be improved by using a promoter such as cadmium. The results obtained with several percentages of cadmium on a copper-nickel catalyst supported on asbestos are summarized in Table (8), and plotted in Fig.(20). The percentage of cadmium in all the cases was based on the total weight of copper and nickel in the catalyst. From Fig.(21) it may be seen that a concentration of 15% cadmium in the catalyst gave a conversion of 93% as against 90% obtained without a promoter. This was a distinct improvement, and therefore it was concluded that if a copper-nickel catalyst is to be used, it is best to promote it with cadmium in the proportion indicated.

The effect of cadmium as promoter on a copper-chromium catalyst was then investigated. Here too the ratio of copper to chromium was maintained at 1:1 with a total concentration of 20% and a cadmium concentration of 20% based on copper and chromium. It was found that the conversion increased from 89% to 90.5%.

The effect of thorium as promoter on the same copper-chromium catalyst was then investigated. The result obtained with 15% thorium is tabulated in Table (8), from which it may be seen that thorium actually reduced the conversion from 89 to 78%.

Further runs with thorium were therefore not carried out.

(c) Life test on selected catalyst

From the foregoing section it may be concluded that a catalyst prepared from copper and nickel in the proportion of 1:1 and in a concentration of 20% on asbestos as carrier, using 15% cadmium (based on total weights of copper plus nickel) as promoter gives the most favourable results. It was therefore decided to conduct a series of life tests on this catalyst.

To start with, the life test was carried out by operating the reactor for about 6 hours in a day, shutting it off, and continuing the run the next day. By this method of operation the catalyst was found to retain its activity for over 25 hours. Subsequently this method of life test was abandoned since it was thought that frequent heating and cooling might have a detrimental effect on catalyst life.

A continuous run was then carried out at 302°C and at  $W/F = 34.54$ , and it was found that this catalyst gave a conversion of 96% for 59 hours, after which it fell rapidly. This is shown graphically in Fig.(22).

Since kinetic studies had not been made at this stage, we were not sure whether we were not operating at too high a value of  $W/P$ . If this were so, the catalyst was being used in excess of the



required quantity, and therefore the life value at this  $W/F$  would be misleading. Life data should normally be taken at a portion away from the flat region of the  $x$  vs  $W/F$  curve, since in that region we would be sure of utilizing the full catalytic activity.

In the subsequent life test the value of  $W/F$  was 24.8 at the same temperature ( $302^{\circ}\text{C}$ ), and a conversion of about 79% was obtained. From this result it is obvious that we were operating away from the flat portion, and the results obtained would be reliable and true. These results are plotted in Fig.(23). Here the conversion fell after about 55 hours of operation. As 55 hours is too short a life for a catalyst to be of any industrial use, attempts were made to regenerate the catalyst. This consisted in heating the catalyst at  $400^{\circ}\text{C}$  in a stream of air for nearly  $1\frac{1}{2}$  hours. After this treatment, when hydrogen was passed through the catalyst, a considerable quantity of nitrobenzene which had blocked the catalyst pores was removed. When life test was again carried out with this catalyst, it was found to give 79% conversion again for a period of 55 hours. The catalyst was again regenerated in the same manner, and it was found that the conversion could be brought back to 79%. All these values are plotted in Fig.(23).

(d) Final choice of catalyst

On the basis of the preliminary catalyst screening data, and the life test reported above, the catalyst finally chosen for detailed studies was:

Catalyst: Copper plus nickel in the ratio of 1:1  
and in a concentration of 20%.

Carrier: Asbestos.

Promoter: Cadmium in 15% concentration on the  
weight of copper plus nickel.

(e) Kinetic studies

A complete kinetic analysis of the reaction would involve (1) evaluation of mass transfer effects, (2) investigation of the effect of space velocity and temperature on conversion, and (3) development of an appropriate rate equation.

In the studies reported below, factors 1 and 2 have been fully evaluated, while a preliminary study has been made of factor 3.

(1) Effect of mass transfer

Before developing a rate equation for any given reaction, it is necessary to ensure that this is done under conditions where mass transfer is not effective. The principal factor influencing mass transfer is the velocity of reactants through the reactor. If this velocity were maintained sufficiently high, so that

concentration gradients across the film surrounding the catalyst particles may be neglected, then the effect of mass transfer can also be considered to be negligible, and the concentration of the reactants and products in the bulk of the fluid may be considered to be the same as that on the catalyst surface. Maintenance of this condition before the development of a rate equation is essential since the rate equation is based on concentrations on the catalyst surface.

In making kinetic studies under conditions where the effect of mass transfer is uncertain, two distinct effects have to be considered: (1) the mass transfer effect; (2) and the kinetic effect. In order to evaluate the mass transfer effect it is obvious that the kinetic effect should be maintained constant. In the case of reactions controlled by mass transfer the effect of temperature will not be as significant as in the case of reactions controlled by kinetic effects.

In the reaction under study the kinetic effect was maintained constant by operating the reactor at the same value of  $W/F$ . At this value of  $W/F$  the effect of velocity change was determined by varying both  $W$  and  $F$  but keeping the ratio constant. In practice this was found to be difficult, and therefore a series of runs

were made with different catalyst weights in the reactor, and plots of  $W/F$  vs conversion were determined for each. Based on these plots, conversion at any desired value of  $W/F$  was determined as a function of feed velocity. The results are tabulated in Table (9) and plots of  $W/F$  vs conversion for catalyst weights of 15, 20 and 25 gm. are shown in Fig.(24a). Beyond  $W/F=25$  the three curves tend to merge together, but below this value the effect of mass transfer is apparent, the conversion being sufficiently higher for larger weights of catalyst and therefore for higher values of feed rate (or velocity). A plot of feed velocity vs conversion for  $W/F=25$  appears in Fig.(24b), from which it is apparent that even at this low value of  $W/F$  the effect of mass transfer can be neglected if the velocity is maintained above 1.85 ft./sec.

In all the kinetic runs reported below, it was therefore ensured that the feed velocity was always above this value. Practically this was achieved by using a catalyst weight of 20 gm.

(ii) Effect of hydrogen to nitrobenzene ratio

According to the data available in the literature a considerable excess of hydrogen has to be used. In order to determine exactly the ratio of hydrogen to nitrobenzene that would give maximum conversion, a series of experiments was carried out at a temperature of 302°C and  $W/F=34.54$  in which the ratio of hydrogen to

nitrobenzene was varied approximately from 3 to 5. These results are plotted in Fig.(25), from which it may be seen that the ratio of 4.5:1 is optimal.

(iii) Development of a rate equation

Several experiments were carried out at a ratio of 5:1 (hydrogen:nitrobenzene) in which both the space velocity and temperature were systematically varied. At each of four chosen temperatures, 250, 302, 325 and 350°C, 6 to 8 runs were carried out to determine the courses of W/F vs conversion curves. The results are tabulated in Table (10) and plotted in Figs.(26,27,28). The curve for 350°C is not shown since at this high temperature the catalyst was too active and undesirable side products were produced.

The simple correlation suggested by Charde and Slipceevich\*

$$r = 0.475 \sqrt{p_{NO_2} p_{H_2}}$$

was not found to represent our data satisfactorily. It is believed that the correlation suggested by these workers may be in error for the following reasons:

- (1) adsorption effects have not been taken into account;
- (2) the life of the catalyst according to the graph

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\* See reference (11) in Chapter II.

shown in their paper was less than  $1\frac{1}{2}$  hours, and it is likely that this interfered with an accurate correlation of the data; and (3) according to the figures published by them conversions above 80% were never obtained, so that the correlation could not be tested beyond this conversion.

Our own attempts to work out the catalytic mechanism of the reaction were not successful since all the  $W/F$  vs conversion curves could be broken into two regions, each constituting a straight line. The conversion at each temperature increased linearly up to a certain point beyond which there was practically no increase in conversion. Simplified equations were developed for several cases including (1) surface reaction, (2) adsorption of hydrogen, (3) adsorption of nitrobenzene, and (4) reaction between dissociated hydrogen and nitrobenzene. None of these equations was found to represent the data satisfactorily. Attempts to develop a rate equation at this stage were not pursued since it was decided to investigate the effect of pressure which required a metallic reactor.

Tables

TABLE OF SYMBOLS

- B - reactant component nitrobenzene
- C - reactant component hydrogen
- $C_p^{\circ}$  - heat capacity, cal./°K./mole
- $\Delta G_f^{\circ}$  - free energy of formation, K-cal./mole
- $\Delta G_r^{\circ}$  - free energy of reaction, K-cal./mole
- $\frac{G_T^{\circ} - H_0^{\circ}}{T}$  - free energy function, cal./°K./mole
- $\Delta H_c^{\circ}$  - heat of combustion, K-cal./mole
- $\Delta H_f^{\circ}$  - heat of formation, K-cal./mole
- $\Delta H_r^{\circ}$  - heat of reaction, K-cal./mole
- $H_T^{\circ} - H_0^{\circ}$  - enthalpy function, K-cal./mole
- $\Delta H_v^{\circ}$  - heat of vaporization, K-cal./mole
- K - equilibrium constant
- $K_{\gamma}$  - fugacity coefficient
- n - number of moles
- R - gas constant, cal./°K./mole
- R - product component aniline
- S - product component water
- $S^{\circ}$  - entropy, cal./°K./mole
- T - temperature, °K.
- x - moles of aniline formed at equilibrium per mole of nitrobenzene fed
- W/F - gm./gm. mole/hr.



GREEK SYMBOLS

$\pi$  - total pressure, atmos.

$\mathcal{V}$  - fugacity

SUBSCRIPTS & SUPERSCRIPTS

B,C,R & S - components taking part in the reaction

b,c,r & s - stoichiometric proportions of B,C,R & S  
taking part in the reaction

**Table of Symbols**

TABLE (1)  
 THERMODYNAMIC FUNCTIONS OF NORMAL HYDROGEN  
 IN THE IDEAL GASEOUS STATE<sup>(6)</sup>

$T$	$C_p^\circ$	$S^\circ$	$H_T^\circ - H_0^\circ$	$\frac{C_T^\circ - H_0^\circ}{T}$	$\Delta G_T^\circ$
298.16	6.892	31.211	2,023.8	-24.423	- 7.281
300	6.895	31.253	2,036.5	-24.465	- 7.339
400	6.974	33.250	2,731.0	-26.422	-10.568
500	6.993	34.809	3,429.5	-27.950	-13.974
600	7.008	36.085	4,129.5	-29.203	-17.520
700	7.035	37.167	4,831.5	-30.265	-21.184
800	7.078	38.108	5,537.4	-31.186	-24.950
900	7.139	38.946	6,248.0	-32.004	-28.803
1,000	7.217	39.704	6,965.8	-32.738	-32.735
1,100	7.308	40.395	7,692.0	-33.402	-36.740
1,200	7.404	41.033	8,427.5	-34.010	-40.812
1,300	7.505	41.629	9,173.2	-34.573	-44.944
1,400	7.610	42.190	9,928.7	-35.098	-49.134
1,500	7.713	42.720	10,694.2	-35.590	-53.382

TABLE (2)

THERMODYNAMIC FUNCTIONS OF ANILINE IN THE IDEAL GASEOUS STATE<sup>(3)</sup>

T	$C_p^\circ$	$S^\circ$	$H_T^\circ - H_0^\circ$	$\frac{G_T^\circ - H_0^\circ}{T}$	$\Delta H_f^\circ$	$\Delta G_f^\circ$
298.15	25.91	76.28	4,349	-61.69	+20.80	+39.90
300	26.07	76.44	4,397	-61.78	+20.78	+40.01
350	30.28	80.78	5,007	-64.19	+20.12	+43.36
400	34.17	85.08	7,421	-66.53	+19.54	+46.64
450	37.68	89.31	9,218	-68.83	+19.03	+50.10
500	40.81	93.45	11,182	-71.09	+18.59	+53.53
600	46.09	101.37	15,536	-75.48	+17.88	+60.59
700	50.32	108.81	20,365	-79.72	+17.34	+67.76
800	53.79	115.76	25,575	-83.79	+16.95	+74.97
900	56.71	122.27	31,105	-87.71	+16.69	+82.28
1,000	59.18	128.37	36,903	-91.47	+16.55	+89.55

TABLE (3)

THERMODYNAMIC FUNCTIONS OF WATER IN THE IDEAL  
GASEOUS STATE<sup>(6)</sup>

T	$C_p^\circ$	$S^\circ$	$H_T^\circ - H_0^\circ$	$\frac{G_T^\circ - H_0^\circ}{T}$	$\Delta H_T^\circ$	$\Delta G_T^\circ$
298.16	8.025	45.106	2,367.7	-37.165	-57.7979	-54.6351
300	8.026	45.154	2,382.0	-37.214	-57.8028	-54.6159
400	8.185	47.490	3,194.0	-39.505	-58.040	-53.518
500	8.415	49.344	4,025.5	-41.293	-58.273	-52.360
600	8.677	50.903	4,882.2	-42.766	-58.493	-51.154
700	8.959	52.269	5,771.5	-44.024	-58.696	-49.913
800	9.254	53.490	6,689.6	-45.128	-58.882	-48.643
900	9.559	54.599	7,634.7	-46.116	-59.055	-47.347
1,000	9.861	55.618	8,608.0	-47.010	-59.214	-46.030
1,100	10.145	56.564	9,606.3	-47.831	-59.360	-44.700
1,200	10.413	57.451	10,630.0	-48.593	-59.497	-43.357
1,300	10.668	58.287	11,679.0	-49.303	-59.622	-41.999
1,400	10.909	59.078	12,753.0	-49.969	-59.735	-40.636
1,500	11.134	59.830	13,848.0	-50.598	-59.841	-39.263

TABLE (4)

HEAT OF REACTION AS A FUNCTION OF TEMPERATURE

$T$	$\frac{1}{T} \times 10^2$	$\frac{\Delta H_R^0}{T}$	$\Delta H_R^0$
298	0.3356	-376.5437	-112.210
400	0.2500	-375.6416	-150.26
500	0.2000	-374.9051	-187.45
600	0.1667	-374.2994	-224.58
700	0.1429	-373.9070	-261.73
800	0.1250	-373.4135	-298.73
900	0.1111	-373.1021	-335.79
1,000	0.1000	-372.8566	-372.86

TABLE (5)

EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE

T	$\Delta G_T^\circ$	$-\frac{\Delta G_T^\circ}{T}$	Log K	K
300	-56.1460	187.15	40.8293	$6.750 \times 10^{40}$
400	-48.6448	121.612	26.7914	$6.184 \times 10^{26}$
500	-41.8950	83.79	18.353	$2.254 \times 10^{18}$
600	-35.3619	58.9365	12.9139	$8.202 \times 10^{12}$
700	-29.1377	41.625	9.09716	$1.251 \times 10^9$
800	-21.5442	26.93	5.9077	$8.8065 \times 10^5$
900	-10.689	11.877	2.620	$4.169 \times 10^2$
1,000	2.255	-2.255	-0.4923	$3.219 \times 10^{-1}$
1,100	23.786	-21.623	-4.7315	$1.856 \times 10^{-5}$
1,200	38.283	-31.9025	-6.9956	$1.010 \times 10^{-7}$
1,300	52.965	-40.742	-8.908	$1.236 \times 10^{-9}$
1,400	67.850	-48.25	-10.5471	$2.837 \times 10^{-11}$
1,500	83.938	-55.9959	-12.2537	$5.576 \times 10^{-13}$

RESULTS FOR MISCELLANEOUS CATALYSTS

Weight of catalyst = 20 gm.

Nitrobenzene rate = 0.1067 gm.mole/hr.



Sr. No.	Catalyst	Ignition temp. °C	Activation temp. °C	Reaction temp. °C	Conversion %	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)

CHARCOALS

1	Activated cocconut shell charcoal	-	-	350	3	-
2	10% cupric chloride impregnated on activated cocconut shell charcoal	-	-	a) 340	25	Conversion fell from 25 to 9.5 in 4½ hrs.
				b) 400	44.1	Conversion fell from 44 to 30 in 3 hrs.

3 10% cadmium chloride impregnated on activated cocconut shell charcoal

- - - 312 41 -

BAUXITE

1	Shevroy A bauxite (-14,+30 mesh)	-	450	300	nil	-
2	6% Ag on bauxite	a) 300	300	300	30.5	Conversion fell from 30.5 to 19.9 in 3 hrs.
		b) 350	300	300	25	-



(1)	(2)	(3)	(4)	(5)	(6)	(7)
				<u>OTHERS</u>		
1	Copper chromite	450	360	302	90.7	Conversion fell from 90.7 to 60 in 3 hrs.
2	Cuprous ammonium nitrate on asbestos	-	250	300	40	Conversion fell from 40 to 16.6 in 2 hrs.
3	Copper metal powder	-	350	300	nil	-
4	Copper from copper nitrate	400	300	280	-	Conversion fell rapidly (after few minutes) from practically 100 to nil as observed from change of colour of product.

TABLE (7)  
RESULTS FOR SUPPORTED CU, NI, CR CATALYSTS

Weight of catalyst 20 gm.  $C_6H_5NO_2:H_2 = 1:4.5$

Nitrobenzene rate 0.1067 gm.mole/hr.

Cr. No.	Catalyst	Ignition temp. °C	Activation temp. °C	Reaction temp. °C	Conversion %	Remarks
<u>COPPER</u>						
1	20% Cu on pumice	200	350	300	44	Conversion fell from 44 to 36 in 6 hrs.
2	10% Cu on asbestos	200	350	a) 400	60.25	Conversion fell from 60.25 to 49 in 6 hrs.
				b) 302	85.5	No fall in conversion for 7 hours.
3	15% Cu on asbestos	200	350	302	85	Conversion fell from 85 to 82.5 in 7 hrs.
4	20% Cu on asbestos	200	350	300	85	Conversion fell from 85 to 80 in 7 hrs.
<u>NICKEL</u>						
1	20% Ni on asbestos	425	a) 325	302	85	Conversion fell from 85 to 84 in 6 hrs.
			b) 275	302	55	Considerable NH <sub>3</sub> formation; smell of hydrocarbon was predominant in the product.
<u>CHROMIUM</u>						
1	20% Cr on asbestos	400	375	302	86.7	Conversion unaltered over 4 hrs.

## RESULTS FOR MIXTURES OF Cu-Ni AND Cu-Cr CATALYSTS ON ASBESTOS AS CARRIER (PROMOTED &amp; UNPROMOTED)

Weight of catalyst = 20 gm.

 $C_6H_5NO_2:H_2 = 1:4.5$ 

Nitrobenzene rate = 0.1067 gm.mole/hr.

Sr. No.	Catalyst	Ignition temp. °C	Activation temp. °C	Reaction temp. °C	Conversion %	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)

COPPER-NICKEL

1	5% Cu+15% Ni on asbestos	425	325	302	86	Constant conversion for 5 hrs; catalyst promising
2	10% Cu+10% Ni on asbestos	425	325	302	89.5	--do--
3	15% Cu+5% Ni on asbestos	425	325	302	87.5	--do--
4	5% conc. of Cu+Ni (1:1) on asbestos	425	325	302	64	catalyst promising
5	10% conc. of Cu+Ni (1:1) on asbestos	425	325	302	82	--do--
6	15% conc. of Cu+Ni (1:1) on asbestos	425	325	302	89.5	--do--

TABLE (8) contd.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
7	20% conc. of Cu+Ni (1:1) on asbestos	425	325	302	90	catalyst promising
6	25% conc. of Cu+Ni (1:1) on asbestos	425	325	302	88.7	--do--
<u>COPPER--CHROMIUM</u>						
1	5% Cu+15% Cr on asbestos	400	375	302	89	--do--
2	10% Cu+10% Cr on asbestos	400	375	302	89.5	--do--
3	15% Cu+5% Cr on asbestos	400	375	302	87.5	--do--
4	10% conc. of Cu+Cr (1:1) on asbestos	400	375	302	79.5	--do--
5	15% conc. of Cu+Cr (1:1) on asbestos	400	375	302	87	--do--
6	20% conc. of Cu+Cr (1:1) on asbestos	400	375	302	89.5	--do--
7	25% conc. of Cu+Cr (1:1) on asbestos	400	375	302	87.5	--do--

(1)	(2)	(3)	(4)	(5)	(6)	(7)
<u>COPPER-NICKEL PROMOTED WITH CALCIUM</u>						
1	6% Cd on 10% Cu+10% Ni with asbestos carrier	425	325	302	90.5	Catalyst promising
2	11% Cd on 10% Cu+10% Ni with asbestos carrier	425	325	302	92.5	--do--
3	15% Cd on 10% Cu+10% Ni with asbestos carrier	425	325	302	93	Catalyst promising (Full life test studied)
4	25% Cd on 10% Cu+10% Ni with asbestos carrier	425	325	302	91	--do--
<u>COPPER-CHROMIUM PROMOTED WITH THORIUM</u>						
1	15% Th on 10% Cu+10% Cr with asbestos carrier	400	375	302	76	--
<u>COPPER-CHROMIUM PROMOTED WITH CALCIUM</u>						
1	20% Cd on 10% Cu+10% Cr with asbestos carrier	400	375	302	90.5	--

TABLE 192

EVALUATION OF THE MASS TRANSFER EFFICI. - DATA USING SEVERAL CATALYST WEIGHTS



Temperature = 302°C

Sr.No.	Weight of catalyst gm.	Feed Rate gm.mole/hr.			Conversion %
		nitrobenzene (3)	hydrogen (4)	combined (5)	
(1)	(2)	(3)	(4)	(5)	(6)
1	15	0.1443	0.6416	0.7959	51
2	15	0.1314	0.5810	0.7123	62.5
3	15	0.1185	0.5337	0.6522	76
4	15	0.1088	0.4896	0.5984	86
5	20	0.1704	0.7668	0.9372	74
6	20	0.1443	0.6416	0.7959	86
7	20	0.1185	0.5810	0.7123	91.5
8	20	0.1088	0.4896	0.5984	93.5
9	20	0.0956	0.4307	0.5263	94
10	25	0.241	1.08	1.321	65
11	25	0.1964	0.8837	1.080	87

TABLE (9) contd.

(1)	(2)	(3)	(4)	(5)	(6)
12	25	0.1704	0.7663	0.9372	90.5
13	25	0.1443	0.6416	0.7959	94
14	25	0.1313	0.5810	0.7123	95.5
15	25	0.1088	0.4896	0.5984	96
16	25	0.0956	0.4307	0.5263	96

TABLE (10)

EFFECT OF SPACE VELOCITY ON CONVERSION AT DIFFERENT  
TEMPERATURES

Minimum feed velocity = 1.05 ft./sec.

$C_6H_5NO_2 : H_2 = 1:5$

Sr.No. (1)	Temperature °C (2)	W/F (3)	Conversion % (4)
1	275	12.78	29
2	275	14.62	32.5
3	275	19.64	49
4	275	22.47	50.5
5	275	26.48	57.78
6	275	34.37	67.58
7	302	19.41	63
8	302	22.46	66
9	302	23.38	76
10	302	26.32	83
11	302	29.25	88
12	302	34.5	96
13	302	39.6	96

---contd.



TABLE (10) contd.

(1)	(2)	(3)	(4)
14	325	7.8	86
15	325	10.5	92
16	325	22.4	95.5
17	325	26.15	96
18	325	34.2	96
19	325	39.6	96
20	350	12.7	69
21	350	14.8	83.5
22	350	26.4	94.5
23	350	34.4	95.5
24	350	39.6	95.5

**Figures**

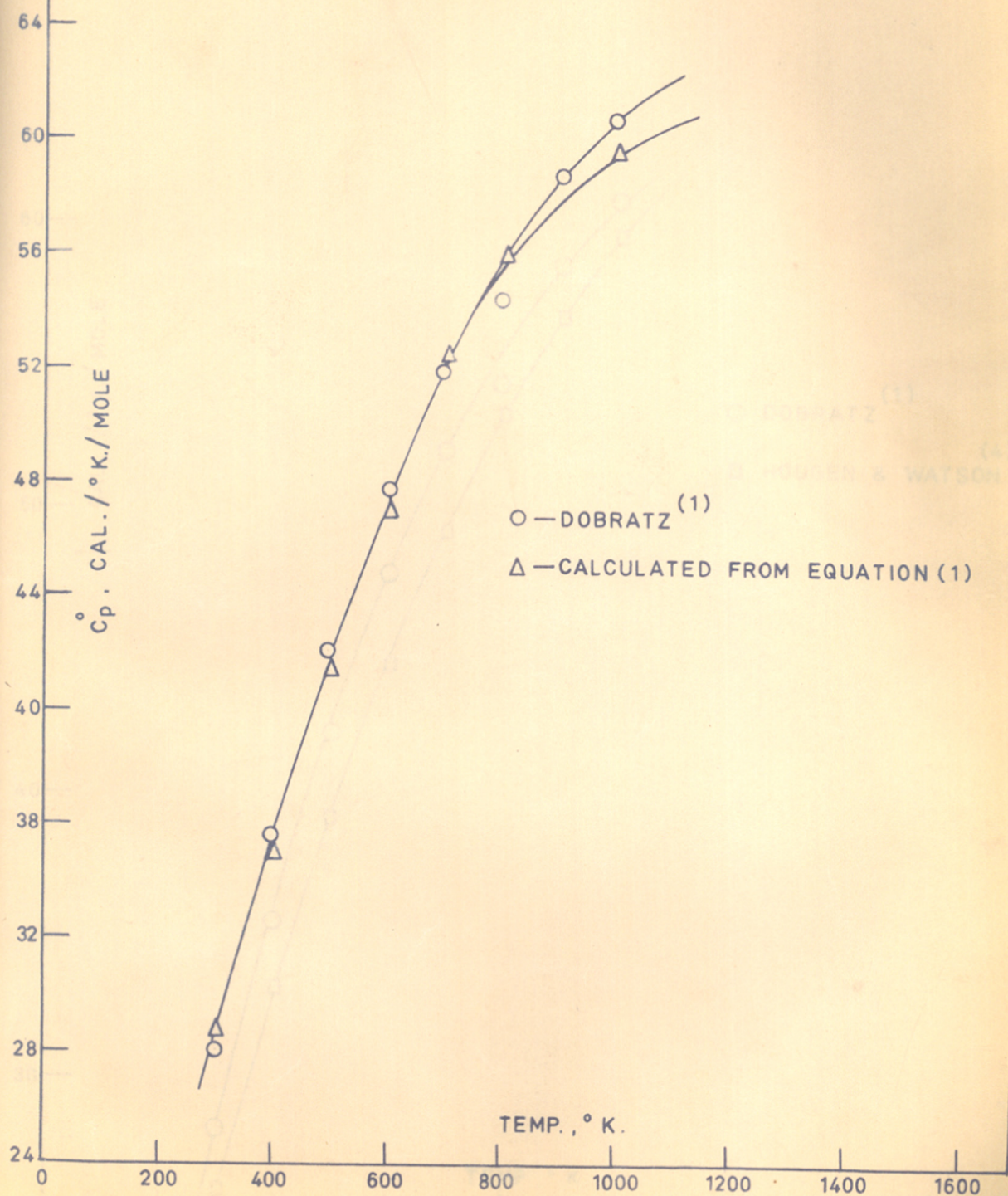


FIG. 1. COMPARISON OF THE CALCULATED VALUES (BY DOBRATZ'S METHOD<sup>(1)</sup>) OF THE HEAT CAPACITY OF NITROBENZENE WITH THE VALUES CALCULATED FROM EQN.(1)

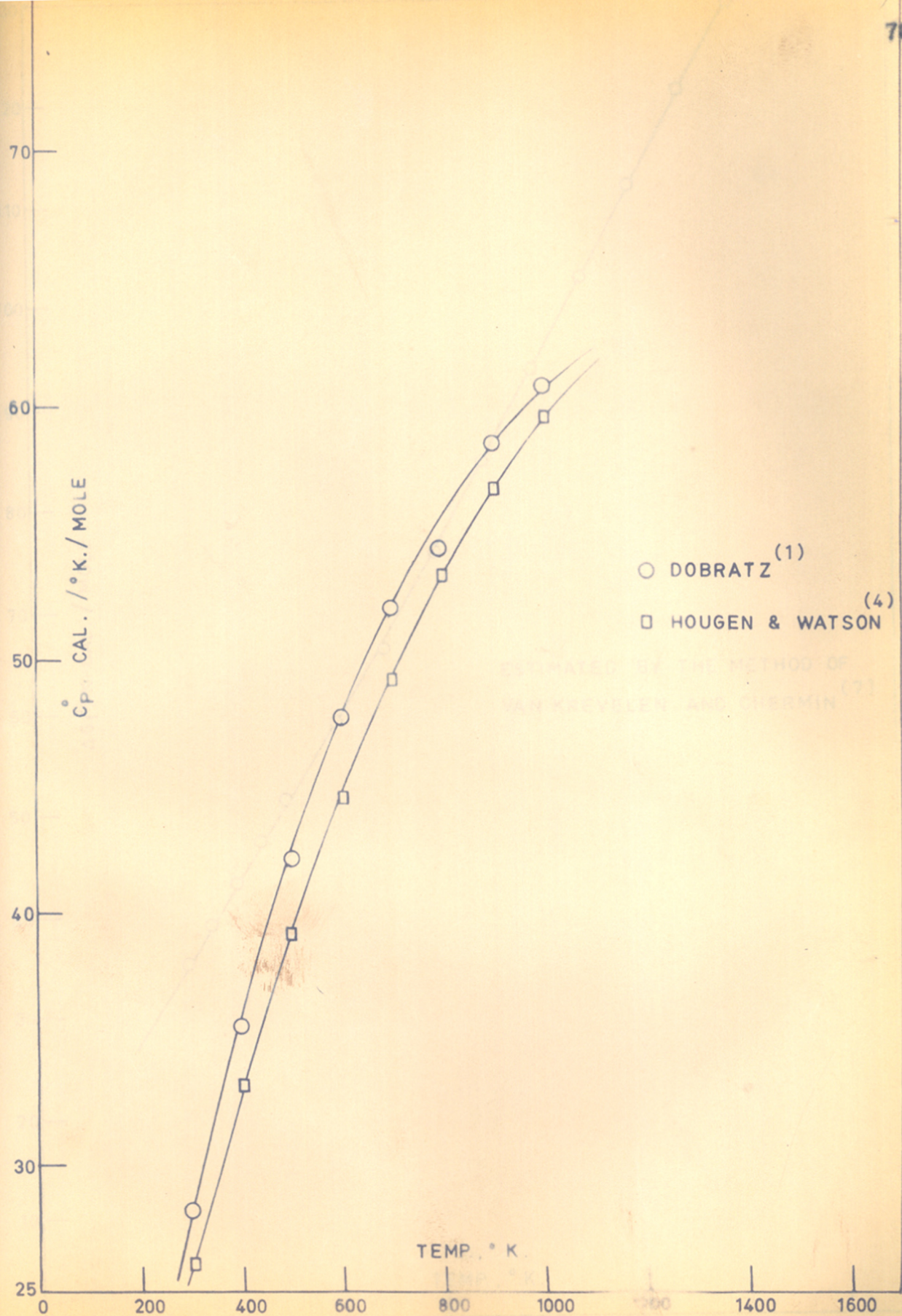


FIG. 2. ESTIMATED VALUES OF THE HEAT CAPACITY OF NITROBENZENE AS A FUNCTION OF TEMPERATURE

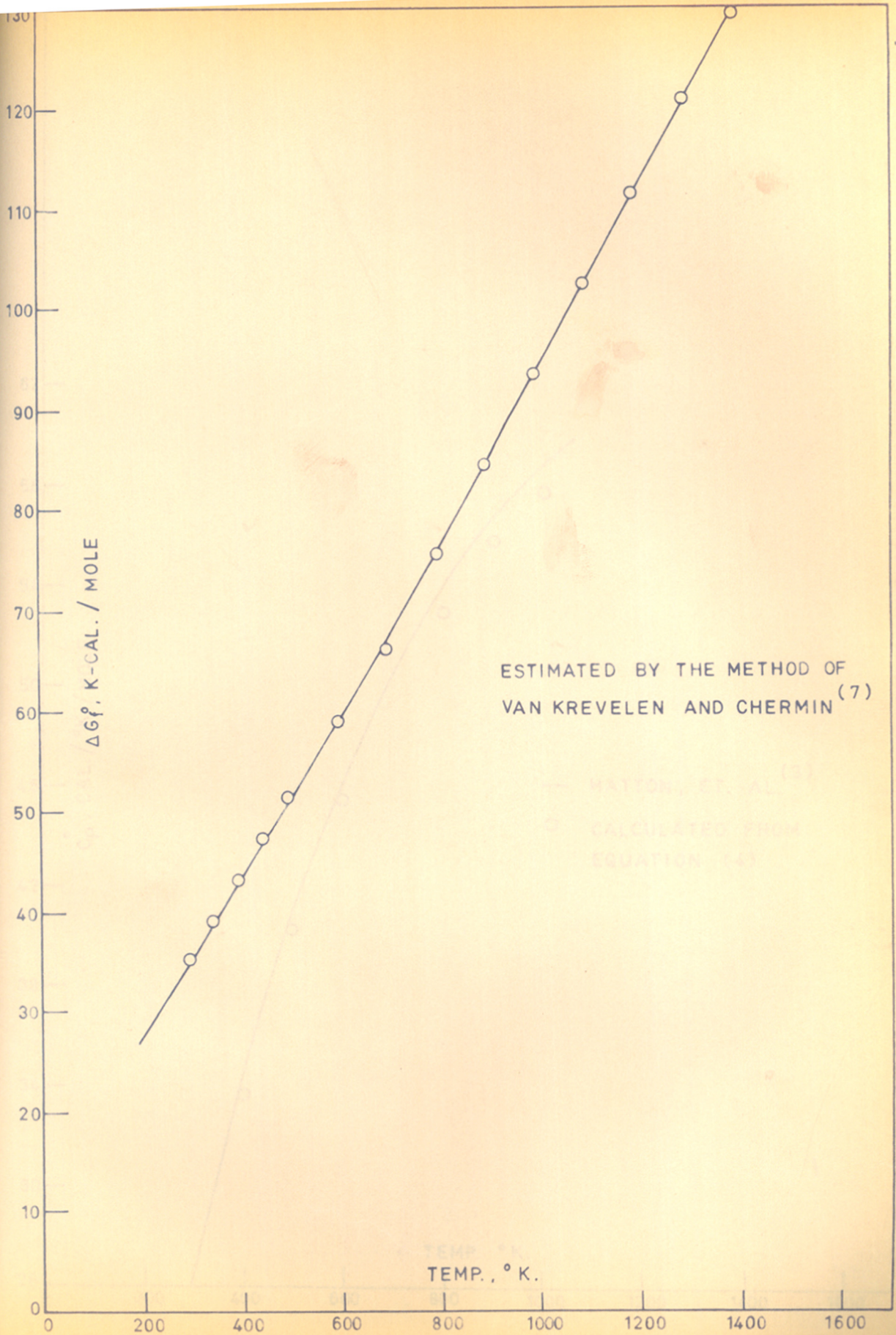


FIG. 3. FREE ENERGY OF FORMATION OF NITROBENZENE AS A FUNCTION OF TEMPERATURE

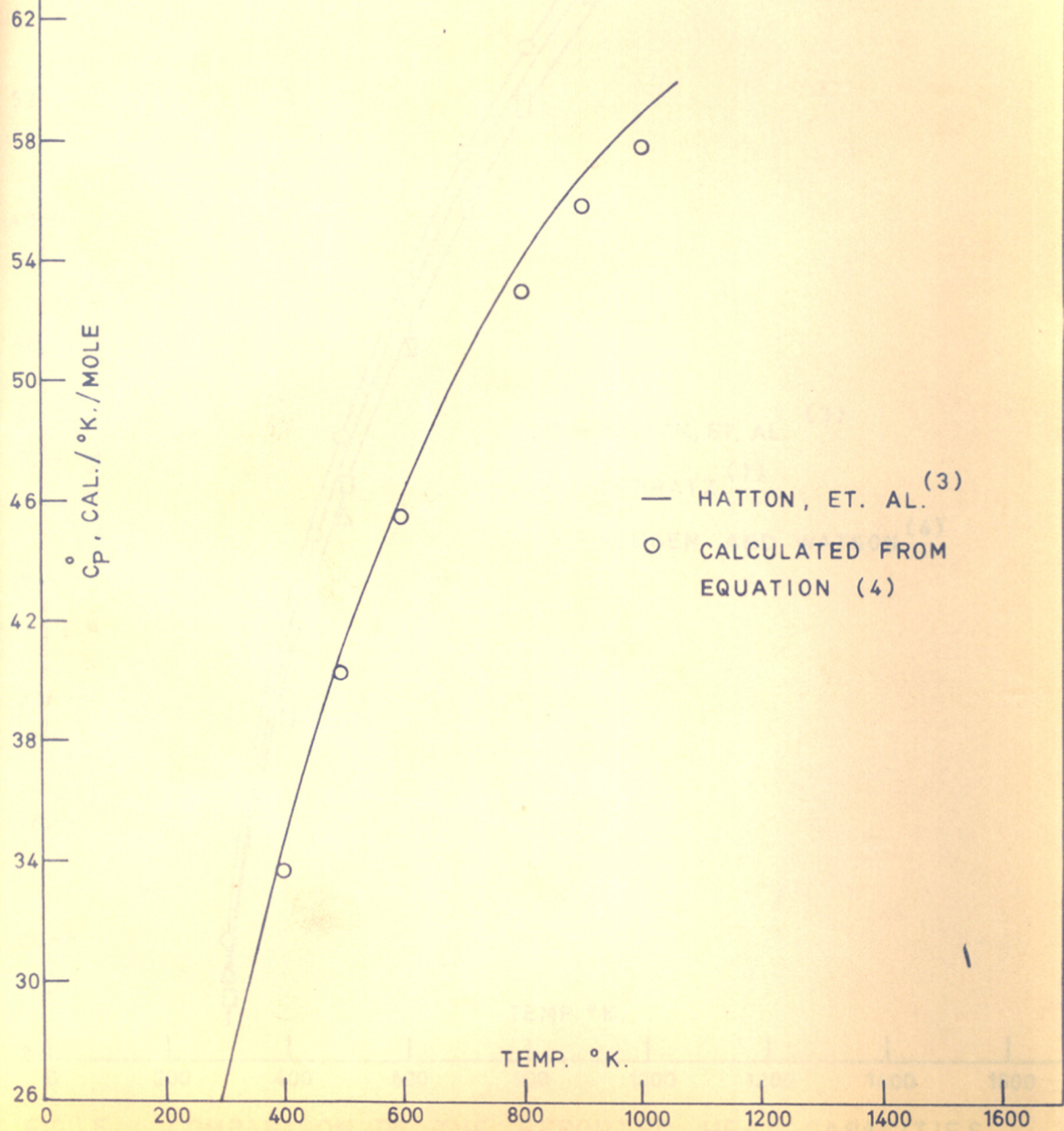


FIG. 4. COMPARISON OF THE REPORTED HEAT CAPACITIES OF ANILINE WITH THE VALUES CALCULATED FROM EQN.(4)

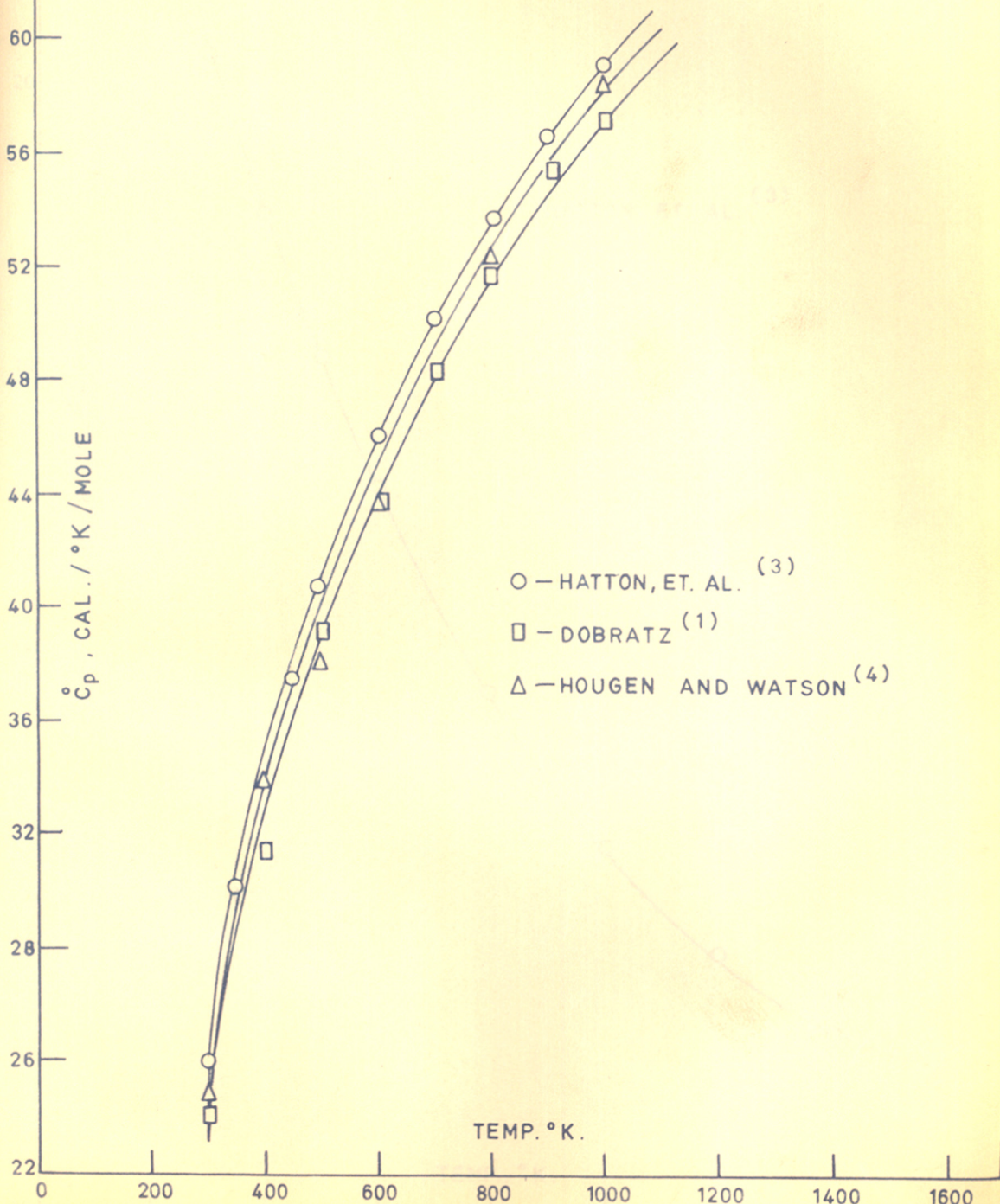


FIG. 5. COMPARISON OF THE REPORTED HEAT CAPACITIES OF ANILINE WITH THE VALUES CALCULATED BY DOBRATZ'S (1) AND HOUGEN & WATSON'S (4) METHODS

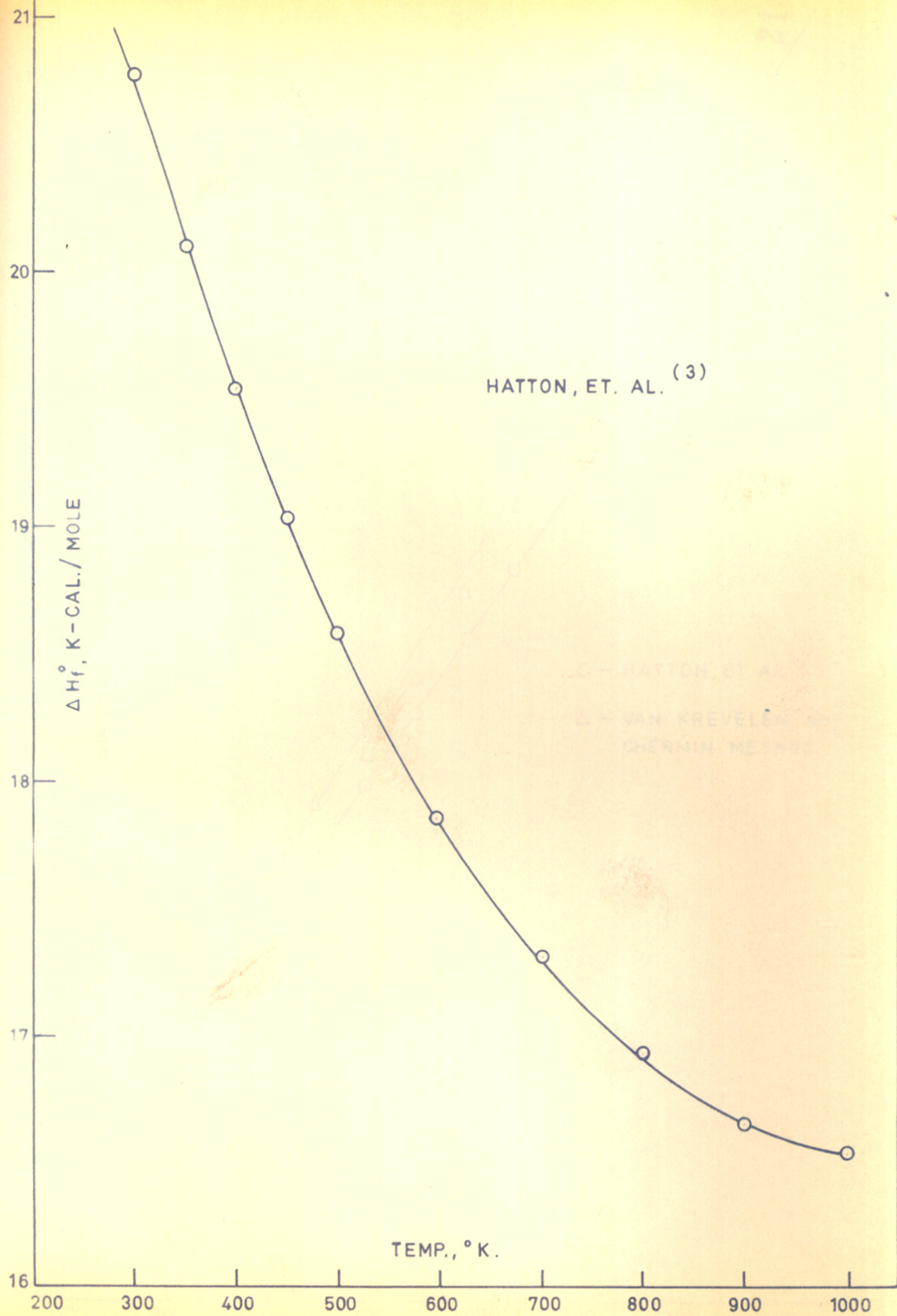


FIG. 6. HEAT OF FORMATION OF ANILINE AS A FUNCTION OF TEMPERATURE



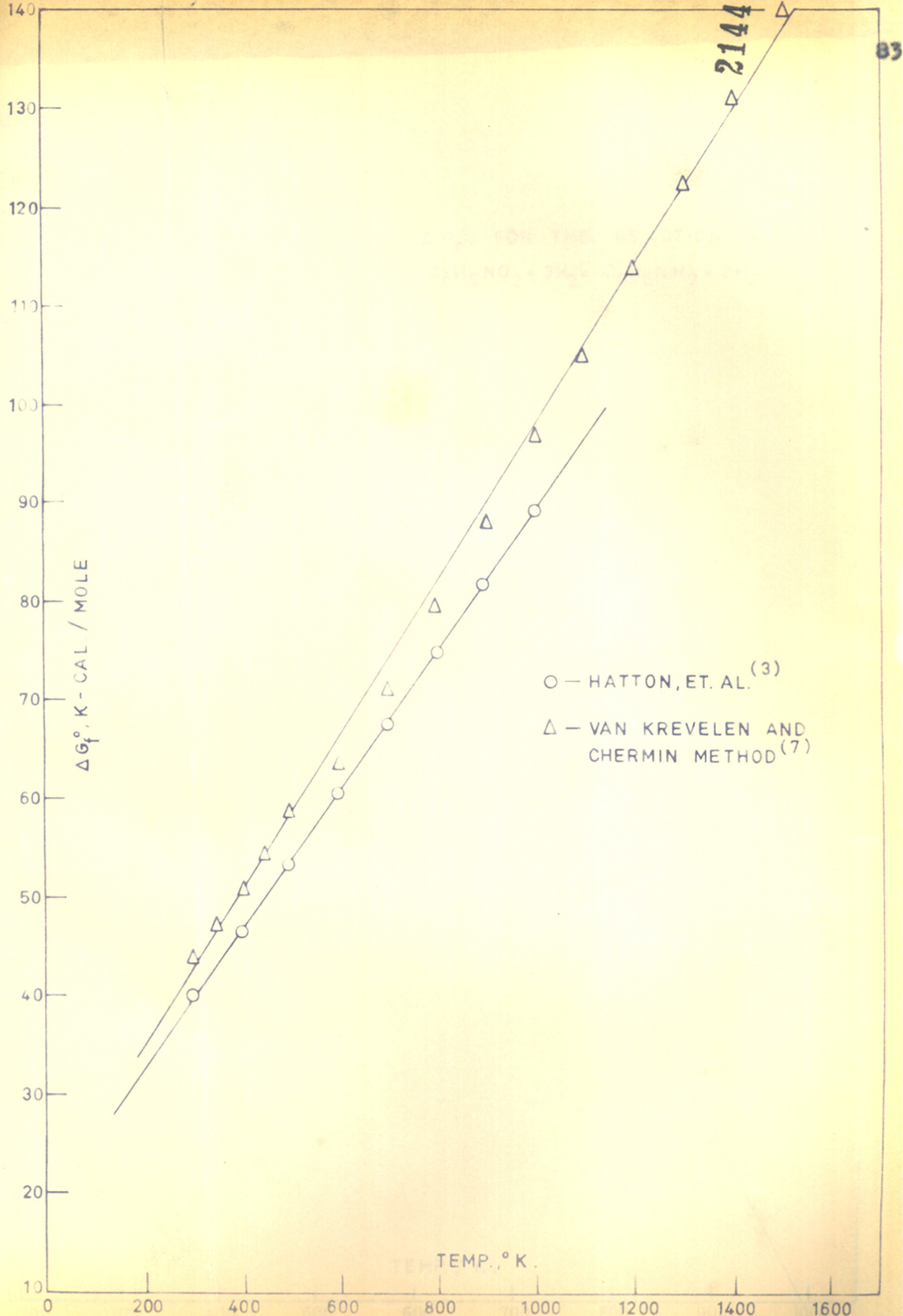


FIG. 7 FREE ENERGY OF FORMATION OF ANILINE AS A FUNCTION OF TEMPERATURE

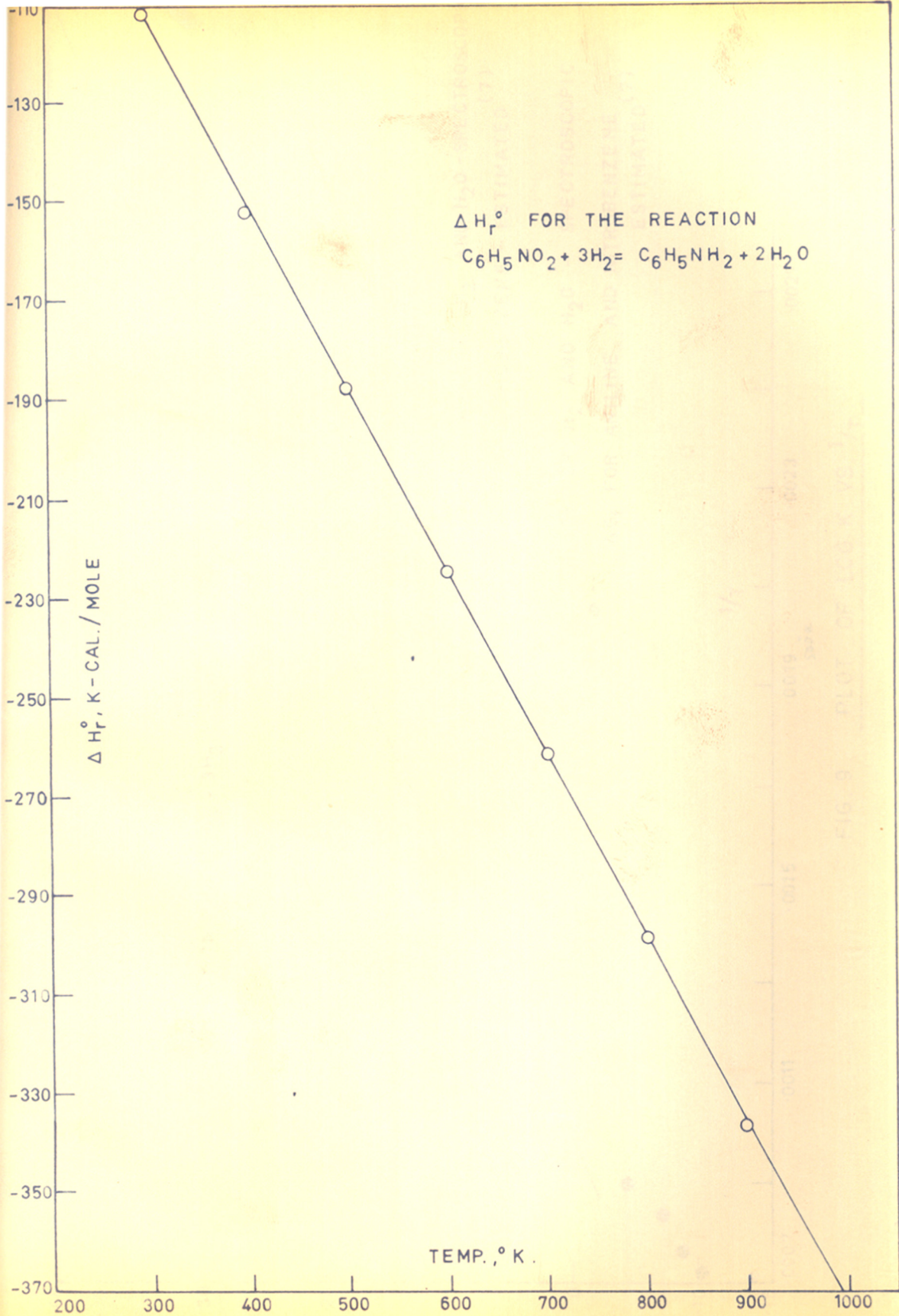


FIG. 8. HEAT OF REACTION AS A FUNCTION OF TEMPERATURE

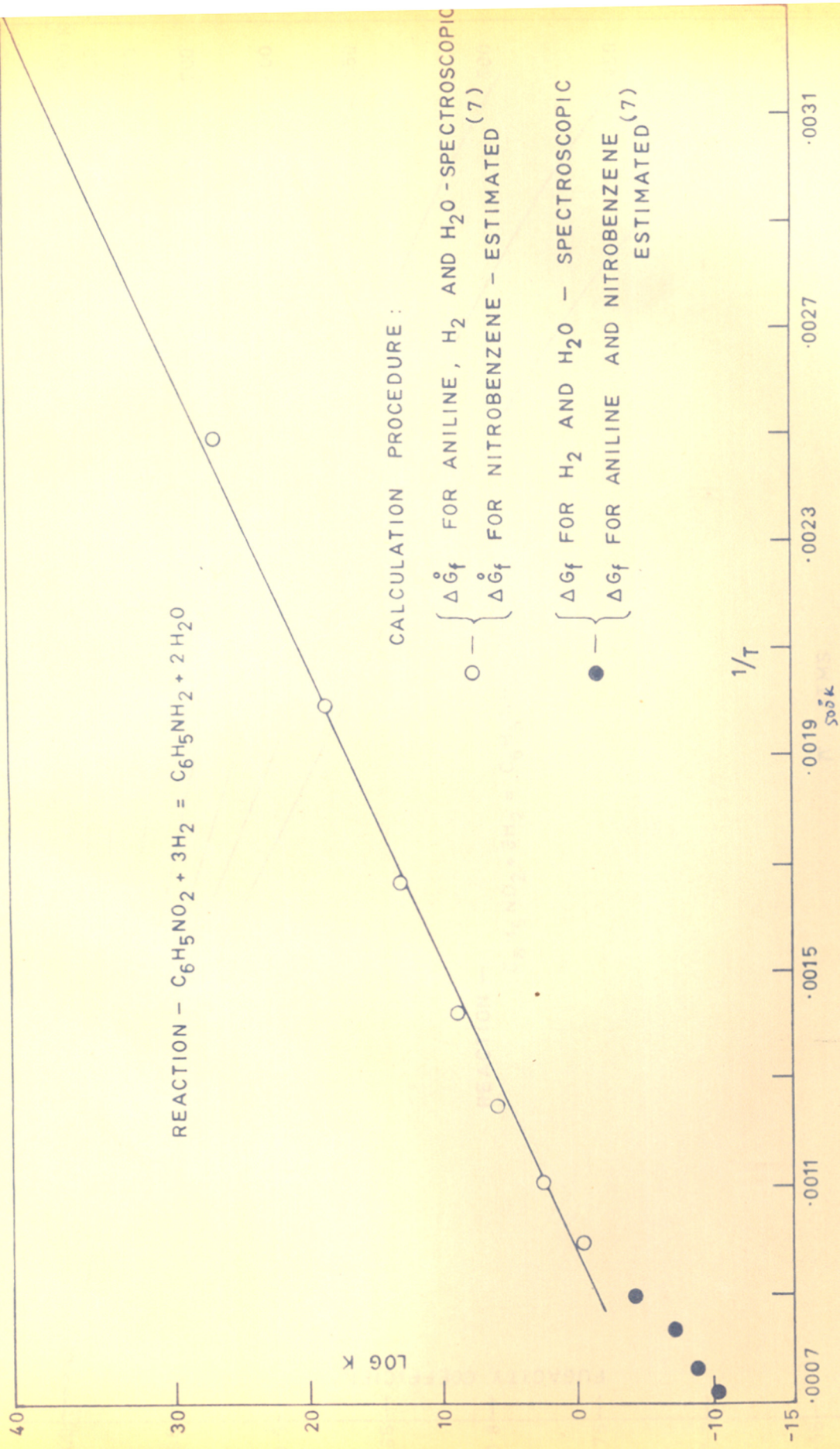


FIG. 9. PLOT OF LOG K VS.  $1/T$

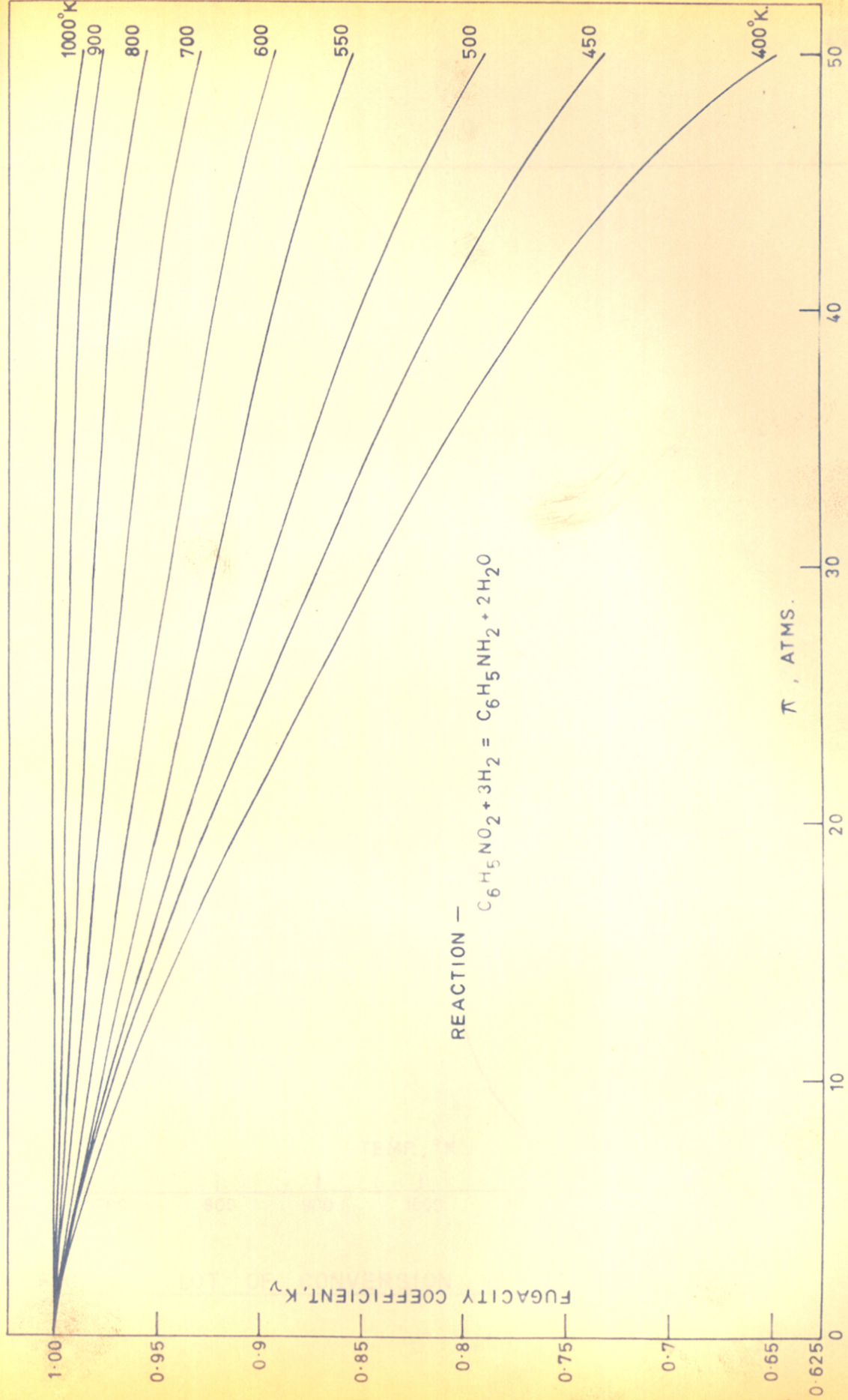


FIG. 10. FUGACITY COEFFICIENT TERM  $K_y$  AS A FUNCTION OF TEMPERATURE AND PRESSURE

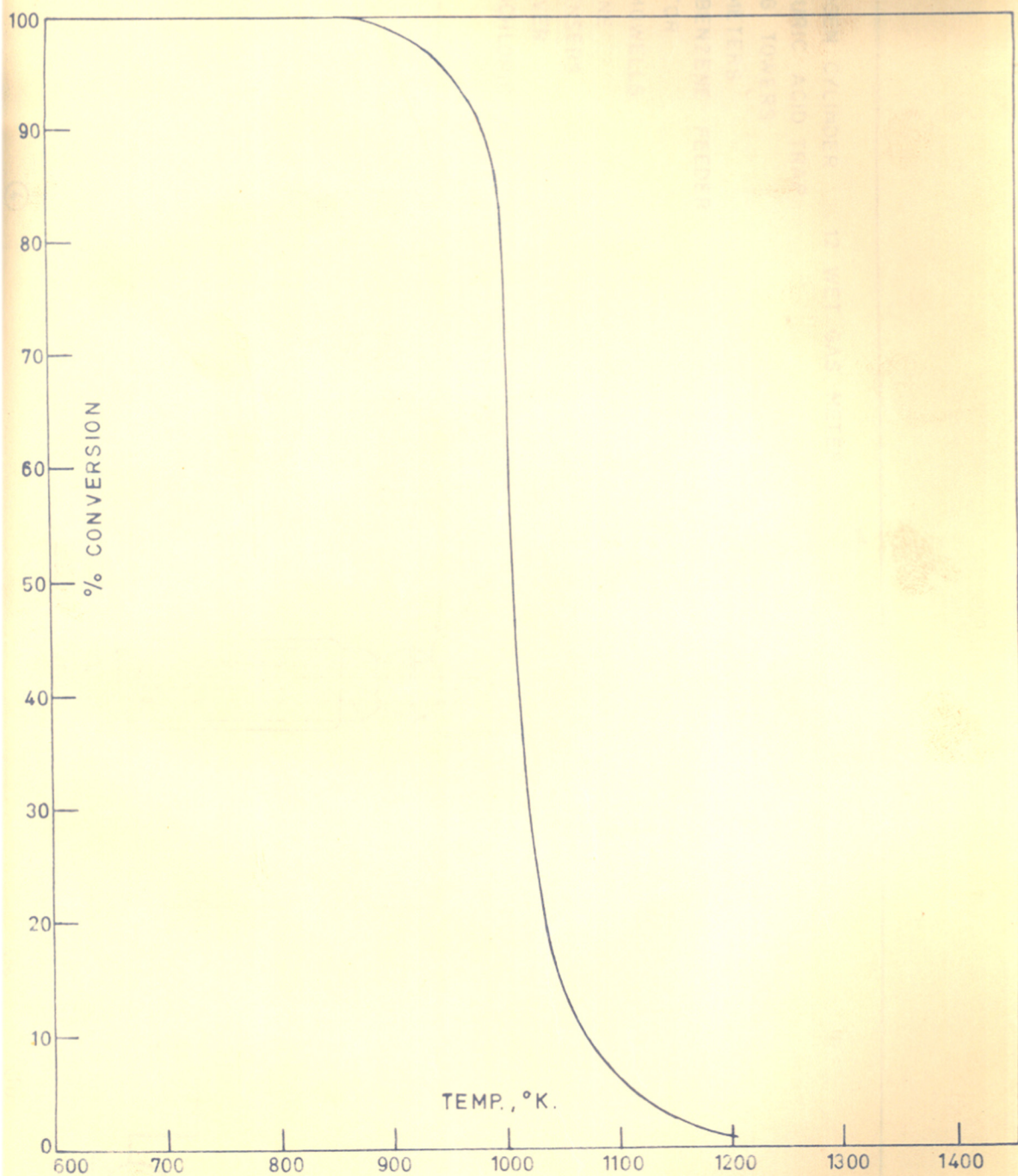


FIG. 11. PLOT OF CONVERSION VS. TEMPERATURE

- 1 HYDROGEN CYLINDER
- 2 SULPHURIC ACID TRAP
- 3 DRYING TOWERS
- 4 MANOMETERS
- 5 NITROBENZENE FEEDER
- 6 REACTOR
- 7 THERMOWELLS
- 8 CYCLONE
- 9 CONDENSERS
- 10 RECEIVER
- 11 HYDROCHLORIC ACID TRAP
- 12 WET GAS METER

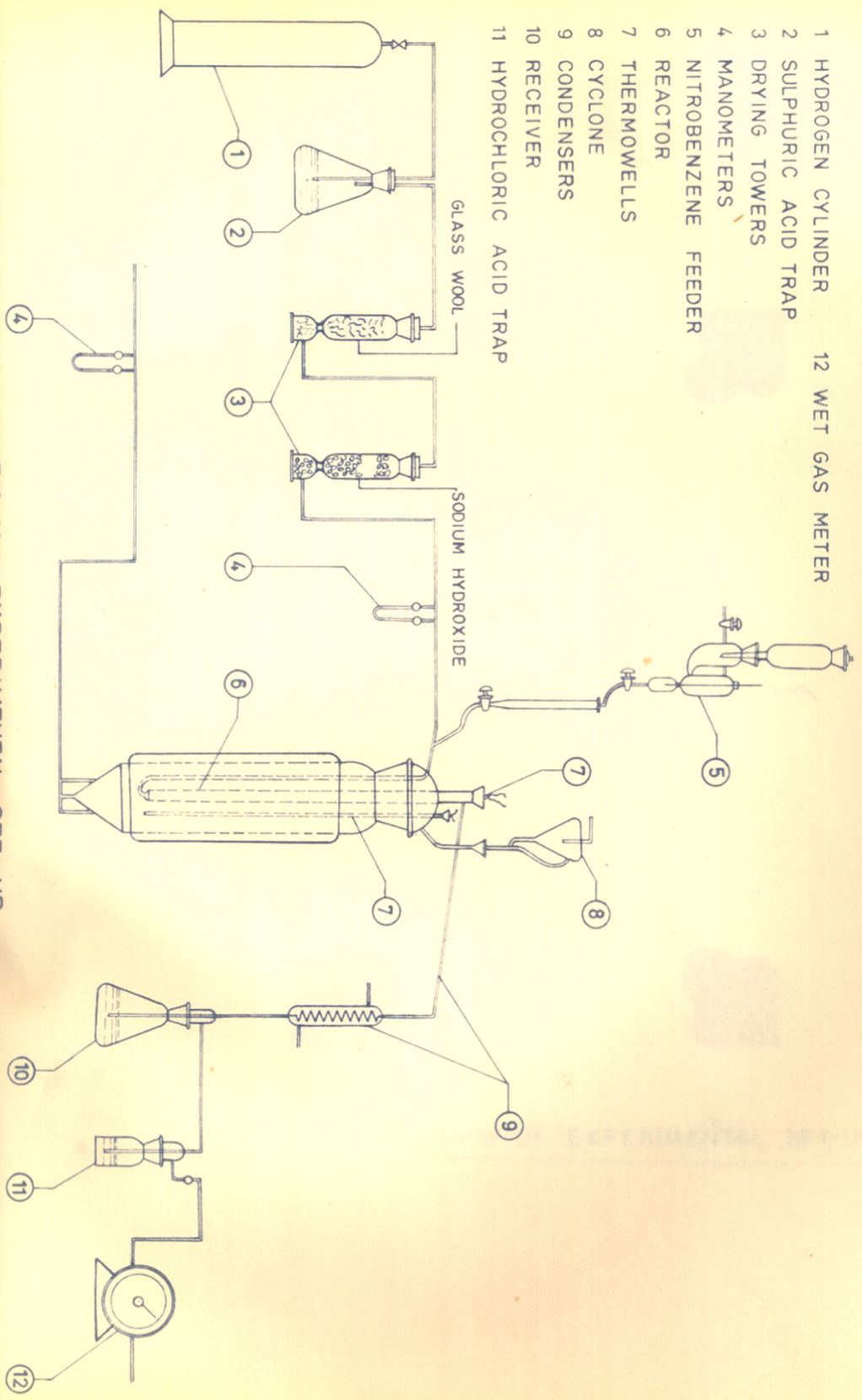
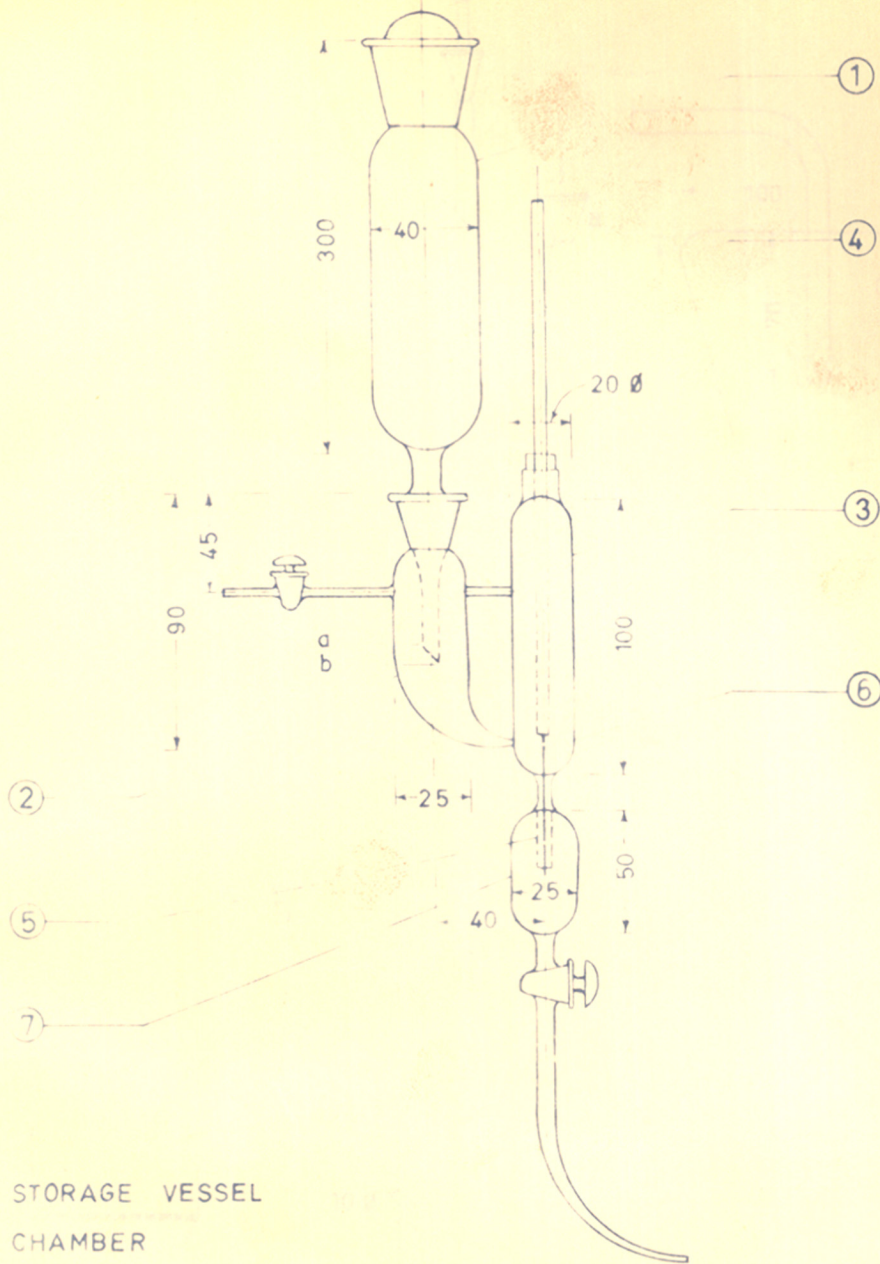


FIG. 12a. EXPERIMENTAL SET-UP



Fig. 12 b. PHOTOGRAPH OF EXPERIMENTAL SET-UP

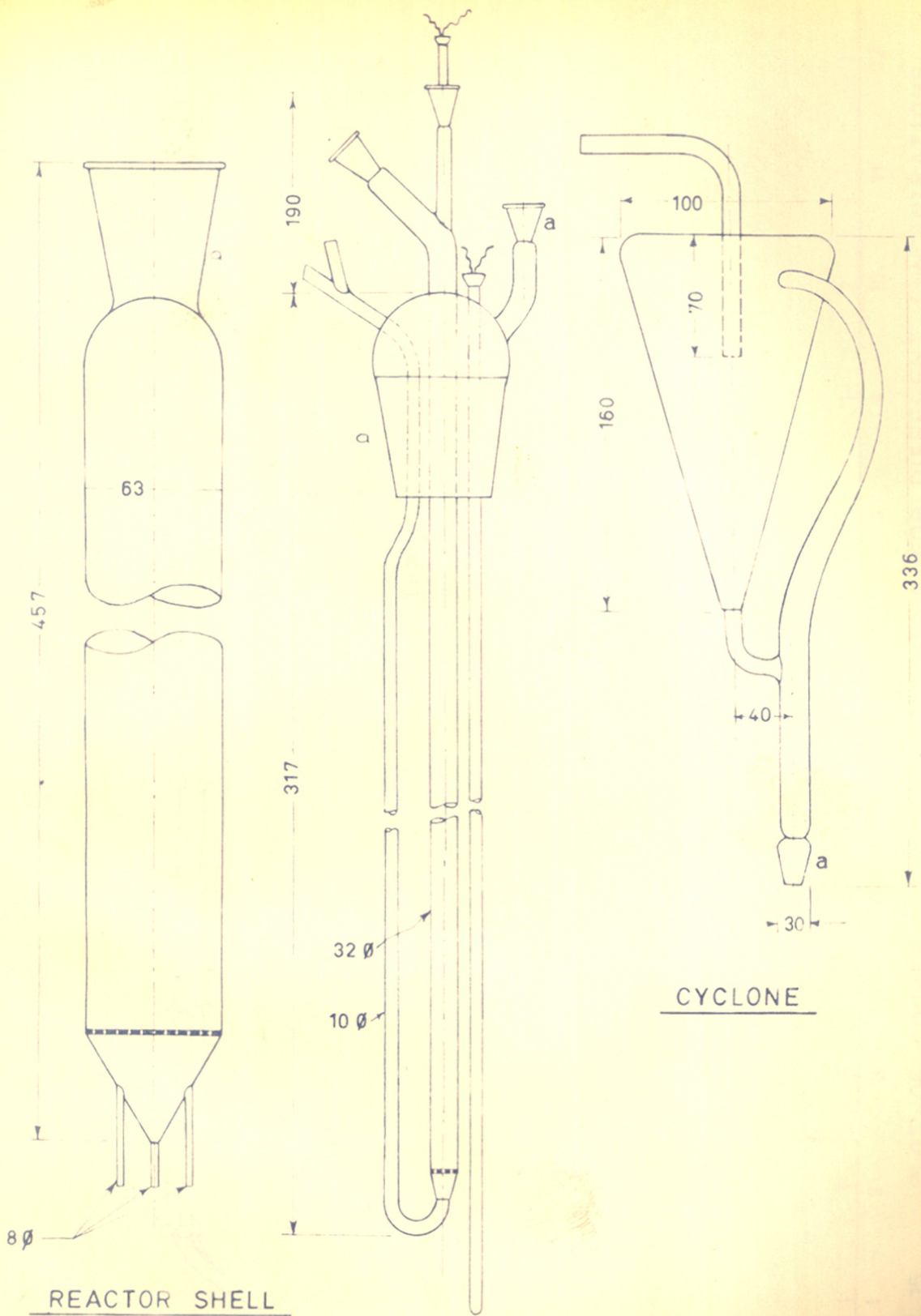


- 1 STORAGE VESSEL
- 2 CHAMBER
- 3 CYLINDRICAL TUBE
- 4 GLASS ROD
- 5 CAPILLARY
- 6 NICROME WIRE
- 7 ADAPTER

### LIQUID FEED

FIG. - 13





REACTOR SHELL

REACTOR

CYCLONE

FIG. - 14.

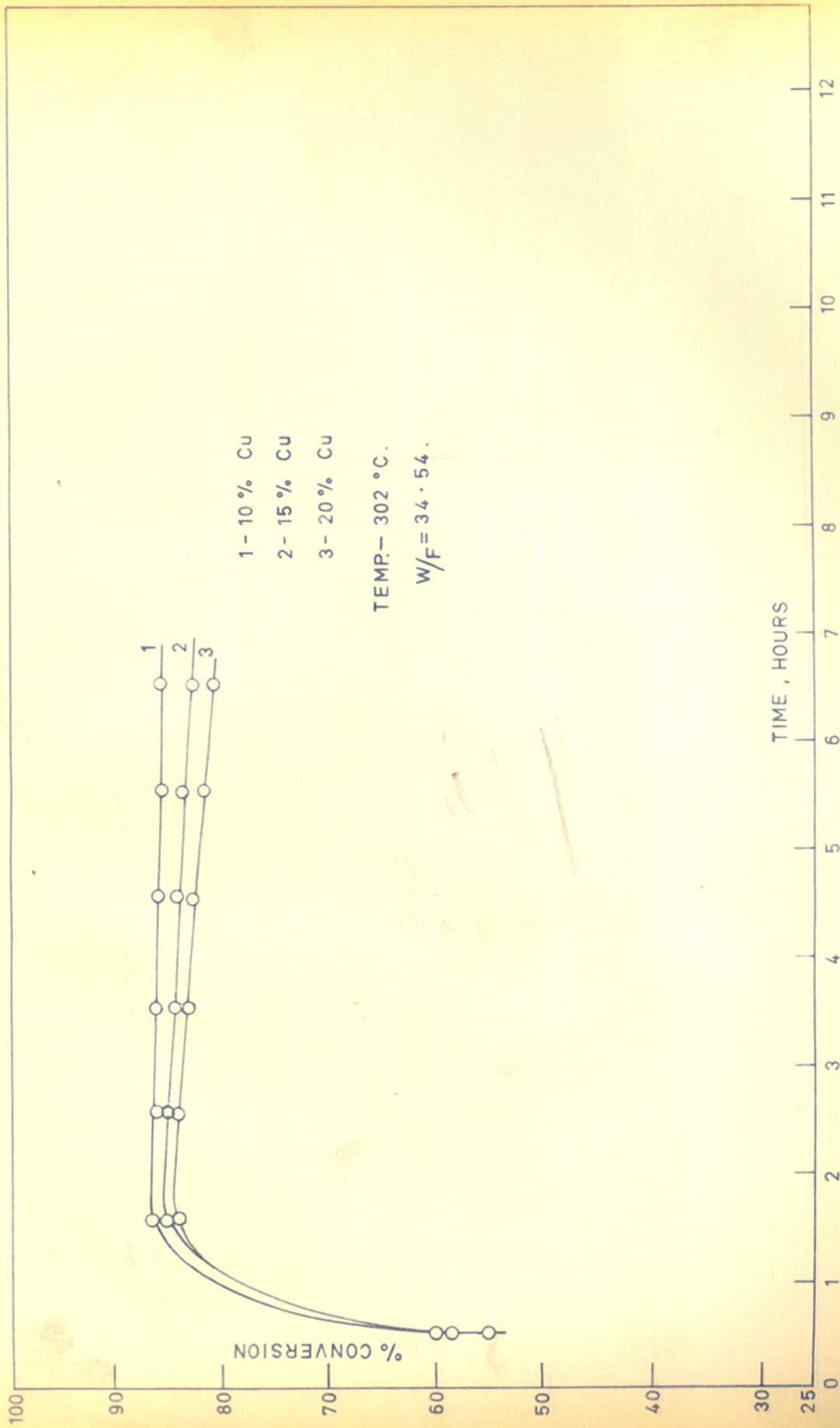


FIG. 15. PLOT OF CONVERSION VS. PROCESS TIME FOR DIFFERENT CONCENTRATIONS

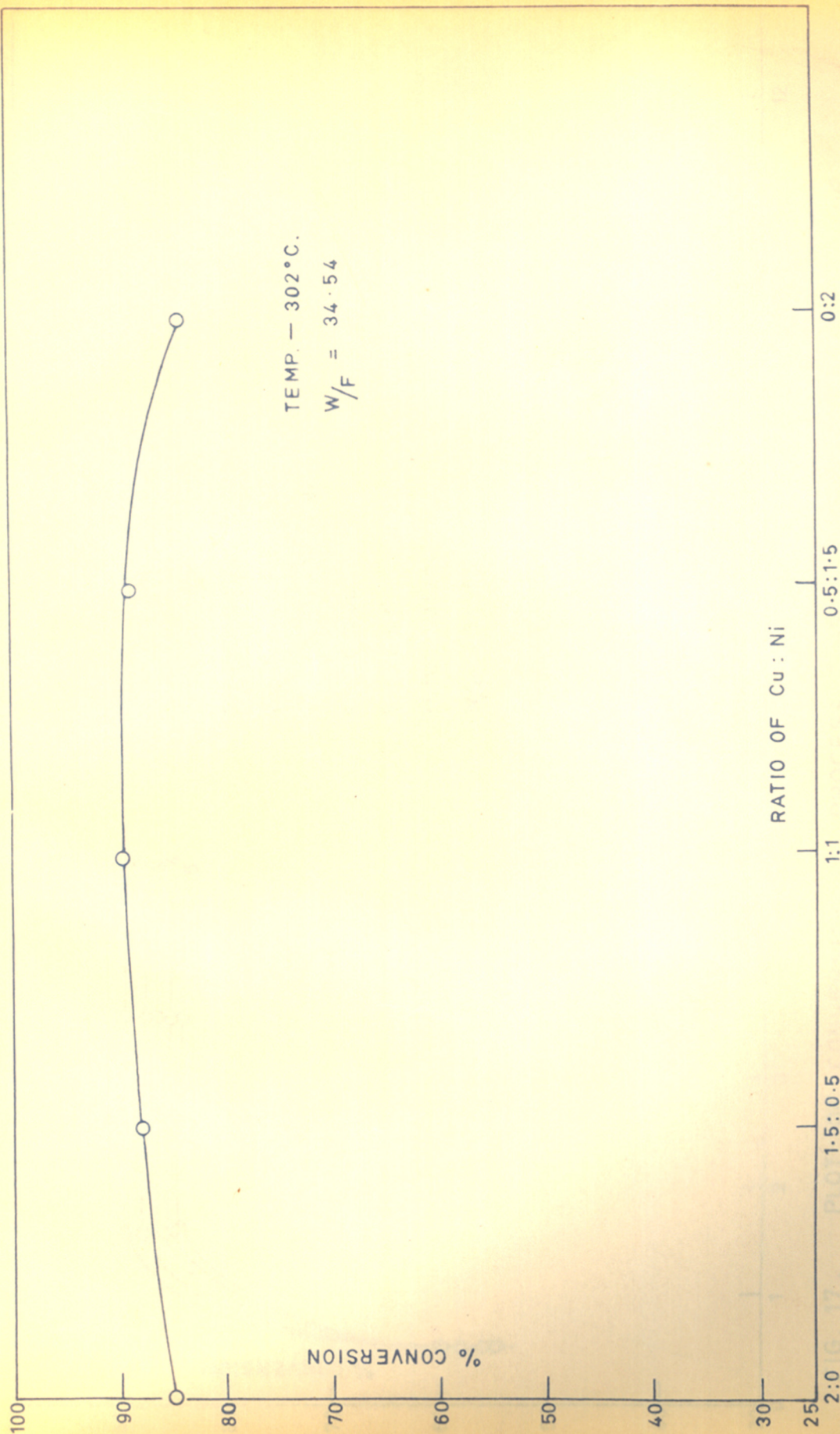


FIG. 16. PLOT OF CONVERSION VS. COPPER TO NICKEL RATIO ON ASBESTOS AS CARRIER  
 IN A TOTAL CONCENTRATION OF 20%

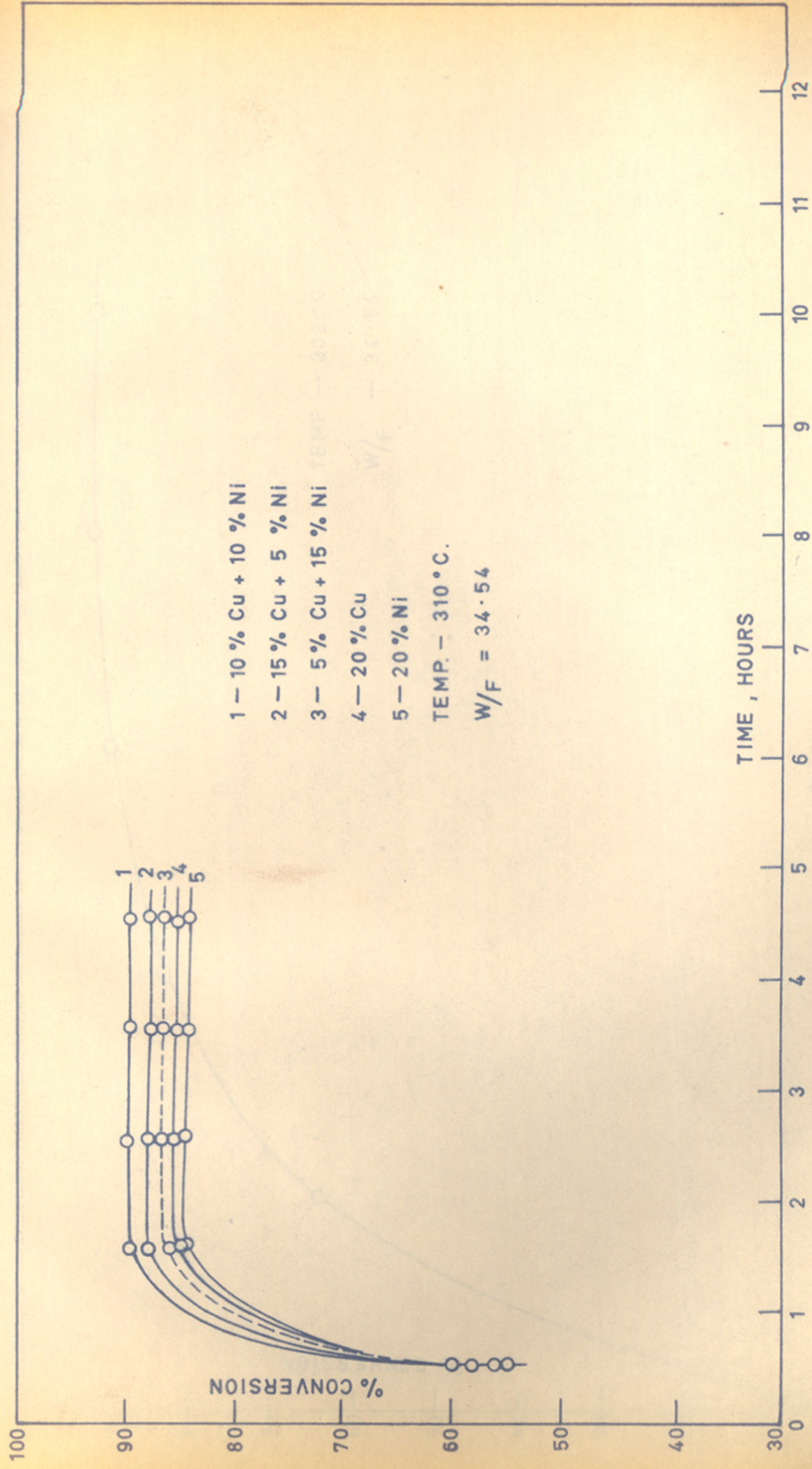


FIG. 17. PLOT OF CONVERSION VS. PROCESS TIME FOR DIFFERENT RATIOS OF  
COPPER TO NICKEL ON ASBESTOS AS CARRIER IN A TOTAL CONVERSION  
OF 20%

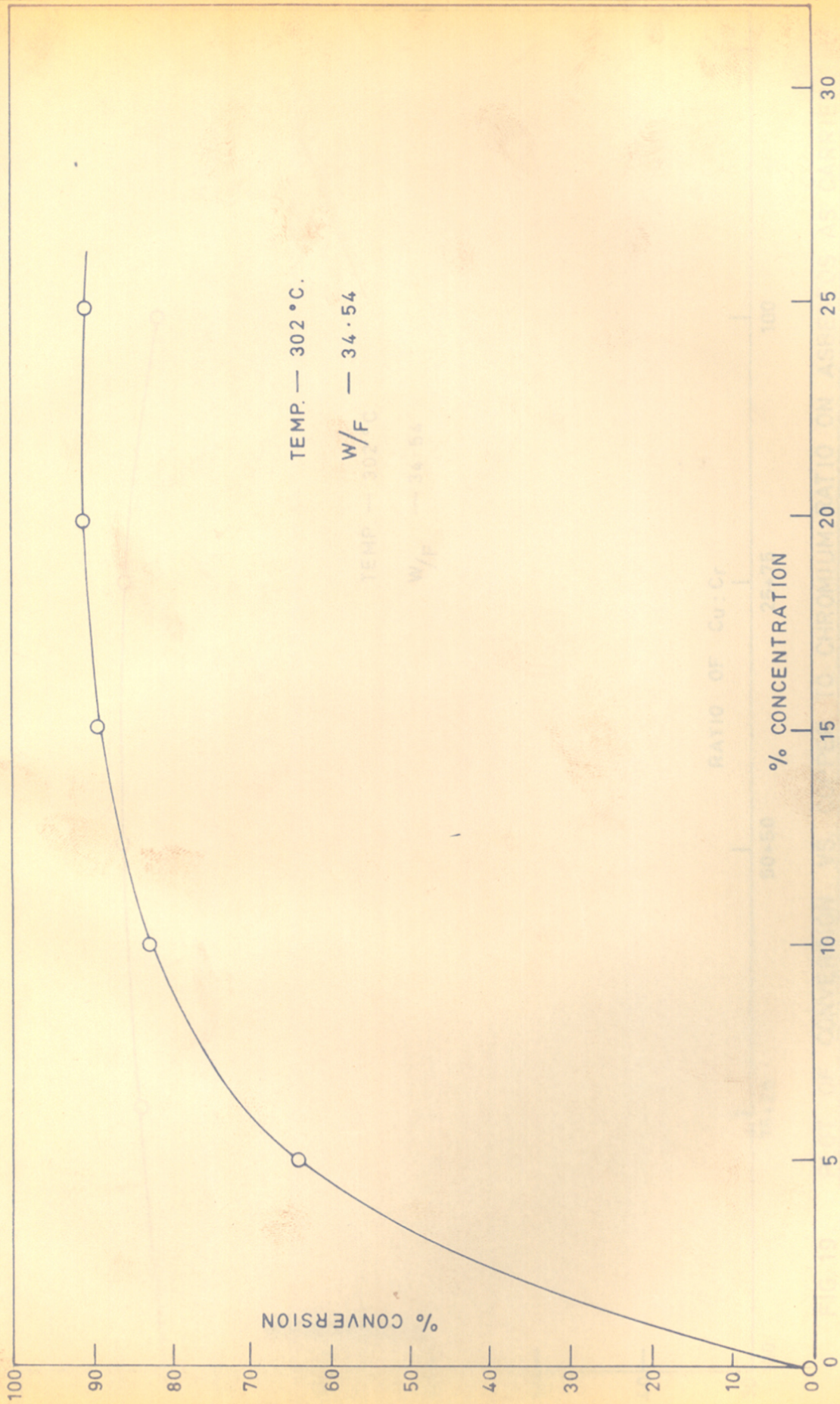


FIG. 18. CONVERSION VS. CONCENTRATION OF COPPER AND NICKEL  
(RATIO - 1:1)

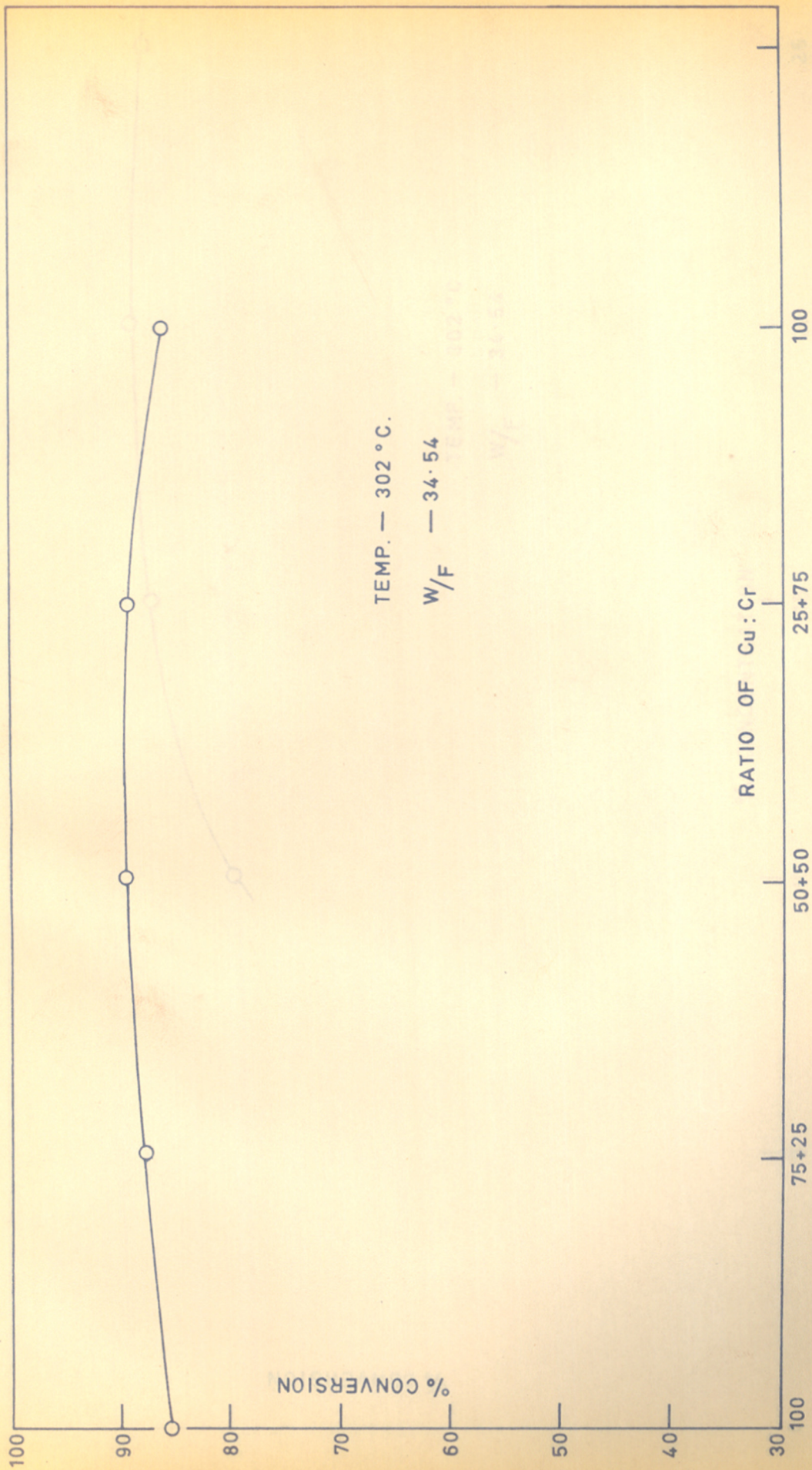


FIG. 19. PLOT OF CONVERSION VS. COPPER TO CHROMIUM RATIO ON ASBESTOS AS CARRIER  
IN A TOTAL CONCENTRATION OF 20 %

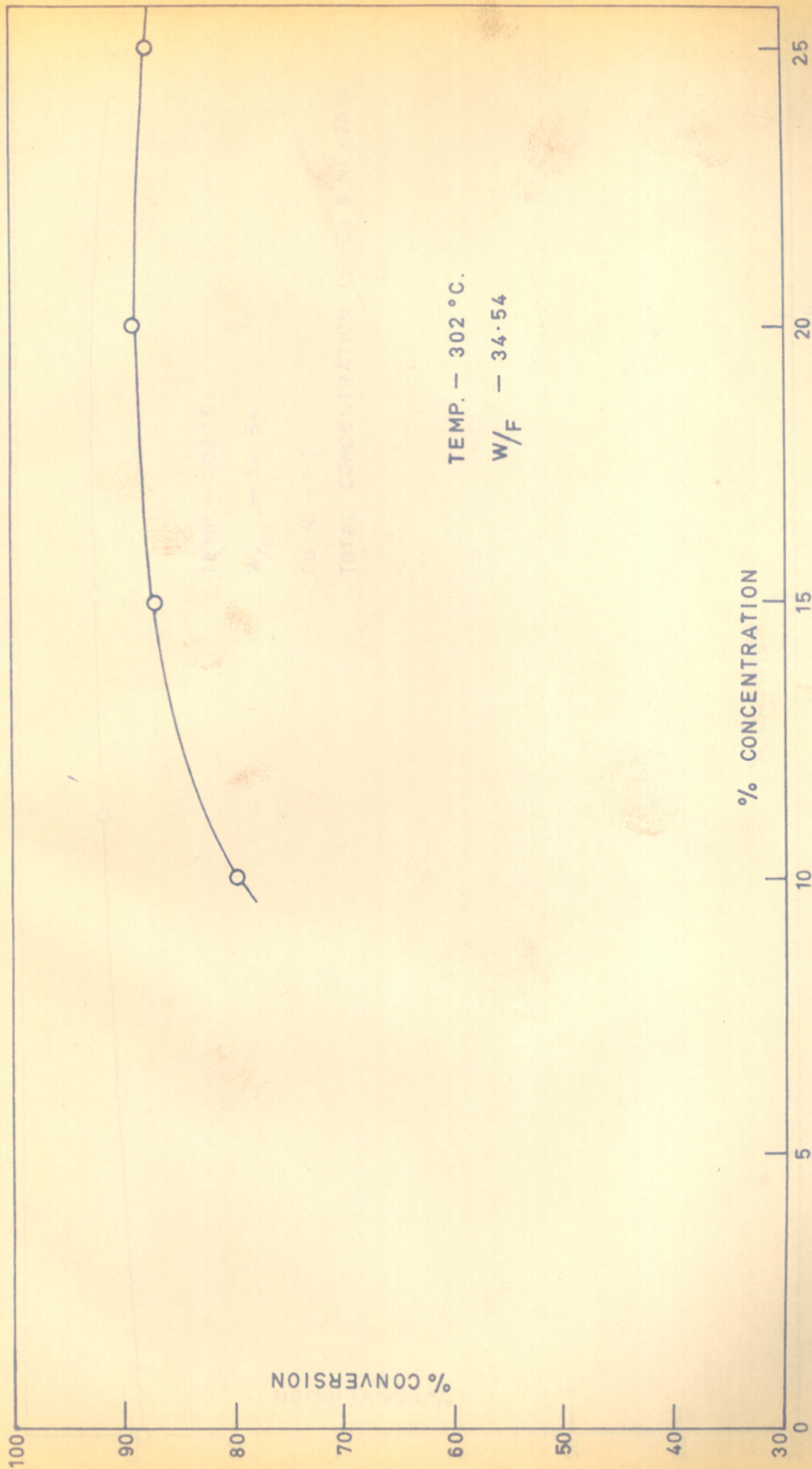


FIG. 20 . CONVERSION VS. CONCENTRATION OF COPPER AND CHROMIUM (RATIO-1:1)

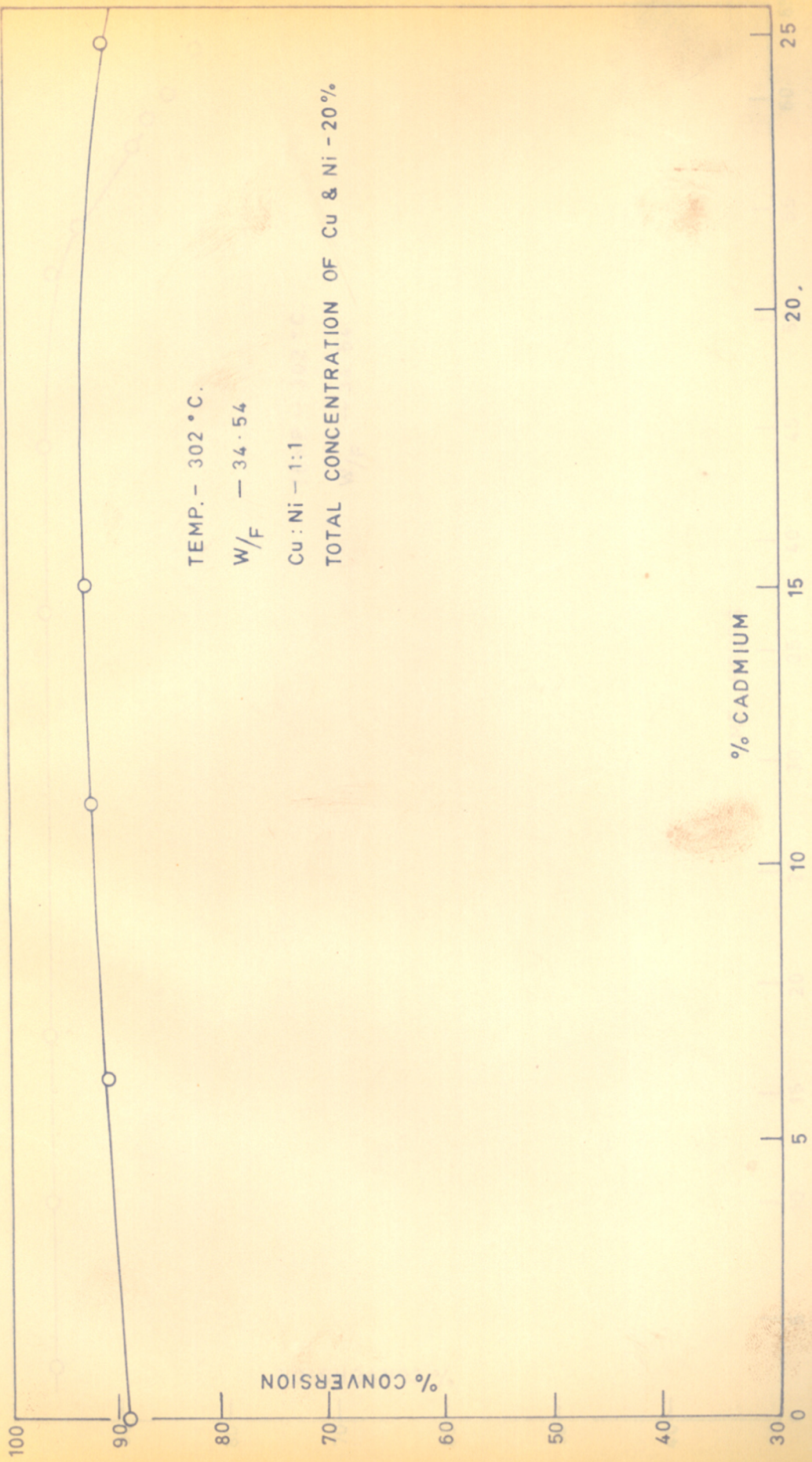


FIG. 21 . . . EFFECT OF CADMIUM AS PROMOTOR ON A COPPER-NICKEL CATALYST  
 SUPPORTED ON ASBESTOS



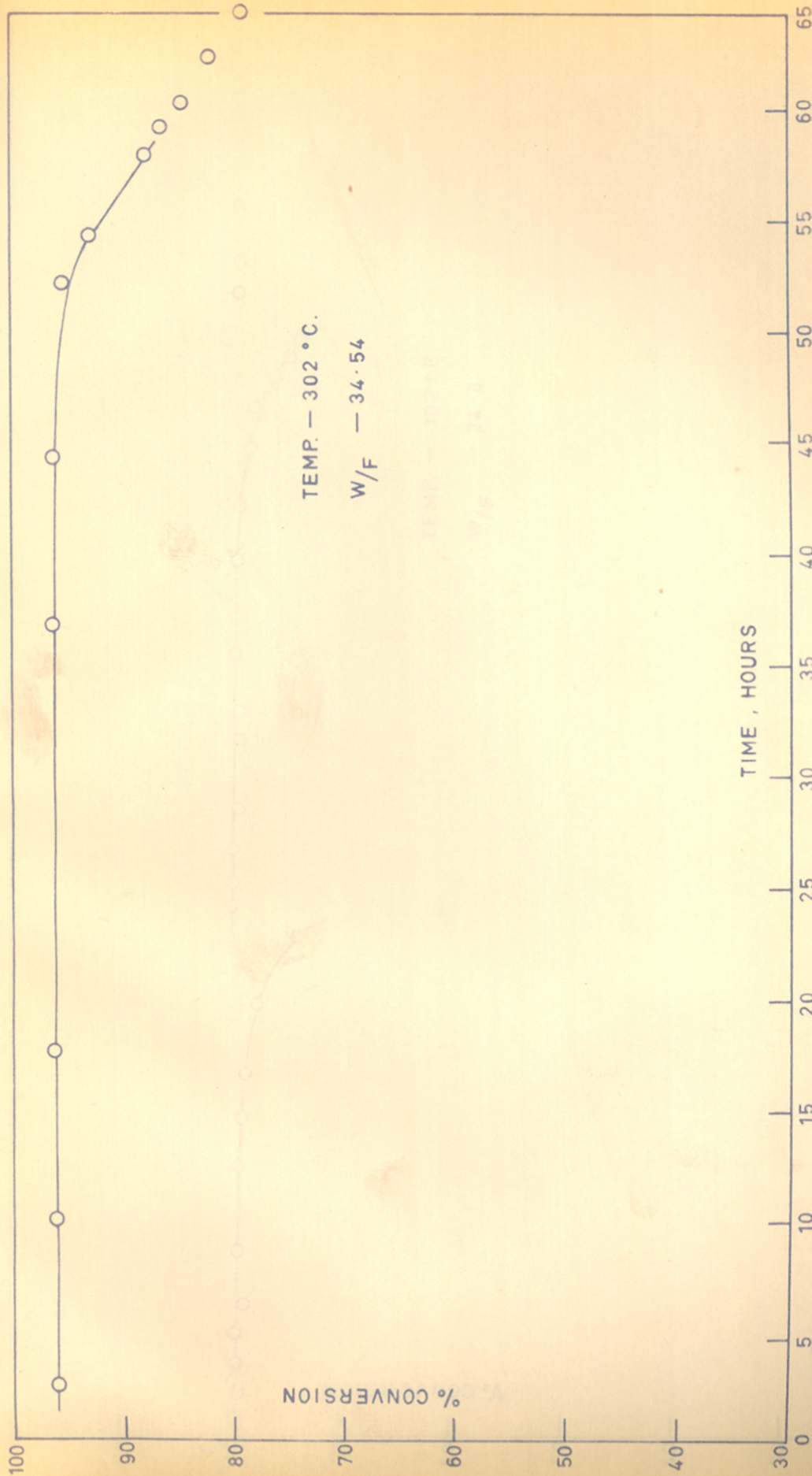


FIG. 22. PRELIMINARY LIFE TEST

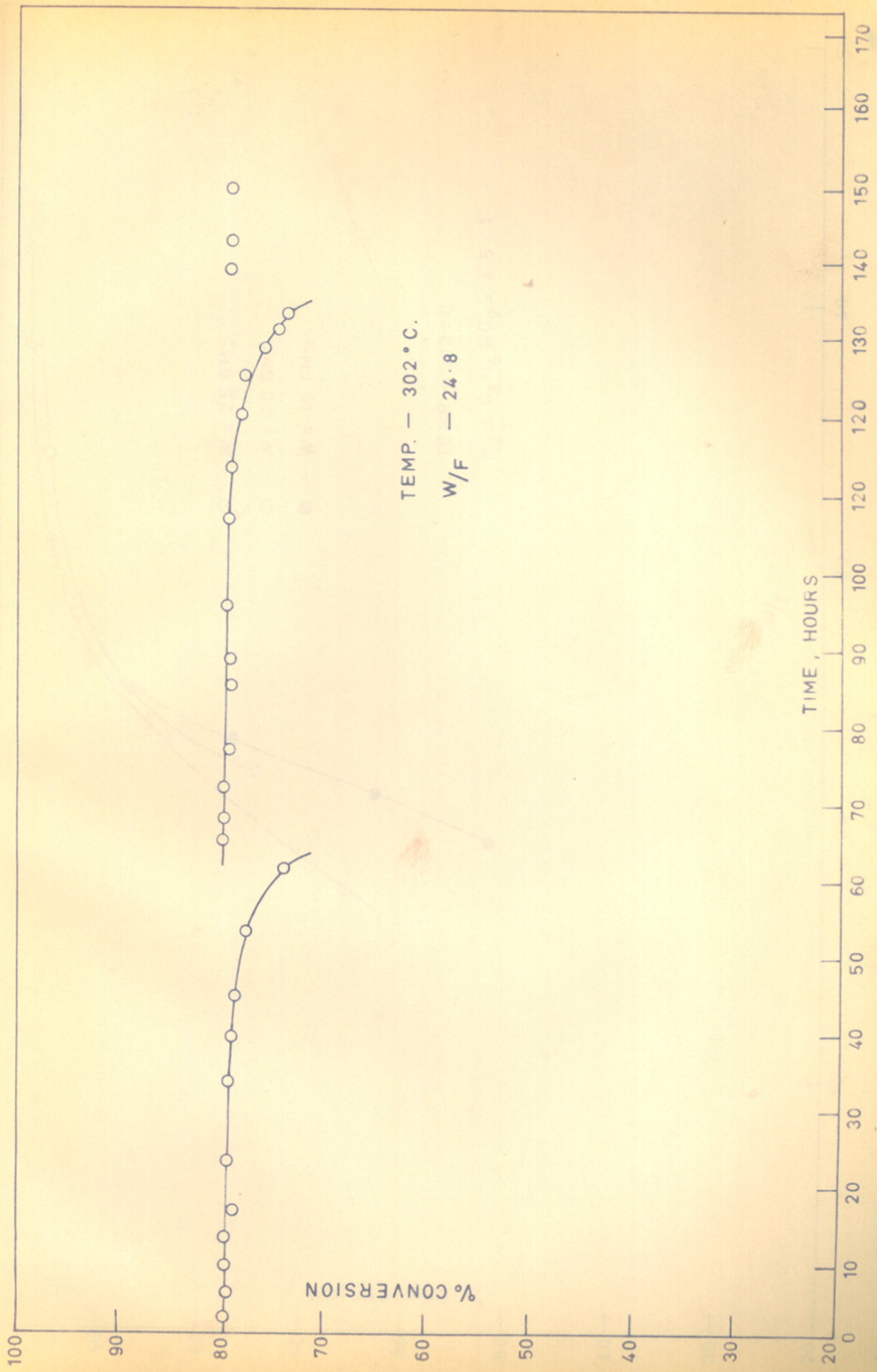


FIG. 23 FINAL LIFE TEST

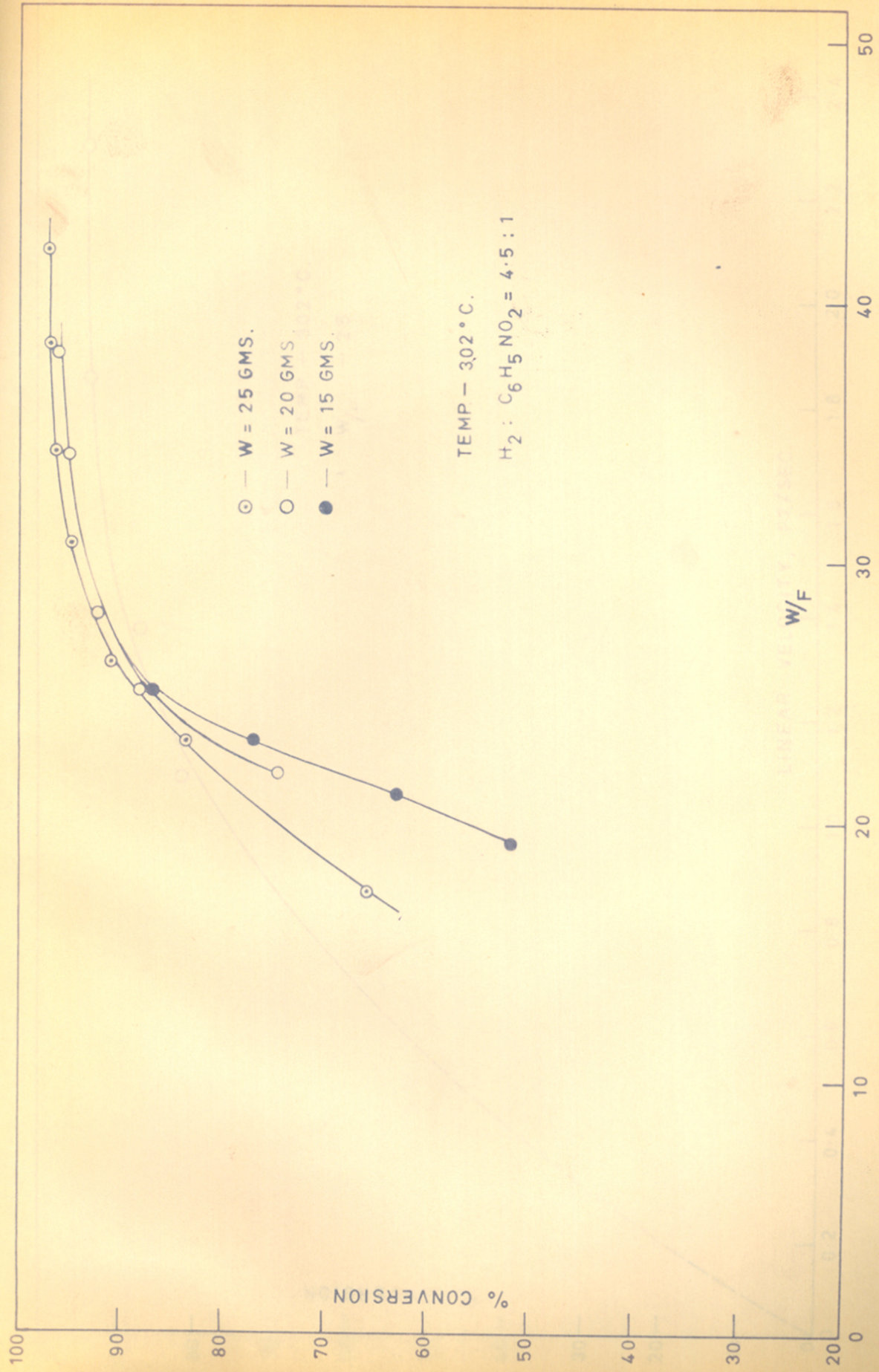


FIG.-24A EFFECT OF MASS TRANSFER

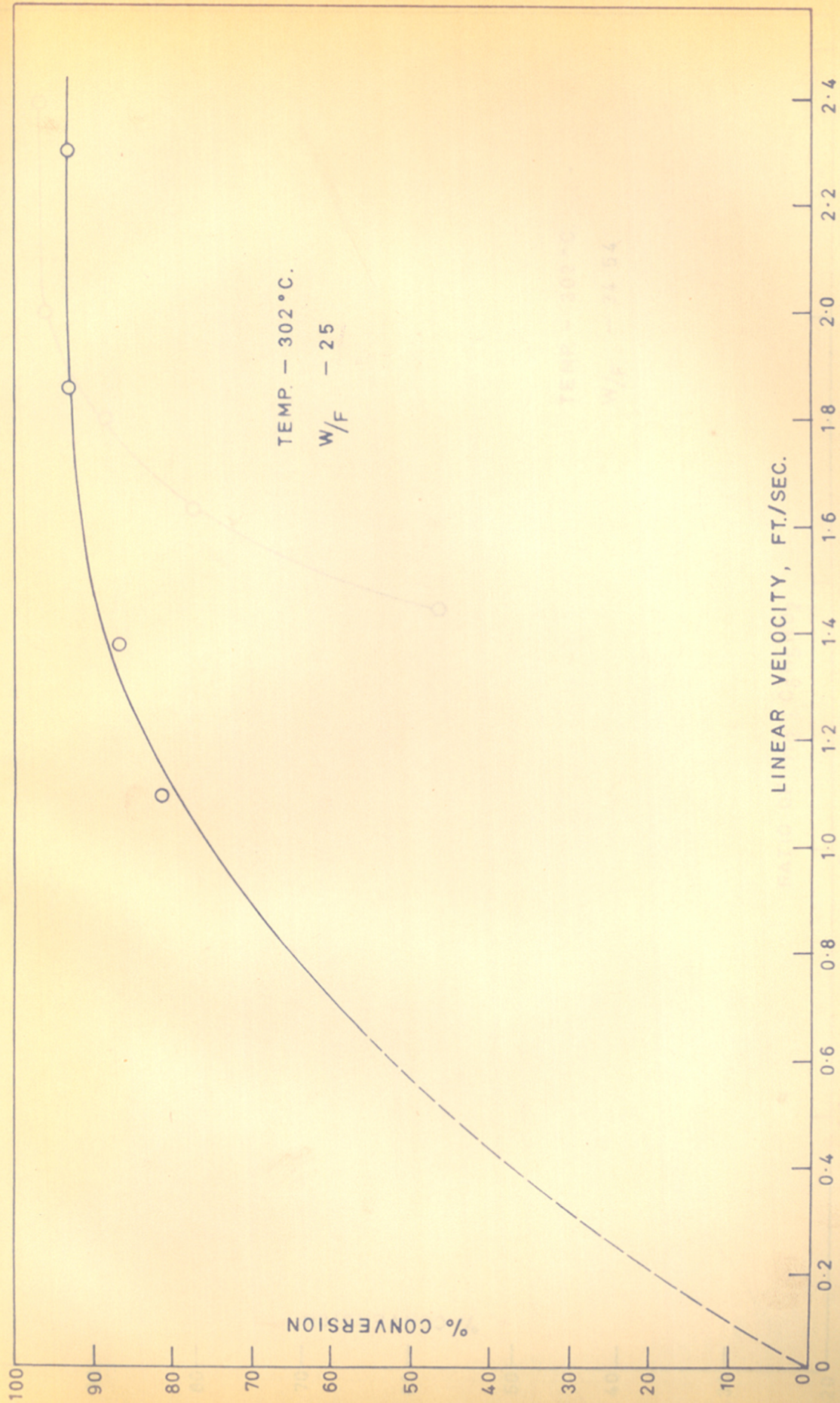


FIG. 24B. EFFECT OF MASS TRANSFER

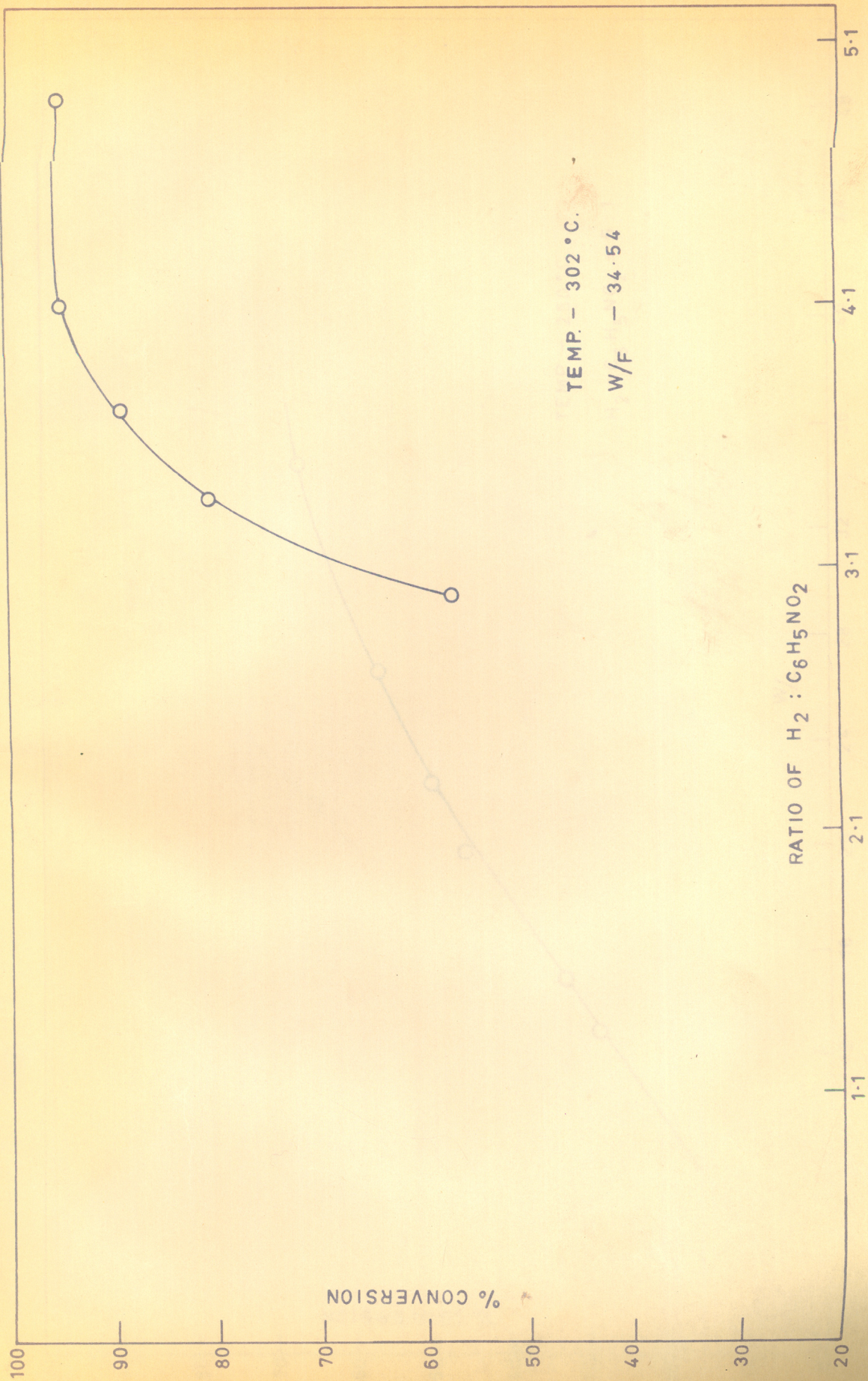


FIG. 25. EFFECT OF HYDROGEN TO NITROBENZENE RATIO ON CONVERSION

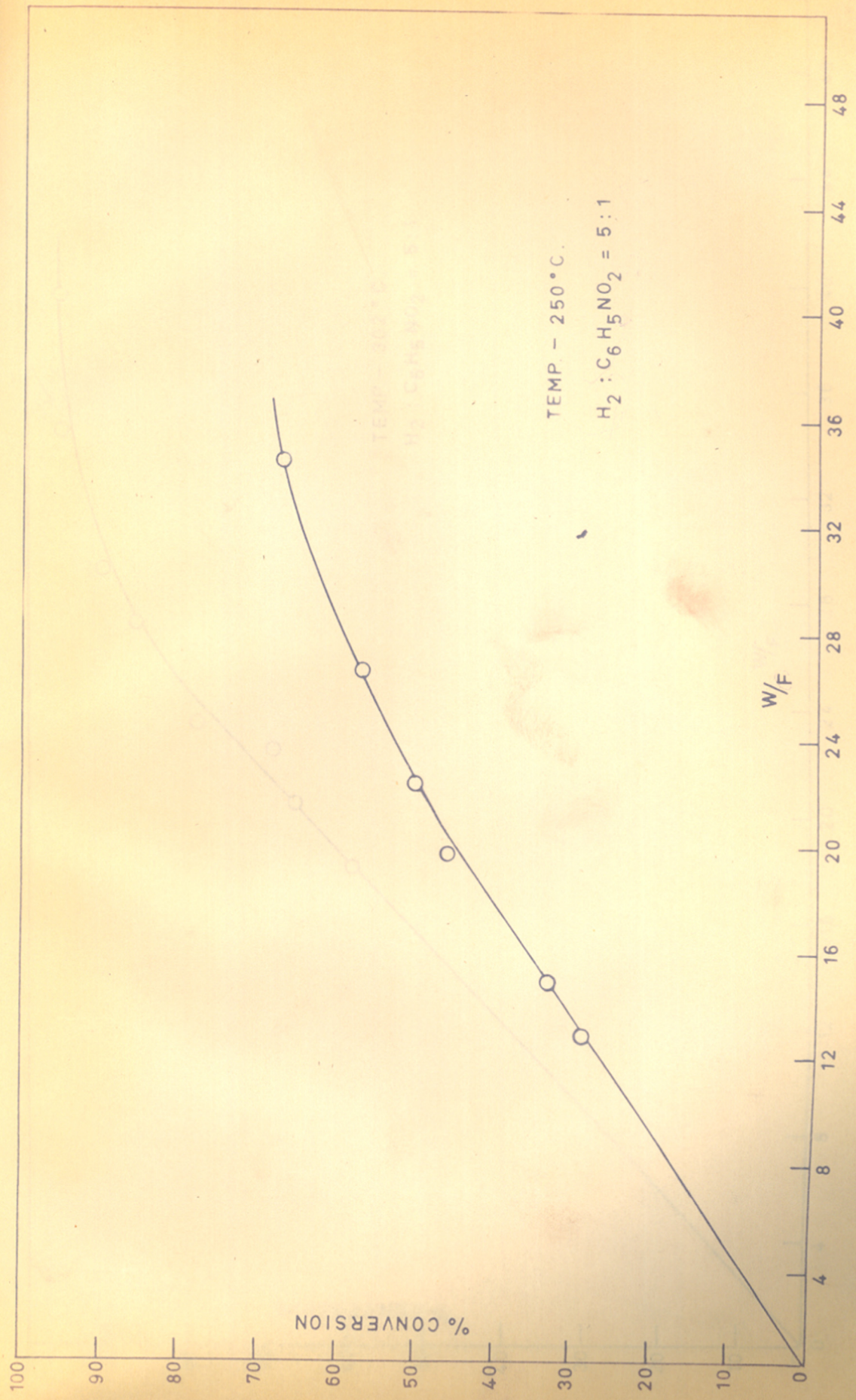


FIG.-26. PLOT OF W/F VS. CONVERSION

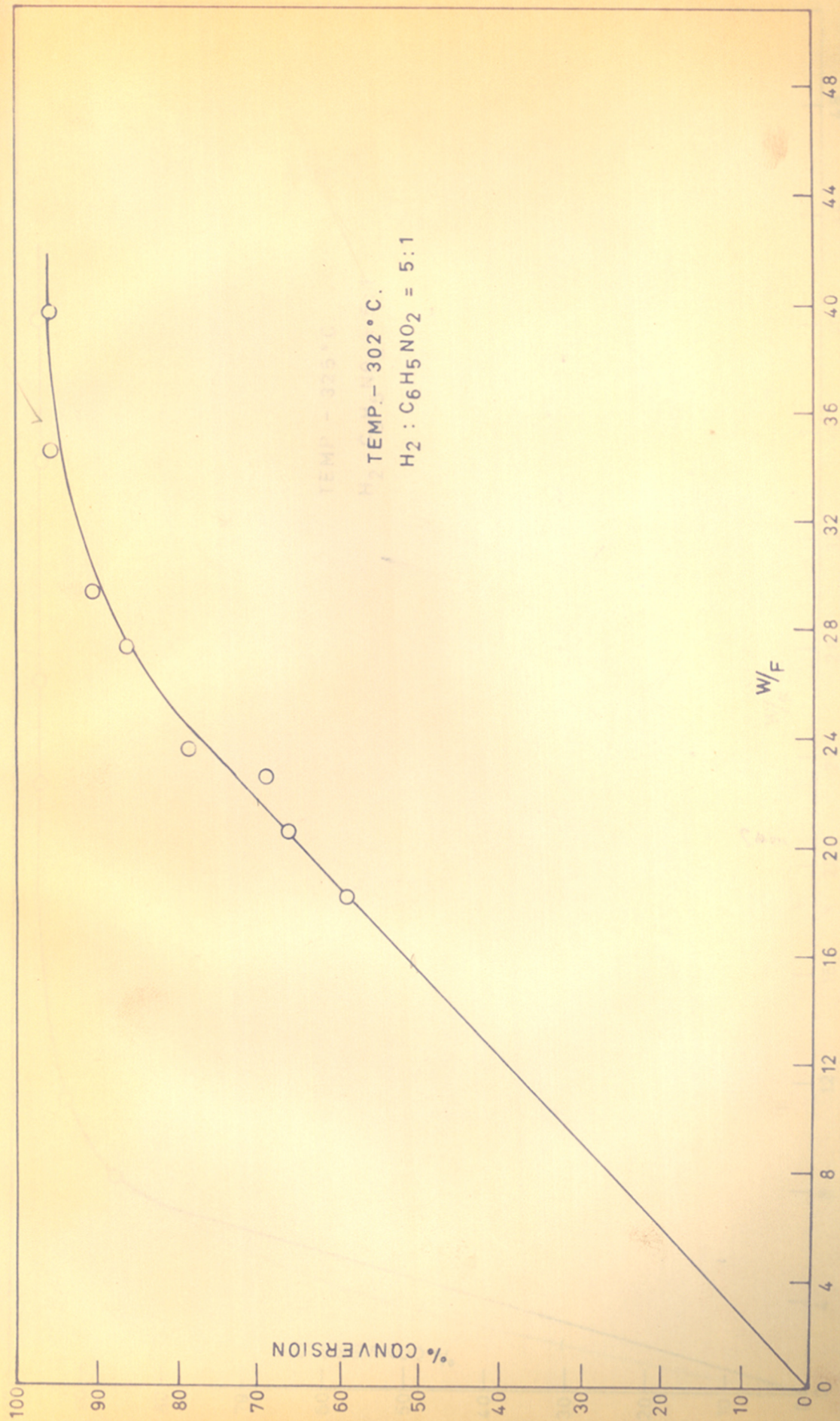


FIG.-27. PLOT OF  $W/F$  VS. CONVERSION

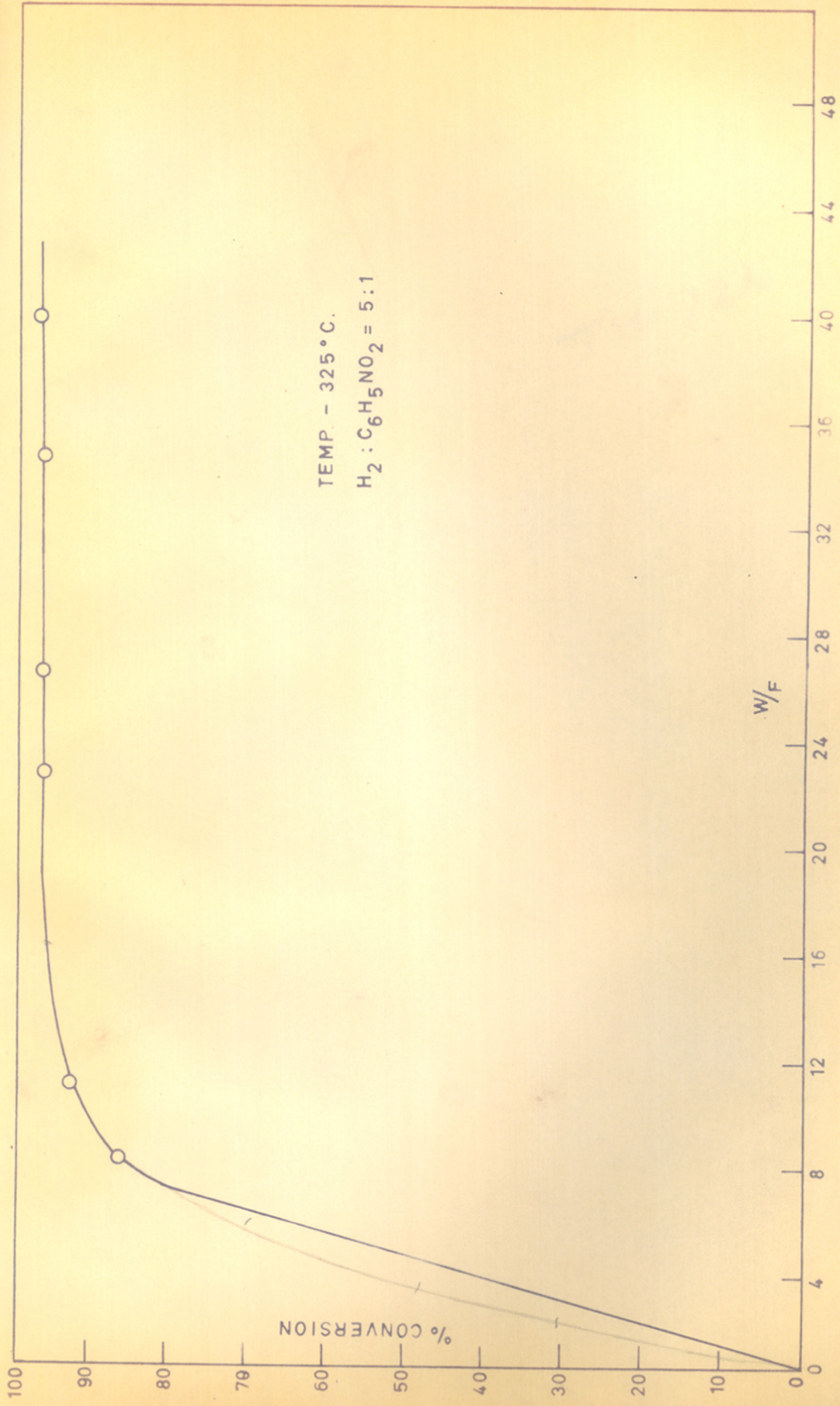


FIG. - 28 PLOT OF W/F VS CONVERSION